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Low-grade metamorphic rocks of the Tethys subduction–collision zone in the Medvednica Mt. (NW Croatia)

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Abstract: The low-grade metasedimentary rocks of Medvednica Mt. (Northwest Croatia) are associated with ortho-greenschists (metabasalts). The Lower to Upper Triassic age of the protolith of the low-grade metamorphic rocks belonging to the Stari Potok, Adolfovac, Tusti Breg, Bliznec, Mrzljak, and Sljeme lithostratigraphic units is determined on the basis of conodonts and field relationships. The metamorphic age of the Triassic metasedimentary rocks from the Risnjak lithostratigraphic units is assumed to be Jurassic. Petrographic and geochemical analyses of ortho-greenschists point to a tholeiite basic magmatic protolith rock having T-MORB (transitional midocean-ridge basalt) characteristics. The ortho-greenschists of the Sljeme lithostratigraphic unit underwent retrograde metamorphism and show metamorphic zoning from the epidote–amphibolite facies to the lower parts of the greenschist facies. However, the greenschists of the Tusti Breg and Bliznec units are characterized by prograde metamorphism ranging from lower to higher greenschist facies. This metamorphism is associated with Jurassic subduction (165–150 Ma) and closure of the Western Tethys. Retrograde metamorphism took place during the collision of the Adriatic and Eurasian plates in the Lower Cretaceous (125–110 Ma).

Keywords: Mt. Medvednica, greenschists, prograde–retrograde metamorphism, T-MORB, subduction–collision, Western Tethys.

Introduction

It is generally accepted that the outcome of metamorphism depends on a combination of several factors, such as pressure, temperature, the amount of fluid involved, and the chemical characteristics of the protolith. Some types of metamorphism are characteristic of certain plate tectonic settings. Namely, in each orogenic cycle, there are conditions which result in metamorphic processes, especially along the subduction zones. The low-grade metamorphism that occurs at low pressures and temperatures can turn the igneous rocks of the oceanic crust into metamorphic rocks, which are known as ortho-greenschists. Thus, the primary mineral composition of magmatic rocks is replaced to a certain degree by characteristic metamorphic mineral paragenesis, which may indicate the grade and time of metamorphism. This is extremely important in the elucidation of metamorphic complexes and understanding of their geodynamic history. On the other hand, protoliths of metamorphic rocks, particularly those of ortho-greenschists, play an important role in the determination of a geodynamic setting of their genesis in the scope of tectonomagmatic reconstruction of geologic processes.

Different pre-Neogene tectonostratigraphic and tectonometamorphic units of continental and oceanic origin have been formed during the geodynamic history of the Northwestern

Dinaridic branch of the Tethys. In the northwestern area of Croatia, these units crop out in intra-Pannonian *inselbergs* (for example, Mt. Medvednica, Mt. Ivanščica, and Mt. Kalnik; Fig. 1). Mt. Medvednica is situated in the southwestern segment of the Zagorje-Mid-Transdanubian Zone (ZMTDZ) at the juncture of three geotectonic units: the Southern Alps, the Tisza Continental Block, and the Dinarides (Pamić & Tomljenović 1998) (Fig. 1) and belongs to the suture zone, i.e., a mixture of these units. Its northwestern slope belongs to the westernmost segment of the Western Vardar Ophiolitic Unit, whereas its southwestern segment is a part of the Bükk–Jadar–Kopaonik tectonic unit (sensu Schmid et al. 2008). The Paleozoic to Triassic metamorphic complex builds up the south-western segment of Mt. Medvednica (Belak et al. 1995; Belak 2005), whereas the Jurassic ophiolite mélange crops out on its northwestern slopes (Babić et al. 2002; Slovenec & Pamić 2002; Fig. 1). Certain tectonically-disintegrated lithological units of the ophiolite mélange of Mt. Medvednica and Mt. Kalnik could be analogous to units from the above-mentioned metamorphic complex, thereby representing their protholiths. These presumptions are based on mutual geodynamical evolution of the aforementioned magmatic–sedimentary successions of the Dinaridic segment of the northwestern part of the Tethys during the Mesozoic, which includes: (1) incipient opening of the ocean system

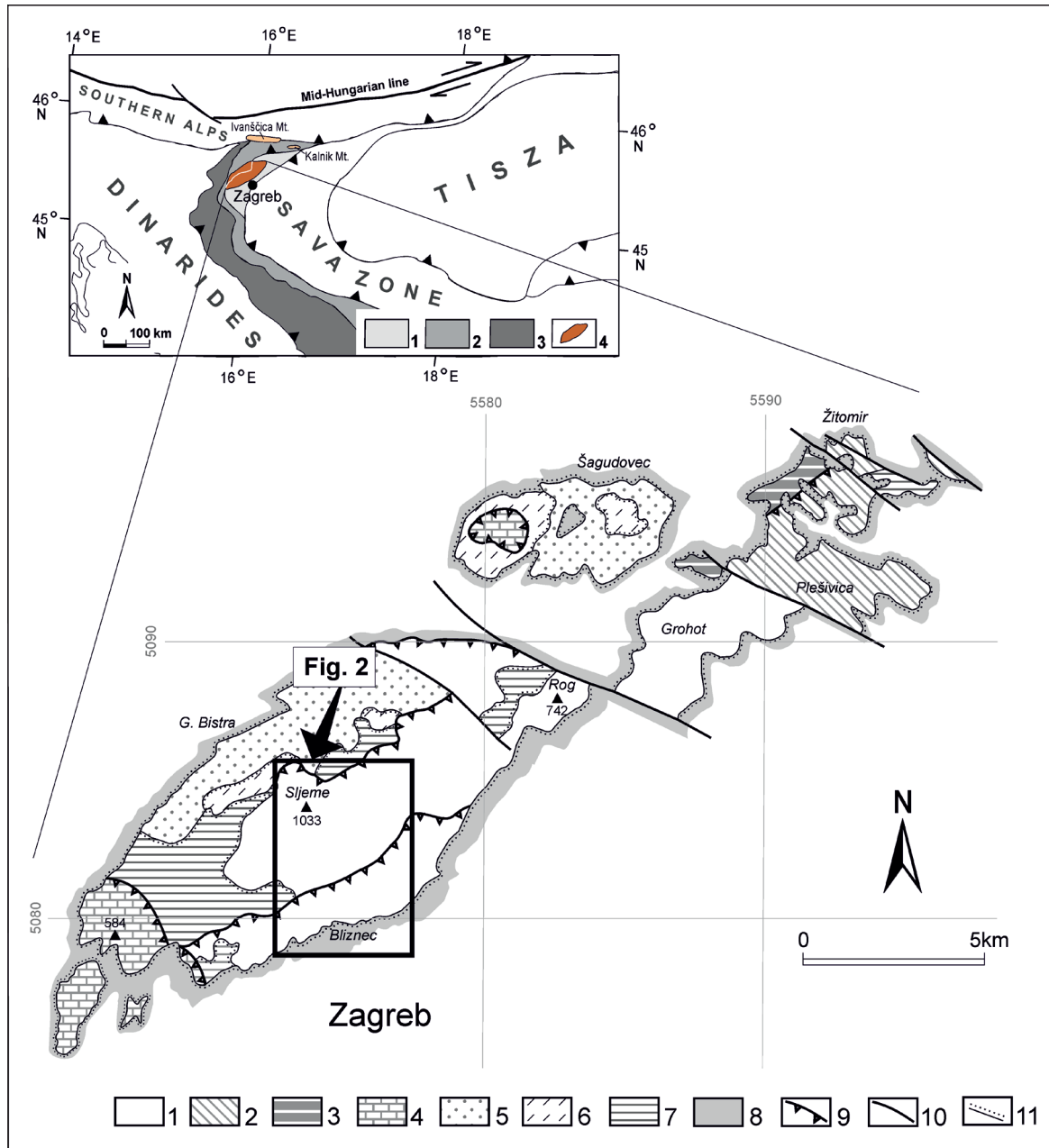


Fig. 1. Simplified geological sketch map of the Mt. Medvednica (Belak 2005). Legend: 1 – Low-grade Paleozoic–Triassic metamorphic complex; 2 – Drenova Unit (mostly marbles, calcschists and serpentized peridotites, metapsamites, metapelites and subordinated blueschist); 3 – Lower Triassic clastics sediments; 4 – Triassic carbonates of the Sava nappe; 5 – Jurassic ophiolite mélangé; 6 – Albian–Cenomanian sediments; 7 – Cretaceous–Paleocene sediments; 8 – Miocene–Quaternary sediments; 9 – major reverse or thrust faults; 10 – strike slip or normal faults; 11 – discordant boundary. Inset: geotectonic sketch map of the major tectonic units (simplified after Schmid et al. 2008, 2020). Legend: 1 – Bükk, Jadar, Kopaonik; 2 – Ophiolites oceanic accretionary prism: Meliata, Darnó-Szarvaskő, Dinaric, Western Vardar, Mirdita; 3 – Pre-Karst & Bosnian Flysch; 4 – Mt. Medvednica.

(Late Anisian; OIB), (2) oceanic crust formation (Ladinian–Bajocian; E-, T-, N-MORB), and (3) intraoceanic (supra-subduction) convergence (Bathonian–Oxfordian; IAT; e.g. Slovenec et al. 2010, 2011). According to this scenario, the igneous rocks represent lithospheric remnants of a single Tethys oceanic basin (Bortolotti et al. 2004; Schmid et al. 2008; Slovenec & Lugović 2009). The oceanic crust fragments and associated sediments were significantly disintegrated

during subduction/obduction processes in the early Mesozoic, forming ophiolite mélanges as well as slices of metamorphic rocks preserved in the metamorphic complex (e.g., Slovenec & Lugović 2009; Slovenec et al. 2010, 2011). The best example of the above-mentioned geological development is recorded in the intra-Pannonian *inselbergs* of northwestern Croatia, such as Mt. Medvednica and Mt. Kalnik.

This study represents the new geochemical and petrological data on the Triassic protolith of the low-grade metamorphic rocks of Mt. Medvednica (NW Croatia). The aim of the paper is to determine the chronostratigraphic age of the protoliths of the studied metamorphic rocks, including the time and grade of metamorphism, as well as define the mineralogical, petrological, and geochemical characteristics of ortho-greenschists of Mt. Medvednica and elucidate the geotectonic setting of their formation. On the basis of the results, the protolithic age of the metamorphic rocks was reinterpreted, and thus metamorphism was associated with Alpine orogeny during the closure of the Western Tethys. Additionally, in order to examine the hypothesis of the single Tethyan ocean area during the Mesozoic era (e.g. Bortolotti et al. 2004; Schmid et al. 2008; Slovenec & Lugović 2009), the analysed ortho-greenschists and their protoliths from the metamorphic complex of Mt. Medvednica were compared with analogous rocks in ophiolite mélanges from the neighbouring magmatic–sedimentary complexes (ophiolite mélanges) of the Zagorje–Mid-Transdanubian Zone (ZMTDZ). The analysis of geochemical affinities and geological characteristics of analogous rocks from the ZMTDZ will contribute to a better knowledge of the geodynamic processes that took place in the western part of the Tethys during the Mesozoic era.

Geological setting

Mt. Medvednica, located in the northwestern part of the ZMTDZ (*sensu* Pamić & Tomljenović 1998), is characterized by a complex composition and structure, whose core is made up of tectonically-disturbed different rocks of Paleozoic, Mesozoic, and Paleogene age, and surrounded by younger Neogene and Quaternary sedimentary rocks. The Pre-Neogene core of Mt. Medvednica is made up of the following main tectonostratigraphic units (Fig 1): (1) The Paleozoic–Triassic metamorphic complex mainly represented by metalimestones, metapelites, metapsammities (phyllites, slates), marbles, chloritoid schists, chlorite–stilpnomelane schists, metaradiolarites, and ortho-greenschists (Belak et al. 1995; Belak 2005); (2) The Drenova Unit, which is composed mainly of marbles and calcschists and, to a lesser extent, blueschists, metapelites, chloritoid schists, metapsammities, and serpentinites (Belak & Tibljaš 1998; Belak 2005; Belak et al. 2022 *in press*); (3) The Middle and Upper Triassic limestones and dolomites with subordinate Lower Triassic clastic and carbonate sediments (Šikić et al. 1978); (4) Triassic carbonates of the Sava nappe; (5) The Jurassic ophiolite mélange (Babić et al. 2002; Slovenec & Pamić 2002) with chaotically-distributed Triassic–Jurassic ophiolitic blocks (cumulate peridotites, basalts, diabases, and gabbros) and fragments of greywackes and radiolarites (Halamić et al. 1998, 1999; Slovenec 2003; Slovenec et al. 2007; Slovenec & Lugović 2008, 2009, 2012); (6) Albian–Cenomanian limestones, shales, sandstones, and siltstones (Šikić et al. 1978; Crnjaković 1979); (7) Upper Cretaceous–Paleocene conglomerates, sandstones, marls, and

Scaglia type limestones (Crnjaković 1979; Šikić et al. 1979; Marinčić et al. 1995; Pavelić et al. 1995).

A significant part of the Pre-Neogene core of Mt. Medvednica consists of low-grade, ortho- and para-greenschists of the Paleozoic–Triassic metamorphic complex, which had been thrust onto the Jurassic ophiolite mélange (Figs. 1 and 2). Although this metamorphic complex had been built from the bottom to the top of eight lithostratigraphic units (Belak 2005; see Fig. 2), the focus of this research is only on four of them: (1) The Tusti Breg Unit, (2) The Bliznec Unit, (3) The Mrzljak Unit, and (4) The Sljeme Unit. These units of Upper Triassic to Middle Jurassic(?) age, which constitute an overwhelming part of the metamorphic complex of the central and southern part of Mt. Medvednica, are characterized by low-grade metamorphic rocks represented by ortho-greenschists.

A number of researchers (e.g., Gorjanović-Kramberger 1907, 1908; Kišpatić 1918; Marić 1959; Šikić et al. 1978; Basch 1983; Pamić 1987) studied the rocks of this complex from the aspect of mineralogy, petrology, biostratigraphy, and geology *sensu lato* assuming that the metamorphic complex of Mt. Medvednica primarily comprises a continuous sequence of Devonian–Lower Permian strata, which had later undergone a unique process of regional, low-grade metamorphism in the frame of Hercynian orogeny. Although Đurđanović (1973) had previously published data on the Triassic age of the major low-grade metamorphic rocks of Mt. Medvednica based on conodont analyses, these data were not accepted in geological literature. However, Belak et al. (1995) determined the Middle- and Upper-Triassic age of the protolith based on the conodont content in the majority of rocks from the metamorphic complex of Mt. Medvednica. The same authors refined constraints on timing of this metamorphism using K–Ar analyses of white mica in chloritoid schist, which yielded ages in the range of 115.5 to 122.8 Ma, and concluded that metamorphism took place during the Early Cretaceous. Judik et al. (2006), Borojević–Šošćarić et al. (2012), and van Gelder et al. (2015) obtained a similar, Early Cretaceous age of metamorphism (110–135 Ma). Belak et al. (1995) associated the low-grade metamorphic rocks of greenschist facies with subduction–collision processes of the Western Tethys, which took place during the Early Cretaceous. However, Belak & Tibljaš (1998) explained the occurrence of high-pressure glaucophane schists in the north-eastern part of the Mt. Medvednica with Middle Jurassic oceanic subduction processes during eo-Alpine orogenesis. According to Babić et al. (2002), these oceanic subduction processes lasted up to the Late Jurassic in the area of north-western Croatia, and compression of the foreland basin existed during the Early Cretaceous. The same authors suggested that Meliata, the Repno complex (Mt. Medvednica and Mt. Kalnik), and the Central Dinaride Ophiolite Belt are all parts of the single ocean environment in the area of the neighbouring Adriatic plate. Based on structural studies, Tomljenović (2002) associated the oldest structural deformations of Mt. Medvednica with the geodynamical evolution of the Dinarides and assumed that the Lower Cretaceous low-grade metamorphic complex of Mt. Med-

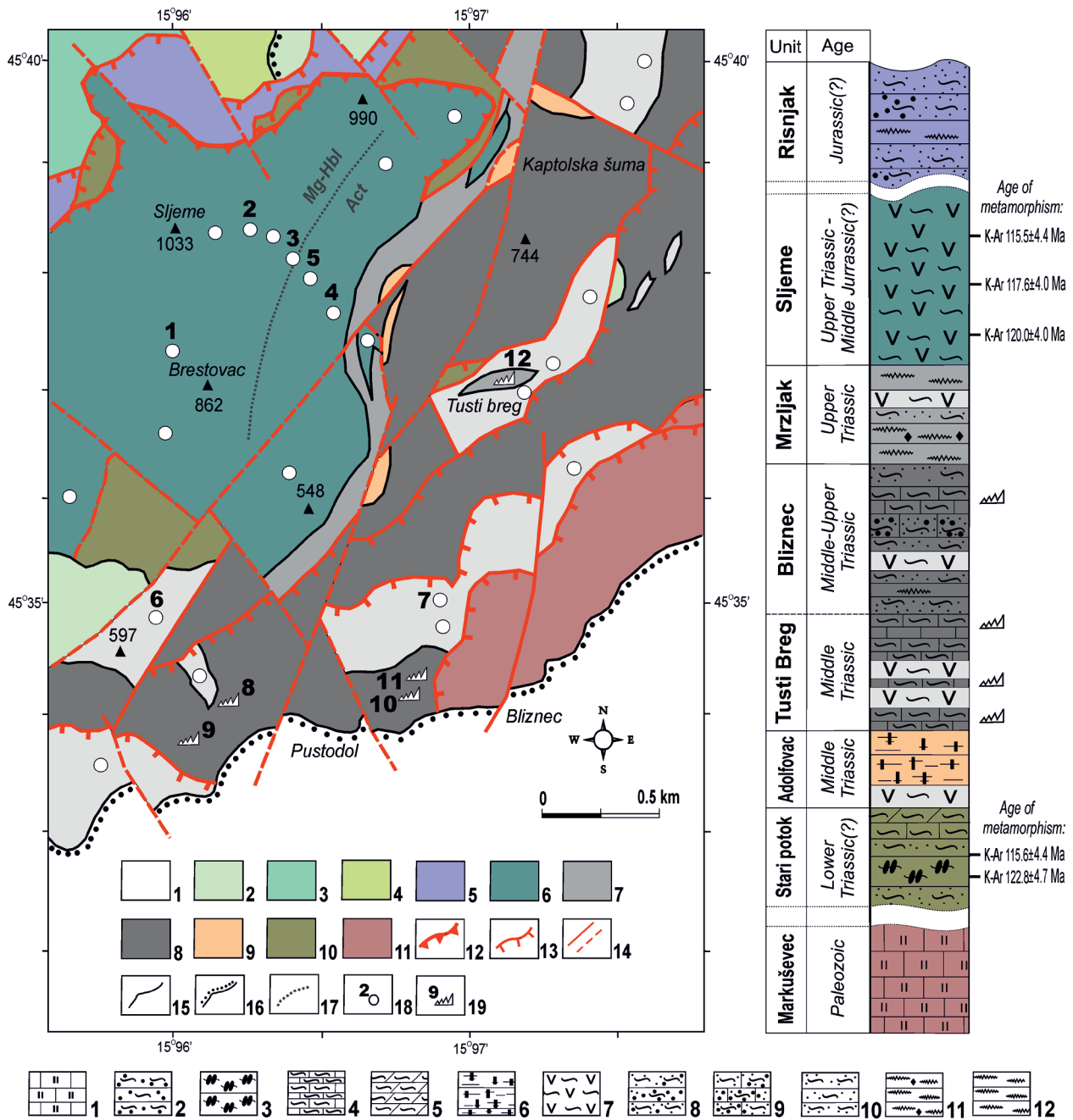


Fig. 2. Geological map and stratigraphic column of the central part of Mt. Medvednica (Belak 2005). Legend (map): 1 – sedimentary rocks (Neogene–Quaternary); 2 – carbonate and clastic rocks (Upper Cretaceous–Paleogene); 3 – basinal fine-clastic rocks (Upper Jurassic–Lower Cretaceous; *Oštrc Unit*); 4 – ophiolitic mélangé (Middle–Upper Jurassic; *Repno Unit*); Metamorphic complex: 5 – interlayering of metapelites, metapsamites and metaradiolarites (Jurassic(?); *Risnjak Unit*); 6 – ortho-greenschists – metabasalts (Upper Triassic–Middle Jurassic(?); *Sljeme Unit*); 7 – quartzschists (metaradiolarites) with magnetite/hematite, metapelites, greenschists (Upper Triassic; *Mrzljak Unit*); 8 – metapelites, metalimestones, calcitic metapsamites/metapelites, greenschists, metaradiolarites (Upper–Middle Triassic; *Bliznec* and *Tusti Breg Units*); 9 – marbles (Middle Triassic; *Adolfovac Unit*); 10 – metalimestones, metapelites, chloritoid schists (Early Triassic; *Stari Potok Unit*); 11 – metalimestones (Paleozoic; *Markuševac Unit*); 12 – thrust fault; 13 – reverse fault; 14 – normal fault; 15 – geological contact line; 16 – erosion and/or tectonic–erosion geological line; 17 – boundary between the lower (*Act*) and upper (*Mg-Hbl*) greenschist facies; 18 – sample location (mineralogical/geochemical analysis: 1=J-898, 2=Slj-6, 3=Želj-23, 4=Želj-26, 5=Run-1, 6=Mel-4, 7=M-710); 19 – sample location (conodont analysis: 8=VR-6C, 9=536, 10=M-2, 11=M-3, 12=M-107B, C and D). Legend (column): 1 – massive to thicklayered metalimestones; 2 – metapsamites; 3 – chloritoid schists; 4 – thin- to middle-layered metalimestones; 5 – recrystallized dolomites; 6 – marbels; 7 – greenschists (metabasalts); 8 – interlayering of metapsamites and metapelites; 9 – interlayering of calcitic metapsamites and metapelites; 10 – metapelites; 11 – quartzschists (metaradiolarites) mineralized with magnetite and hematite; 12 – quartzschists (metaradiolarites).

vednica is associated with a regional compression event caused by ophiolite obduction in a north to north-western direction diagonally over the eastern rim of the Adriatic Plate. This interpretation was accepted by Lugović et al. (2006), Schmid et al. (2008, 2020), and van Gelder et al. (2015).

Methods and analytical techniques

The lithostratigraphic units, geological map, and synthesized geological column of the studied area were determined on the basis of the detailed field examination, which included construction (or recording) of numerous representative geological columns, geological mapping, and careful sampling of the rocks (Fig. 2).

Optical investigations of the minerals and rocks in thin sections were carried out on more than 1000 samples, of which 85 representative samples were chosen for further analyses.

Bulk-rock powders for chemical analyses of 27 samples were obtained from rock chips free of visible veins. Major elements and trace elements of Rb, Ba, Sr, Zr, Cr and Ni were measured by wavelength dispersive XRF using conventional techniques at the Federal Institute for Geosciences and Natural Resources in Hannover (Germany). The trace elements and REE were analysed by ICP-MS at Actlab Laboratories in Ancaster (Canada). International mafic rocks were used as standards (BIR-1a, W-2a, SY-4, GBW, DNC-1, NIST 694). Major element and trace element concentrations were measured with accuracy better than 1% and 5%, respectively.

Minerals in 8 rock samples were analysed at the Mineralogisches Institut, Universität Heidelberg (Germany), using a CAMECA SX51 electron microprobe equipped with five wavelength-dispersive spectrometers. Measurements were performed using accelerating voltage of 15 kV, beam current of 20 nA, beam size of ~1 µm (for feldspars 10 µm), and 10 s counting time for all elements. Natural and synthetic minerals and oxides [wollastonite (Si, Ca), Al₂O₃ (Al), gahnite (Al in spinel), rodonite (Mn), TiO₂ (Ti), Cr₂O₃ (Cr), Fe₂O₃ (Fe), MgO (Mg), NiO (Ni), albite (Na) and orthoclase (K)] were used for calibration. Raw data for all analyses were corrected for matrix effects with the PAP algorithm (Pouchou & Pichoir 1984, 1985), implemented by CAMECA. Mineral formulas were calculated using the MINPET software package written by Linda R. Richard (Gatineau, Québec, Canada).

K–Ar age dating was carried out on 5 samples at the Institute for Nuclear Research, the Hungarian Academy of Sciences, Debrecen (Hungary). K–Ar analyses were performed on greenschist whole rock, as well as on monomineral muscovite fraction from chloritoid schist. A common method using zeolites and heating with Ti and CuO is used for argon separation, whereas isotopic measurement of argon is done by magnetic mass spectrometry (150-mm radius and 90° deflection). The potassium is measured by flame photometry. The error estimation of K–Ar ages (2σ) was determined assuming a 3% error for the determination of potassium, taking in

account 1.5% error for the standards Asia-1/65 and GL-O and 1% error for the argon isotope ratios.

Determination of the primary (protolith) age of the studied rocks had been attempted by the paleontological investigations of the fossil contents of conodonts and radiolarians in the metasedimentary rocks. The chronostratigraphic data were obtained from conodont analyses. Twenty-one rock samples with weights between 0.3–1.0 kg were processed for conodonts and treated in a 15% acetic acid solution following standard conodont preparation techniques. Conodont faunas were recovered in seven samples and were generally poorly preserved. Conodont elements show high Colour Alteration Index (CAI), which is a valuable tool for assessing organic metamorphism (Epstein et al. 1977; Harris 1981; Rejebian et al. 1987). All studied and figured specimens were catalogued and deposited with the Geological Survey of Slovenia, under the numbers GeoZS 2969-2977 and 3099-3110. The conodont specimens were taken under the electron microscope EM JEOL (Department of Biology, University of Ljubljana).

Results

Description of lithostratigraphic units

Stari Potok Unit

The rocks of the Stari Potok Unit, as smaller occurrences, outcrop on the south-eastern and north-western slopes of Mt. Medvednica (Fig. 2). The unit is characterised by chlorite–muscovite–quartz schists (metapsammites), chlorite–muscovite–quartz–chloritoid schists (Fig. 3A), and meta-limestone interlayers (Fig. 3C), while bright, calcite-rich phyllites intercalated with recrystallized limestones, dolomites, and albite–chlorite schists (derived from tuff) and minor greenschists interlayers dominate at the top of the unit.

The rocks lying beneath this unit, being in a tectonical relationship with other units, were not determined. The rocks which overlie the Stari Potok Unit partly belong to the rocks of the Tusti breg Unit, or this contact with other overlying units is characterized by a fault zone (Fig. 2).

Considering the protoliths of these metamorphic rocks, such as sandstones, pelites, and quartz clastites, which prevail in the central parts together with a carbonate component, gradually occur toward the apical parts of the unit where a correlation with the Dinarides–Alps evolution of the Lower Triassic can be noted (Belak 2005). Moreover, conodont analyses and analyses of detrital granitoid zircons of Permian age indicate that the protolith rocks of the Stari Potok Unit may chronostratigraphically correspond to the Upper Permian or younger age; however, they likely belong to the Lower Triassic.

Isotope age is determined using the K–Ar dating method on synmetamorphic white micas in different rocks of this unit. The obtained isotopic analyses (122.8±4.7 Ma on chlorite–quartz–muscovite–chloritoid schist, 115.6±4.4 Ma on chlo-

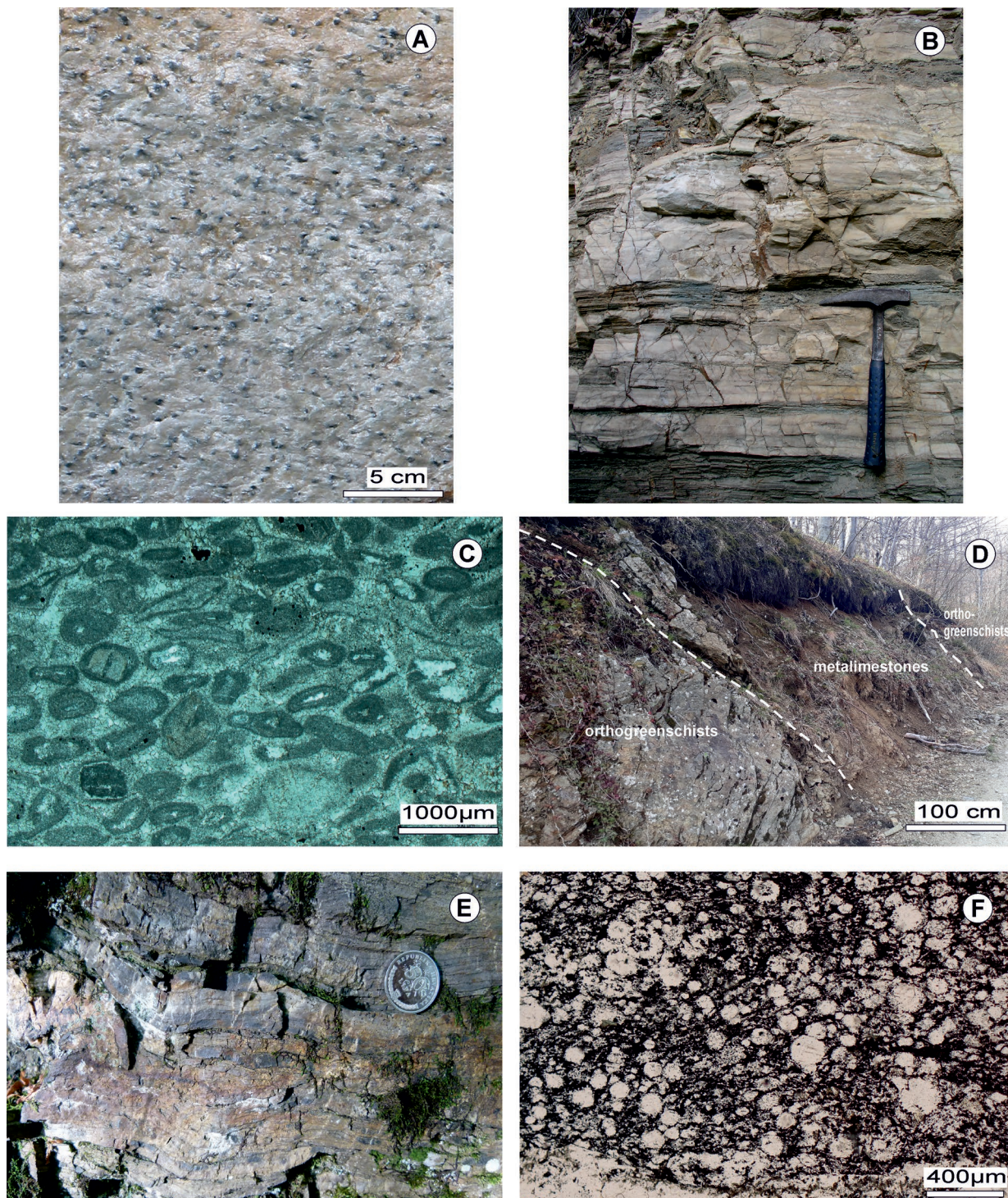


Fig. 3. Field occurrence of: **A** — chloritoid schists (*Stari Potok Unit*); **B** — marbles with green schists interlayers (*Adolfovac Unit*); **C** — metalmestone ooids (*Stari Potok Unit*); **D** — metalimestone interlayer (Anisian – Bithinian to Illyrian) in ortho-green schists (metabazalts) (*Tusti Breg Unit*); **E** — metaradiolarites (*Mrzljak Unit*). Microphotograph of metaradiolarites (**F**) with recrystallized radiolarians in magnetite–hematite matrix (*Mrzljak Unit*).

ritoide–chlorite–quartz–muscovite schist, and 115.5 ± 4.4 Ma on chlorite–quartz–muscovite schist; Fig. 2; Table 1) indicate the metamorphism that occurred during the Early Cretaceous (Aptian). The new results of dating monazite (153 ± 6.9 Ma) in chloritoid schists using the U–Th–Pb method indicate

older metamorphism (Mišur 2017; Mišur et al. 2022 in press).

The mineral paragenesis of the rocks of the Stari potok unit, which consist of chloritoid+white mica+chlorite and quartz, indicates the low-grade metamorphism.

Adolfovac Unit

The Adolfovac Unit, which is built up of marbles, is characterized by sporadic smaller outcrops occurring on the south-eastern part of Mt. Medvednica (Fig. 2).

Thin, ortho-greenschist (metabasalt) interlayers and rare, thin quartz schists (metachert) bands intercalate the marbles in the lower parts of the unit, while chlorite schist (muscovite–chlorite–quartz) interlayers, which originated by metamorphism from basic to intermediate tuff and tuffites (Fig. 3B), occur in the central and apical parts of the unit. Marbles in the upper part of the unit gradually change into grey metalimestone of the Tusti Breg Unit. Taking into account the previously-mentioned continuous lithological sequence of these units, as well as the determined Middle Triassic age of the rocks of the upper part of the Tusti Breg Unit, the protolith age of the Adolfovac Unit is defined chronostratigraphically as the Middle-Triassic.

During magmatic dyke penetration, the rocks of the Adolfovac Unit had undergone contact metamorphism and regional dynamothermal metamorphism of a low grade in the Early Cretaceous.

Tusti Breg Unit

The Tusti Breg Unit occurs on the south-eastern part of Mt. Medvednica and consists of thin layers (5–30 cm) of grey metalimestones intercalated locally with ortho-greenschists (Figs. 2 and 3D). Ortho-greenschists appear as smaller basaltic bodies or as rare dykes. Some dykes break through the metalimestones. The underlying rocks of this unit are made up of rocks of the Stari potok Unit, including rocks of the Adolfovac Unit sporadically, whereas the rocks of the Bliznec Unit overlie the rocks of the Tusti Breg Unit. Middle Triassic age of these rocks is determined on the basis of conodont fossils (Fig. 2). Samples contain conodont elements, but are predominantly fragmented. Associations yield elements of *Gladigondolella* sp., *Paragondolella bifurcata* Budurov & Stefanov, *P. bulgarica* Budurov & Stefanov, and *Paragondolella* sp. (Table 2). This fauna is dated to Anisian, based on the two determined species that co-occur in the Pelsonian (Kovács & Kozur 1980; Kolar-Jurkovšek & Jurkovšek 2019).

Conodonts are partly black to white with CAI (Conodont Alteration Index) values ranging between 5 and 7 (Rejebian et al. 1987). CAI values from CAI 5 (300–480 °C) to CAI value 7 (≥ 490 °C) are characteristic for low-grade metamorphism (Winkler 1979; Kovacs & Árkai 1989; Gawlick et al. 1994). Thermally-modified organic matter and white mica muscovite and paragonite in stilolyte seams of metalimestones point to low grade metamorphism as well. The mineral paragenesis of ortho-greenschists of the Tusti breg Unit reflects the prograde regional dynamothermal metamorphism of the greenschists facies (see the chapter Discussion – Metamorphic zones and geothermobarometric estimations of orthogreenschists).

Table 1: K–Ar white mica and whole rock ages of low-grade metamorphic rocks from Mt. Medvednica metamorphic complex.

Sample	Unit	Rock type	K ₂ O [%]	⁴⁰ Ar (rad) [%]	⁴⁰ Ar (rad) [mol/g]	Age Ma±1s
M-1	SP	MCS	4.738	81.2	8.6570×10 ⁻¹⁰	122.8±4.7
M-2	SP	CMS	2.641	85.4	4.5333×10 ⁻¹⁰	115.6±4.4
M-3	SLJ	MQS	2.171	84.3	3.7257×10 ⁻¹⁰	115.5±4.4
M-4	SLJ	OGS	1.049	65.9	1.8774×10 ⁻¹⁰	120.0±4.0
M-5	SLJ	GS	2.261	85	3.9550×10 ⁻¹⁰	117.6±4.0

SP=Stari Potok, SLJ=Sljeme; MCS=muscovite–chloritoid schist, CMS=chloritoid–muscovite schist, MQS=muscovite–quartzite schist, OGS=ortho-greenschist, GS=greenschist.

Table 2: Conodont distribution in the studied samples of Tusti Breg Unit.

Conodonts	Sample				
	M-2	M-3	M-107B	M-107C	M-107D
<i>Gladigondolella</i> sp.					1
<i>Paragondolella bifurcata</i>	3		2	1	
<i>Paragondolella</i> cf. <i>bifurcata</i>		1			
<i>Paragondolella bulgarica</i>	4				1
<i>Paragondolella</i> cf. <i>bulgarica</i>			1		
<i>Paragondolella</i> sp.	1				

Bliznec Unit

The lower part of the Bliznec Unit consists of black calcite slate and calcite fine-grained metapsammite with thin layers of dark grey metalimestone (Fig. 2). In the central and upper parts of the unit, the carbonate components disappear, and black metapelites including subordinately black, fine-grained metapsammite, thin quartz schist laminae (metachert) and interlayers of greenschists occur. The rocks of the Tusti Breg Unit lie beneath this unit, whereas the rocks of the Mrzljak Unit cover it. The Middle–Upper Triassic age of this unit is determined on the basis of conodont fossils (Fig. 2).

Sample VR-6C: This fauna is marked by abundant platy and ramiform conodont elements. They show high CAI values of 6–6.5. Platform elements are represented by *Paragondolella foliata* Budurov, P. aff. *inclinata* (Kovacs), *Quadralella* ex gr. *polygnathiformis* (Budurov & Stefanov), and *Paragondolella* sp. (Table 3). This conodont fauna characterizes the Uppermost Ladinian–Early Carnian. (Kovács 1983; Chen et al. 2015; Rigo et al. 2018; Kolar-Jurkovšek & Jurkovšek 2019).

Sample-536: Younger Triassic conodonts have been recovered from a single rock sample. The obtained elements are of poor preservation with a high CAI value of 6–7. Specimens are texturally-altered, and due to the significant deformation a single element enabled determination of *Epigondolella quadrata* Orchard. This species ranges from the Late Carnian–Early Norian (Orchard 2014; Rigo et al. 2018; Kolar-Jurkovšek & Jurkovšek 2019).

Mineral paragenesis, vitrinite reflectance, and a kind of coaly substance, as well as the illite Kübler index indicate an epizone or low-grade metamorphism (Belak et al. 1995; Judik et al. 2004, 2008; Belak 2005).

Mrzljak Unit

The lithostratigraphic Mrzljak Unit is characterized by interbeds of quartz schists (metaradiolarite), ortho-greenschists,

Table 3: Triassic Conodonts from the sample VR-6C (Bliznec Unit). **1a–c, 2a–c:** *Paragondolella* aff. *inclinata* (Kovács); **3a–c:** *Paragondolella* sp.; **4a–c:** *Quadralella* ex gr. *polygnathiformis* (Budurov & Stefanov); **5a–c, 6a–c:** *Paragondolella foliata* Budurov; a – oral view, b – aboral view, c – lateral.



and thin paraschist interlayers (metamorphosed shales and fine-grained siliciclastic rocks are enriched locally in a tuff component; Fig. 2). The rocks of this unit are unevenly ferruginous, while in some parts, they are enriched in ore minerals, such as magnetite and hematite. Metaradiolarites correspond to typical, primary well-bedded cherts (radiolarites) intercalated with mm- to cm- thick shale layers; however, they show evidence of deformation-metamorphic textures (crenulation cleavage, slate cleavage; Fig. 3E). A very rich content of recrystallized radiolarians with magnetite and hematite matrix is observed in some microlithons, thereby indicating biogenic genesis with weak terrigenous influence. However, the radiolarian content didn't enable stratigraphic determination. Although the possibility of the existence of similar deep-water facies in (older) Paleozoic cannot be excluded as well, still, the Middle–Upper Triassic age is indicated to the rocks of

the Mrzljak Unit due to its association with the rocks of the Anisian and Upper-Triassic age, as well as the Jurassic age.

Sljeme Unit

The Sljeme Unit has a uniform composition and is built up of ortho-greenschists, which create the main mass of these rocks at Mt. Medvednica and form its main ridge (Figs. 2 and 4A). These ortho-greenschists are characterized by retrograde metamorphism, in which the rocks had undergone lower epidote-amphibolite facies metamorphism followed by lower greenschist facies metamorphism (Fig. 5A–C) (see the chapter Discussion – Metamorphic zones and geothermobarometric estimations of orthogreenschists).

The rocks of the Sljeme unit are in tectonic contact with all units except for the rocks of the Mrzljak Unit.

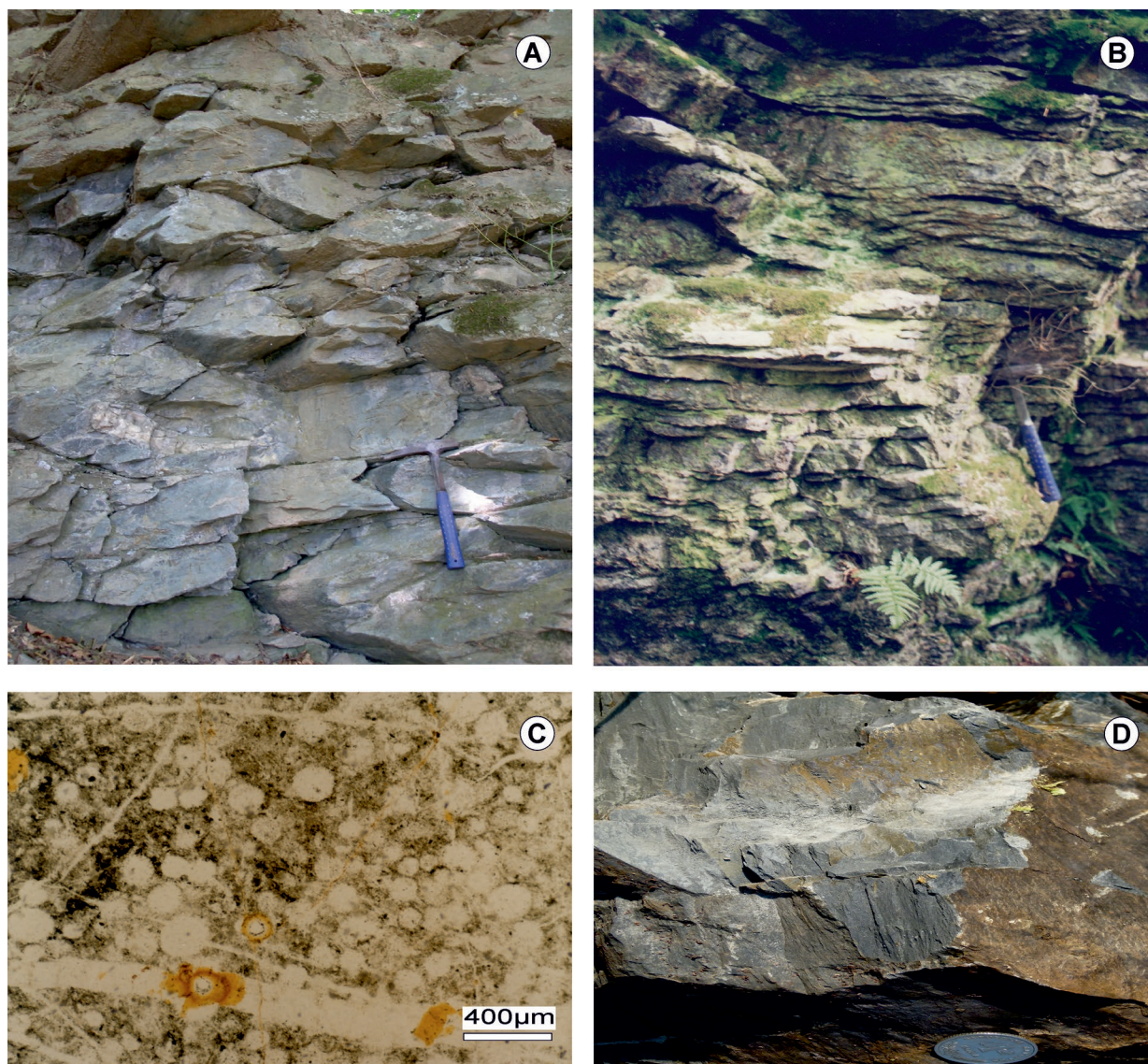


Fig. 4. Field occurrence of: **A** — ortho-greenschists (metabazalts) – relict pillow lava(?) (*Sljeme Unit*); **B** — metaradiolarites (*Risnjak Unit*); **C** — metaradiolarites with recrystallized radiolarians (*Risnjak Unit*); **D** — darkgray metapelites (*Risnjak Unit*).

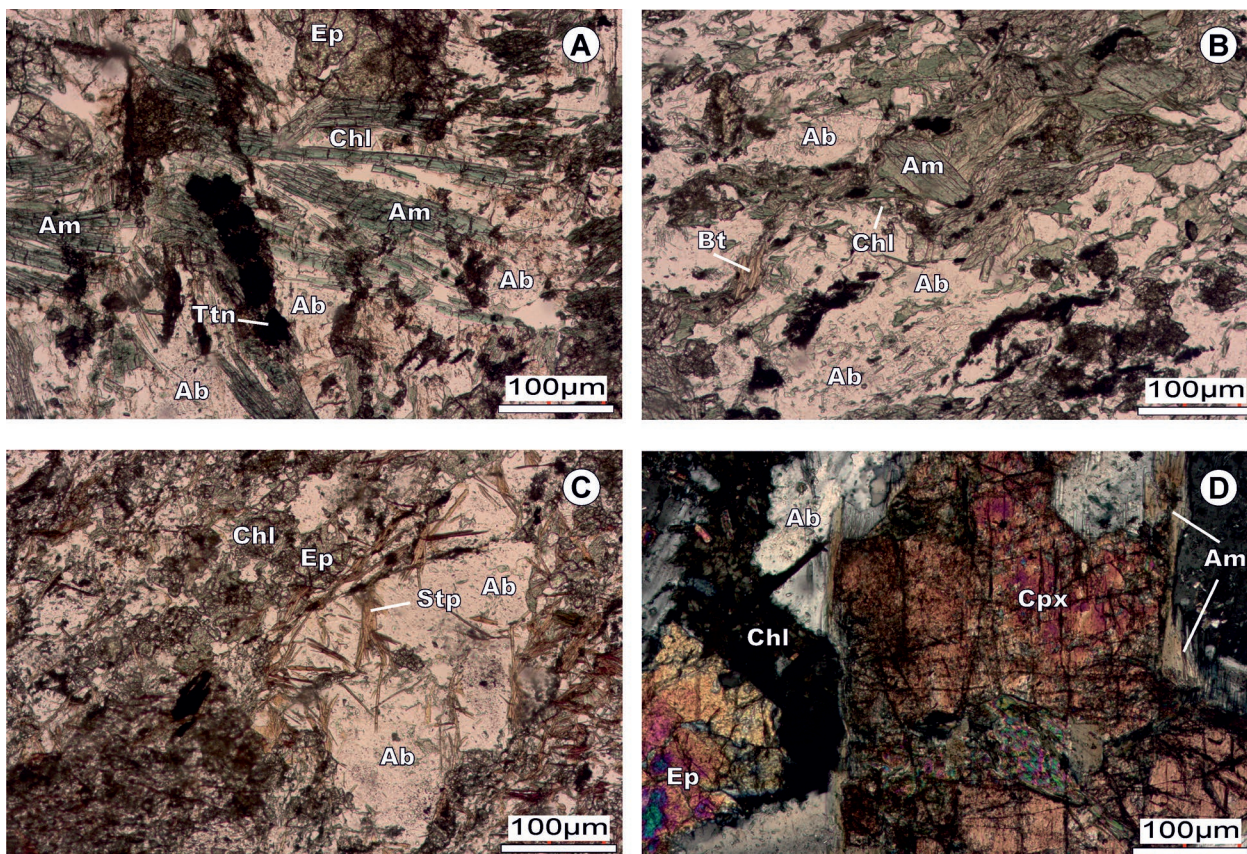


Fig. 5. Microphotographs of thin sections of: **A** — ortho-greenschist – metabasalt (N⁻), sample J-898 (epidote–amphibolite-greenschist facies; *Sljeme Unit*); **B** — ortho-greenschist – metabasalt (N⁻), sample Zelj-23 (greenschist facies – middle parts; *Sljeme Unit*); **C** — ortho-greenschist – metabasalt (N⁻), sample Run-1 (greenschist facies – lower parts; *Sljeme Unit*); **D** — ortho-greenschist – metabasalt (N⁺), sample Md-4 (greenschist facies with relict of clinopyroxene; *Tusti Breg Unit*). Mineral abbreviations after Kretz (1983): Ab=albite, Am=amphibole, Bt=biotite, Chl=chlorite, Cpx=clinopyroxene, Ep=epidote, Pl=plagioclase, Stp=stilpnomelane, Ttn=titanite.

The radiometric data obtained by the K–Ar dating method (115–120 Ma; Table 1) point to the retrograde of Early Cretaceous metamorphism of ortho-greenschists. The protolith rocks of the greenschists represented by basalts and diabase have not been chronostratigraphically determined. However, its Late Triassic to Middle Jurassic(?) protolith magmatic age is assumed on the basis of their very similar geochemical characteristics (see the chapter – Bulk rock chemistry and Tectonomagmatic significance) with Upper-Triassic to Middle Jurassic basalts from ophiolite melange on the Medvednica and Kalnik Mts. (Slovenec & Lugović 2009, 2012; Slovenec et al. 2010, 2011).

Risnjak Unit

The lithostratigraphic Risnjak Unit consists of dark grey metapelites, metapsammites, and metaradiolarites, whose outcrops occur in apical western parts of the south-eastern slope of Mt. Medvednica, as well as on its northern slopes (Fig. 2). The rocks of this unit are overthrust by ortho-greenschists of the Sljeme Unit on the southern side, but reversely displaced in relation to the younger rocks that surround them on the

northern side. Metapelites have pronounced foliation, which is subparallel to the bedding and therefore, the primary characteristics of the bedding plane are difficult to observe (Fig. 4D). The lamination is observable macroscopically and occurs as a millimetre change of colour and separation of green grey to dark grey laminae richer in organic component. Metaradiolarites are composed of recrystallized quartz with rare white mica and chlorite sheets (Fig. 4B). Recrystallized radiolarians are recognizable in some microlithons (Fig. 4C). The association of this facies points to the sedimentation of the rocks in a deeper marine basin, below the carbonate compensation depth (CCD). Due to the fact that there is no chronostratigraphic paleontological data for the rocks of the Risnjak Unit, its belonging to the Mesozoic or Paleozoic deeper marine basins can only be assumed. However, when taking into consideration the lithological characteristics of these rocks, it is evident that the rocks of this unit do not show similarities with Upper-Paleozoic rocks of the Dinarides or Tisza and therefore, their Jurassic(?) age is presumed.

Vitrinite reflectance and a kind of coaly substance, together with the illite Kübler index, point to an epizone or low-grade metamorphism (Belak et al. 1995; Judik et al. 2004, 2008).

Petrography and mineral chemistry of ortho-greenschists

The ortho-greenschists of Mt. Medvednica are fine- to coarse-grained (≤ 0.5 mm up to 5 mm), dark to light green rocks, having different textural and structural characteristics. Their textures vary between nematogranoblastic to lepidogranoblastic with a relict ophitic texture, and some coarse-grained varieties have a blastophitic texture (Fig. 5). Prograde and retrograde metamorphism of ortho-greenschists from Mt. Medvednica is identified on the basis of petrographic investigations of rocks and roentgen diffraction of some mineral phases. The criteria for the choice of rock samples of greenschist facies for detailed chemical analyses of mineral phases were the grade and type of metamorphism. From the rocks that recorded retrograde metamorphism, five samples (J-898, Slj-6, Želj-23, Želj-26 and Run-1) from the Sljeme Unit were chosen for further analyses, whereas sample Md-4 from the Tusti Breg Unit and sample M-710 from the Bliznec Unit were selected as samples that evidence prograde metamorphism.

Amphibole

The representative chemical composition of amphiboles is shown in Suppl. Table S1, and their crystallochemical classification follows Leake et al. (1997), in Figure 6A. In the sample J-898, which recorded retrograde metamorphism from the Sljeme Unit, the core of amphibole corresponds to Mg-hornblende and its rim to actinolite (Fig. 7A). The SiO_2 content varies between 46.54 and 50.87 wt% or 7.049 and 7.494 Si p.f.u. The chemistry of actinolite ranges from limited values being characteristic for Mg-hornblende ($\text{SiO}_2=50.30$ wt%, $\text{Al}_2\text{O}_3=3.50$ wt%, $\text{TSi}=7.512$ a.p.f.u.) up to $\text{SiO}_2=52.56$ wt% and $\text{Al}_2\text{O}_3=1.81$ wt%, with $\text{Si}=7.734$ p.f.u. in tetrahedral coordination. In the classification diagram, analyses of amphiboles from the sample Slj-6 correspond to a broader crystallochemical range of actinolite (Fig. 6A). However, the core analyses of actinolite in this sample indicate chemistry close to the limited values of Mg-hornblende ($\text{SiO}_2=51.06$ wt%, $\text{Al}_2\text{O}_3=3.30$ wt% i $\text{TSi}=7.535$ a.p.f.u.), whereas rims are more acid and contain less aluminium (up to $\text{SiO}_2=54.87$ wt%, $\leq \text{Al}_2\text{O}_3=0.82$ wt% and up to $\text{TSi}=7.896$ a.p.f.u.). The content of TSi in the actinolites (sample Želj-23) varies in the narrow range from 7.660 a.p.f.u. in the core to 7.841 a.p.f.u. toward the grain rim. Amphibole analyses from retrograde metamorphosed lower greenschists facies (sample Želj-26) are plotted in the classification diagram in a narrow actinolite field with low standard deviation of atom contents in the formula, having a mean value of TSi 7.870 a.p.f.u. (Fig. 6A). Mg-hornblende occurs rarely at the rim of the grains in the samples of prograde type of metamorphism of the Tusti Breg and Bliznec Units (sample Md-4) (Fig. 7A). Its chemistry varies in this sample from the limited values with actinolite ($\text{TSi}=7.496$ a.p.f.u.) to values being typical for Mg-hornblende ($\text{TSi}=7.431$ a.p.f.u.). In the same sample, the composition of actinolite varies from limited values of Mg-hornblende ($\text{TSi}=7.496$ a.p.f.u.) at the

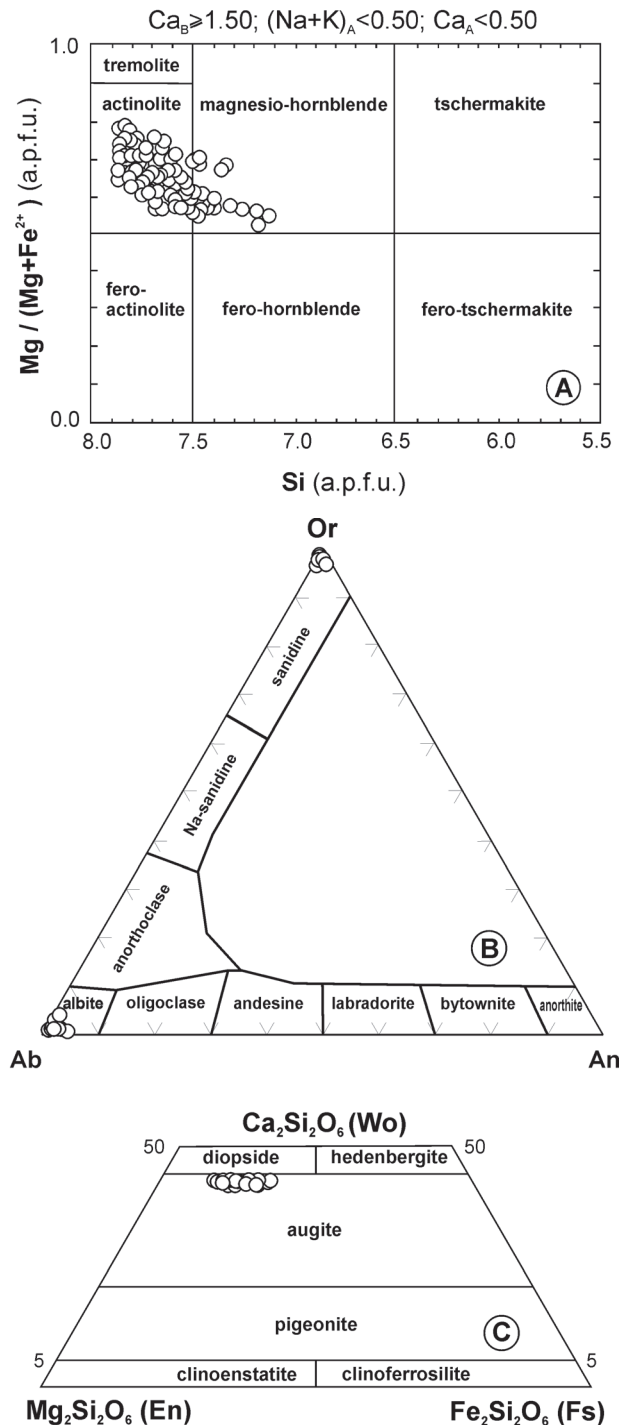


Fig. 6. Classification diagrams for: A — calcium amphibole [$\text{Si-Mg}/(\text{Mg}+\text{Fe}^{2+})$ plot (Leake et al. 1997)], B — feldspar [Ab–An–Or plot (Deer et al. 1992 and Dana et al. 1993)] C — clinopyroxene [En–Fs – Wo ($\text{Mg}_2\text{Si}_2\text{O}_6\text{--Fe}_2\text{Si}_2\text{O}_6\text{--Ca}_2\text{Si}_2\text{O}_6$) plot (Morimoto et al. 1998)], from ortho-greenschists from Mt. Medvednica metamorphic complex.

rims of grains to $\text{TSi}=7.876$ a.p.f.u. in the core. Identical increase of Si content in actinolite from the rim ($\text{TSi}=7.496$ a.p.f.u.) toward the core of the grain ($\text{TSi}=7.935$ a.p.f.u.) is recorded in the sample M-710.

Feldspar

The representative chemical composition of feldspars is presented in Suppl. Table S2 and their classification diagram in Figure 6B. Albites that contain a low amount of anorthite component ($An_{0.0-3.0}$) dominate in all types of greenschists from Mt. Medvednica. However, K-feldspar ($An_{1.2-13.8}Ab_{0.9-1.2}Or_{85.3-97.8}$) occurring as tiny inclusions in albite is found in the lower zone of the greenschist facies. Laminae, which still have a higher anorthite component ($An_{12-18.2}$), have been found to coexist with albite (“peristerite gap”) while studying the spatial distribution of elements in albite in the sample J-898 from the Sljeme Unit. These findings point to the transition between the greenschist facies to the epidote–amphibolite facies, where oligoclase-in isograde coexists with Mg-hornblende, chlorite, and epidote (Spear 1995).

Clinopyroxene

The representative chemical composition of clinopyroxenes is presented in Suppl. Table S3 and their classification diagram in the Figure 6C. Clinopyroxenes that have an augite composition ($Wo_{42.7-44.6}En_{36.4-43.3}Fs_{12.7-20.8}$) are determined only in the ortho-greenschists of the Tusti Breg Unit. They occur as relict magmatic minerals, which are selectively replaced with amphibole, chlorite, and epidote during metamorphism. Metamorphic replacement of augite began from the rim toward the core of the grains. Those augite grains, being more weakly-replaced, vary in size up to 1 mm and show prismatic habitus with albite intergrowths that form a typical ophitic texture (Fig. 5D).

Epidote

The representative chemical composition of the epidote is given in Suppl. Table S4. The epidote grains in the samples of greenschists (J-898, Slje-6, Želj-23, Želj-26 and Run-1) from the Sljeme Unit show a continuous range of Fe^{3+} content, while the occurrence of a miscibility gap (Raith 1976) wasn't observed. Epidote grains are characterized by $Al \leftrightarrow Fe^{3+}$

oscillations with the pistacite molecule Ps_{28-34} and 73.5 to 92 mol.% Al_2FeEp . The epidote composition depends on oxygen fugacity (f_{O_2}), the chemical composition of the rock, and its mineral paragenesis (Holdaway 1972; Liou 1973). Epidotes from the rocks of the Sljeme Unit are not an indicator of metamorphic grade. However, epidotes from greenschists of the Tusti Breg Unit (the samples Md-4 and M-710) have significant substitution $Al \leftrightarrow Fe$ rim-core (Fig. 7B), which is typical for a prograde type of metamorphism (Raith 1976; Liou et al. 1985; Beiersdorfsser & Day 1995). Their core shows variation in the pistacite component $Ps_{29.4-32.6}$ and mol.% $Al_2FeEp_{78.38-86.52}$, whereas their rims are characterized by $Ps_{17.5-28.2}$ and mol.% $Al_2FeEp_{46.91-77.79}$. A similar compositional evolution pointing to prograde metamorphism recorded epidotes in the metamorphic areas of the Penninic series in the Tauern window in Austria, in greenschist, garnet amphibolite, and eclogite facies (Raith 1976). The same author concluded that the Fe^{3+} content in epidote decreases with increasing metamorphic grade, which is not only the consequence of temperature and pressure change, but also of the oxidation state in the rock during prograde metamorphism.

Chlorite

The representative chemical composition of chlorite is given in Suppl. Table S5 and its classification in Figure 8A,B. According to the classification of Hey (1954), the studied chlorites belong to the picnochlorite–ripidolite group with some tendency to brunsvigite, whereas in the classification diagram of Bailey (1980), they plot into the clinochlore field since they have a high content of chamosite molecule, as well as into the chamosite field with a high content of clinochlore molecule. The chlorites from the rocks of the Sljeme Unit do not show the prograde substitution $Mg \leftrightarrow Fe$ (FM) in which the Mg/Fe ratio increases as the grade of metamorphism increases (Cooper 1971). Therefore, the chemical composition of chlorite from the rocks of the Sljeme Unit is not an indicator of the grade of metamorphism, which is perhaps due to the changes of chemical composition and the oxidation state of the rocks in the course of their geodynamic evolution.

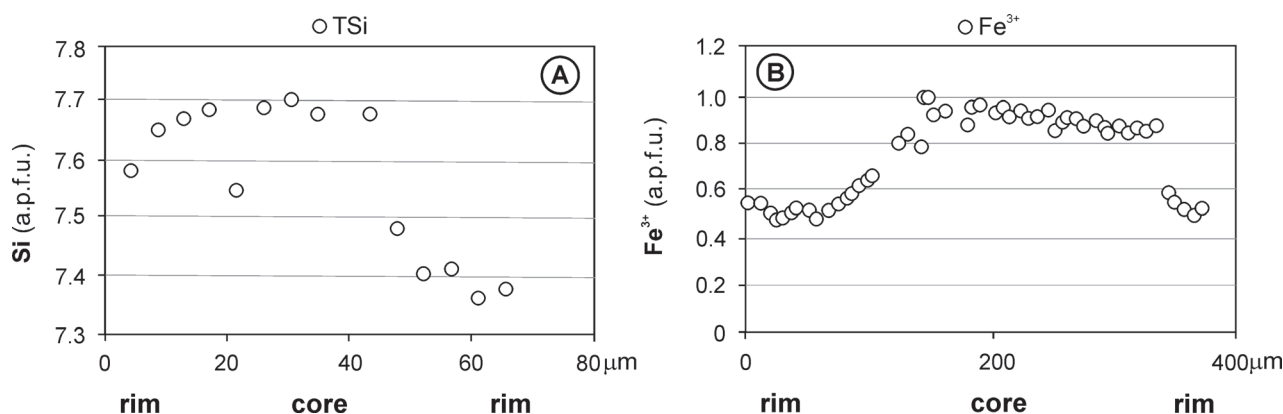


Fig. 7. Chemical profile through the prograde grain of amphibole (A) and epidote (B) in sample Md-4 (Tusti Breg Unit).

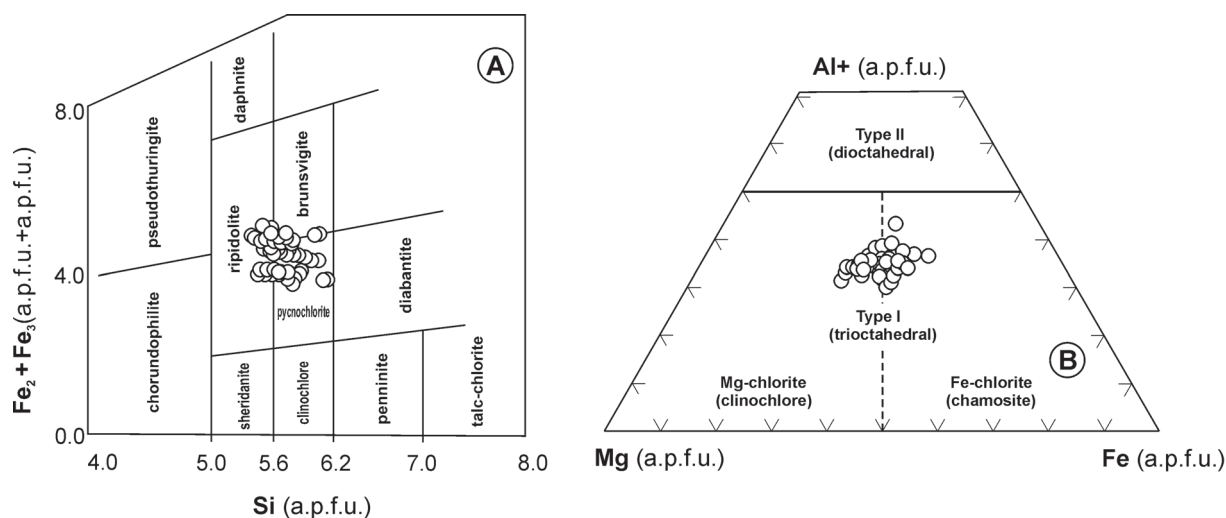


Fig. 8. Classification diagrams for chlorite: **A** — Si–Fe/(Fe+Mg) plot (Hey 1954); **B** — Mg–Fe–^{VI}(Al+Cr+Fe³⁺) plot (Zane & Weiss 1998) from ortho-greenschists from Mt. Medvednica metamorphic complex.

The chlorites from the greenschists of the Tusti Breg and Bliznec Units (samples M-710 and Md-4) also do not define the type of metamorphism. In addition, the chlorites from the greenschists of the Sljeme Unit and the Tusti Breg and Bliznec Units show differences in the Tschermak substitution (TK), which includes: $Al^{IV}Al^{VI}Si_{-1}Mg_{-1}$, $Al^{IV}Cr^{3+}Si_{-1}Mg_{-1}$ and $Al^{IV}_2Ti^{4+}Si_{-2}Mg_{-1}$, as also “dioctahedral” substitution (AM) Al_2Mg_{-3} , producing vacancy in octahedral sheets. The intensity of TK substitution can be represented in a two-component diagram Al^{IV} vs. $(Al^{VI}+2Ti+Cr)$, where the line 1:1 points to the TK substitution and its intensity, and the departure of this line is expressed by the formula: $\Delta = Al^{IV} - (Al^{VI} + 2Ti + Cr)$ (Zane et al. 1998). Higher negative values of Δ indicate stronger “dioctahedral” AM substitution, meaning more “vacancy” in octahedron coordination. The values >0 exclude “dioctahedral” AM substitution and indicate that R^{3+} cations are included as well, which are not present in the Tschermak substitution (e.g. $Fe^{3+} \leftrightarrow Al$). The chlorites from the rocks of the Sljeme Unit are characterized by positive and negative Δ values, whereas chlorites from the rocks of the Tusti Breg and Bliznec Units have negative Δ values.

Biotite and stilpnomelane

The representative chemical compositions of biotite, biotite characterized by deficit in the interlayer charge, and stilpnomelane is given in Suppl. Tables S6 and S7. From the crystallochemical point of view, biotite shows a homogeneous composition, the $Fe/(Fe+Mg)$ ratio varies from 0.52 to 0.53, while in the $Al^{IV} : Fe/(Fe+Mg)$ diagram (not shown; Deer et al. 1962), the studied biotites are plotted between the end members annite and phlogopite. In the greenschists of the Sljeme Unit biotite (sample Slj-6), altered biotite (sample Želj-23) and stilpnomelane (sample Run-1 and Želj-26) were identified. According to Winkler (1979), biotite in the low-grade metamorphism, which coexists with phengite±chlorite and

quartz, corresponds to the Barrow-biotite zone in metapelites, whereas the biotite occurrence in the mineral parageneses in which phengite fails, has a different petrogenetic meaning and may occur in very low-grade metamorphism as well. Biotite from the sample Slj-6 coexists with phengite, chlorite, and Al-rich actinolite, whereas biotite characterized by the inter-layer charge deficit (±stilpnomelan) from the sample Želj-23 occurs together with phengite, chlorite and actinolite (mean rich in Al). In the mineral parageneses where biotite fails, stilpnomelane occurs with phengite, chlorite and actinolite characterized with a low Al content.

K-white mica

The representative chemical compositions of white micas are shown in Suppl. Table S8. The analysed white micas from the greenschist of the Sljeme, Tusti Breg, and Bliznec Units are phengites. Usually, phengites are considered minerals being typical for high pressure/low temperature metamorphic terrains, however, Sassi et al. (1994) advised caution in such conclusion and emphasized that phengite can be formed in conditions from low to middle pressures in the greenschist facies of rocks with an appropriate chemical composition.

Bulk rock chemistry

The chemical composition of representative rock samples is shown in Suppl. Table S9. Volatile components (H_2O+CO_2) vary from 2.23 to 9.26 wt%. The content of main elements in greenschists from the metamorphic complex of Mt. Medvednica is typical for the altered basic magmatic rocks. The chemical composition of the studied metabasalt rocks is additionally influenced by prograde dehydration and retrograde rehydration. There is no significant correlation between Si, Na, and K with other elements, except for K with Rb. Therefore, the $Nb/Y - Zr/TiO_2 * 0.0001$ classification diagram, which is more

appropriate for altered volcanic rocks and based on incompatible trace elements, as well as proposed by Winchester & Floyd (1977), was used instead of the classic TAS classification. In this diagram, the analysed rocks are plotted inside a subalkaline basalt field (Fig. 9A). The affinity of the studied metabasalts toward tholeiitic series is documented in the Y–Zr diagram (Barrett & MacLean 1994; Fig. 9B). In the Ni vs. Ti/Cr diagram, the samples are mostly plotted into a high-Ti (MORB) area (Beccaluva et al. 1983; Fig. 9C). Only the samples of Anisian age from the Tusti Breg Unit, those having the lowest Ni contents, show weak affinity toward low-Ti basalt rock series (Fig. 9C).

The trace element abundance patterns normalized to N-MORB (values from Sun & McDonough 1989) for the studied metabasalts are shown in Fig. 10A, and chondrite normalized (values from Taylor & McLennan 1985) REE patterns are displayed in Fig. 10B. All rocks show light ion lithophile elements (LILE), variable enrichment and uniform, a slightly inclined profile from Th to Lu $[(Th/Lu)_{N-MORB}=0.38-1.34]$ at a concentration level of 1 to 10 times relative to N-MORB, as well as a Ta–Nb negative anomaly of low intensity $[(Nb/La)_{N-MORB}=0.18-0.54]$. The LILE variations are common for altered basic rocks (e.g. Rollinson 1993). The metabasalts display convex REE patterns, enriched 18–40 times relative to chondrite, and show slight enrichment of light rare earth elements (LREE) compared to heavy rare earth elements (HREE) $[(La/Lu)_{CN}=1.14-1.74]$. The LREE enrichment is possible in the course of alteration of the basic rocks (Wood et al. 1976), but also through the process of contamination of N-MORB magma with enriched MORB (Wilson 1989). The analysed samples show slight Eu anomaly ($Eu/Eu^*=0.88-1.17$) typical for low accumulation or fractionation and removal of plagioclase.

Discussion

Metamorphic zones and geothermobarometric estimations of ortho-greenschists

The mineral composition of the studied metabasalt rocks from the metamorphic complex of Mt. Medvednica, which originated under conditions of low-grade metamorphism, is determined by reactions taking place in the multicomponent chemical system. The content of tremolite, edenite, glaucophane, and tschermakite molecules in amphibole is controlled by the interaction with albite, clinozoisite, chlorite, quartz, and H₂O and is typical for the individual metamorphic facies. In this way, the tremolite molecule dominates in the amphiboles of greenschist facies, the glaucophane molecule prevails in the amphiboles of blueschist facies, the tschermakite molecule in the amphiboles of the amphibolite facies, and the edenite molecule in the amphiboles of the epidote–amphibolite facies (Brown 1977; Holland & Richardson 1979).

The following metamorphic zones can be distinguished based on the amphibole composition (Fig. 2), biotite, and stilpno-

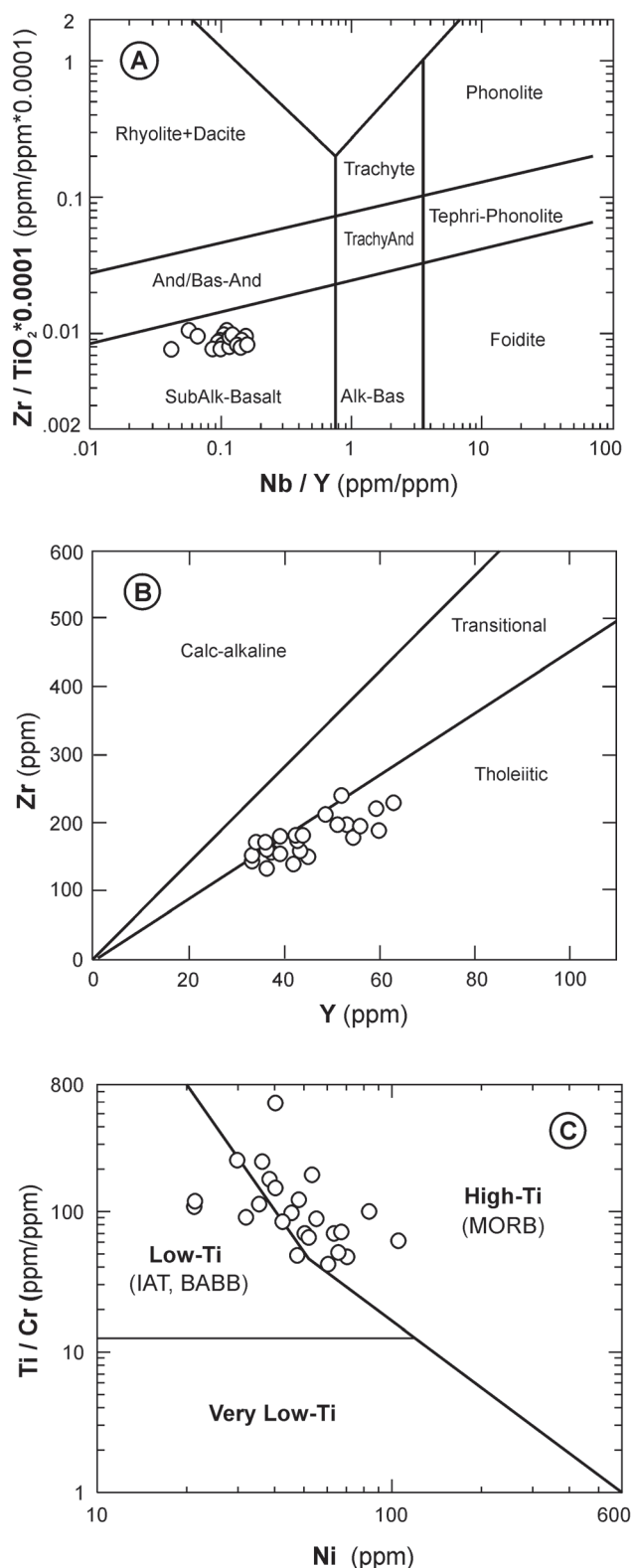


Fig. 9. Classification and discrimination diagrams: **A** — Nb/Y–Zr/TiO₂*0.0001 (Winchester & Floyd 1977); **B** — Y–Zr (Barrett & MacLean 1994); **C** — Ni–Ti/Cr (Beccaluva et al. 1983) for the ortho-greenschists from Mt. Medvednica metamorphic complex. IAT= island-arc tholeiites, MORB=mid-ocean ridge basalts, BABB= back-arc basin basalts.

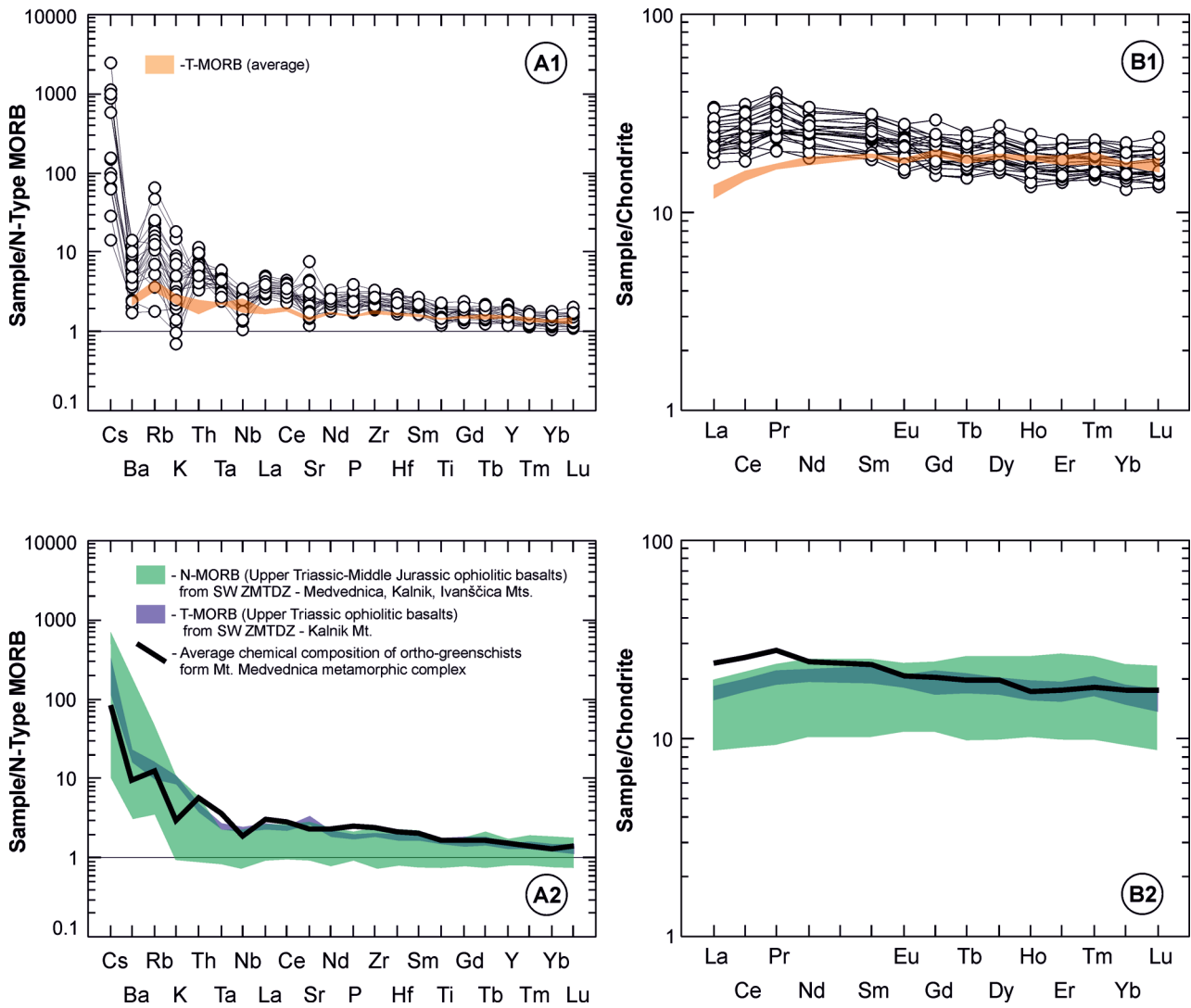


Fig. 10. N-MORB-normalised multielement (A) and REE (B) patterns for the ortho-greenschists from Mt. Medvednica metamorphic complex. Normalisation values are from Sun & McDonough (1989) for N-MORB pattern, and from Taylor & McLennan (1985) for REE pattern. Field for average T-MORB (Klein 2003; Geshi et al. 2007), Upper Triassic T-MOR basalts from the Mt. Kalnik ophiolite mélange and Upper Triassic–Middle Jurassic N-MOR basalts from Medvednica, Kalnik and Ivanščica Mts. ophiolite mélanges (Slovenec & Lugović 2009, 2012; Slovenec et al. 2010, 2011) are plotted for correlation constraints.

melane occurrences in the ortho-greenschists of Mt. Medvednica, thereby showing retrograde metamorphism (the Sljeme Unit): (a) epidote-amphibolite facies, with metamorphic zone: Mg-hornblende+oligoclase_{an18,2}; (b) upper greenschist facies with a metamorphic zone: actinolite (high Al content)+albite+Fe–Mg chlorite+epidote_{ps33}+biotite+phengite; (c) “central” parts of greenschist facies with a metamorphic zone: actinolite (middle Al content)+albite±clinochlore_{xMg0.55–0.59}+epidote_{ps33}+biotite characterized by interlayer charge deficit ±stilpnomelane+phengite; (d) lower greenschist facies, with metamorphic zone: actinolite (low Al content)+albite±orthoclase+clinochlore_{xMg0.52–0.54}+epidote_{ps32}+phengite+ stilpnomelane.

In the ortho-greenschists record of prograde metamorphism (Tusti Breg Unit), the following metamorphic zones are recognized: (a) lower greenschist facies with the metamorphic

zone: actinolite+albite+epidote_{ps-30}+clinochlore_{xMg0.53}; (b) upper greenschist facies with the metamorphic zone: Mg-hornblende+actinolite (high Al content)+albite+epidote_{ps-15}+clinochlore_{xMg0.60}±biotite.

In the Sljeme Unit, the metamorphic zone (a) is typical for the lower parts of the epidote–amphibolite facies at a temperature of 450 °C to 500 °C and pressure of 4–5 kbar (e.g. Brown 1977; Plyusnina 1982; Gerya et al. 1997). The metamorphic zone (b) points to the upper parts of the greenschist facies with a temperature of 450 °C and pressure of 3–4 kbar (e.g. Plyusnina 1982; Brown 1977; Fig. 11; Suppl. Table S1). The temperature of 400 °C and pressure of 3–4 kbar (e.g. Brown 1977; Bucher & Frey 1994) correspond to the metamorphic zone (c) in the central parts of the greenschist facies, whereas the temperature between 350 and 400 °C and pressure

of 2–5 kbar (e.g. Brown 1977; Bucher & Frey 1994; Spear 1995) is typical for the metamorphic zone (d), which characterizes the lower parts of the greenschist facies.

In the Tusti Breg Unit, with recorded prograde metamorphism, the metamorphic zone (a) of the lower greenschist facies is characterized by a temperature of about 350 °C and a pressure of ≤ 2 kbar (e.g. Brown 1977; Bucher & Frey 1994; Spear 1995; Fig. 11; Suppl. Table S1), whereas the metamorphic zone (b) of the upper greenschist facies indicates a temperature of about 450 °C and a pressure of ~ 2 kbar (e.g. Brown 1977; Plyusnina 1982; Gerya et al. 1997; Fig. 11).

Amphiboles from the greenschists of the Sljeme Unit (samples J-898, Slj-6, Želj-23 i Želj-26) are characterized by a higher content of glaucophane, edenite, and tschermakite molecules in the core, as well as an increase of tremolite molecules toward the rims (Suppl. Table S1).

However, the amphiboles of the ortho-greenschists from the Tusti Breg Unit (the samples Md-4 i M-710) have a very low content of the glaucophane component with significant tschermakite substitution (Suppl. Table S1). These greenschists have a preserved relict ophitic texture and therefore, they could not have originated through the retrograde process from amphibolite; however, their genesis is linked to prograde metamorphism up to the lower part of the epidote–amphibolite facies.

Chemical analyses of amphiboles from the rocks of the Sljeme Unit show increased Na content in B site (rarely up to barrosite values) in the core of the mineral grains, which could point to the origin of the retrograde greenschist from the blueschist facies or from the transitional zone between the blueschist and greenschist facies (Fig. 12). In amphiboles from the ortho-greenschist of the Tusti Breg- and Bliznec Units, the tschermakite substitution and small increase of Na in A_{site} (edenite component) are evident, while the Na content in B_{site} in all of the analysed amphiboles varies from actinolite to Mg-hornblende ($j < 0.1$ a.p.f.u.). This, according to Brown (1977), indicates pronounced low pressure, i.e., temperature influence in the metamorphic reaction, and can indicate “acceleration” or skipping of the reaction. The actinolite core could be preserved due to the sluggishness of the reactions (Grapes & Graham 1978). The P–T path of greenschists from the Mt. Medvednica is shown in Figure 12.

Tectonomagmatic significance

The studied ortho-greenschists correspond predominantly to the high-Ti metabasalts, which typically evolve in the area of mid-oceanic-ridges (MORB-type; Beccaluva et al. 1983; Fig. 9C). Only a smaller number of samples from the Tusti Breg Unit shows weak affinity to basalts, which may have originated in an orogenic tectonic setting. All rocks show weakly-expressed negative Nb anomaly (Fig. 10A1), which is typical for magmas related to a suprasubduction zone (SSZ; e.g. Pearce 1982). The Nb anomaly is most pronounced in the metabasalts from the Tusti Breg Unit. This can point to the rare presence of earlier subducted components in the melt

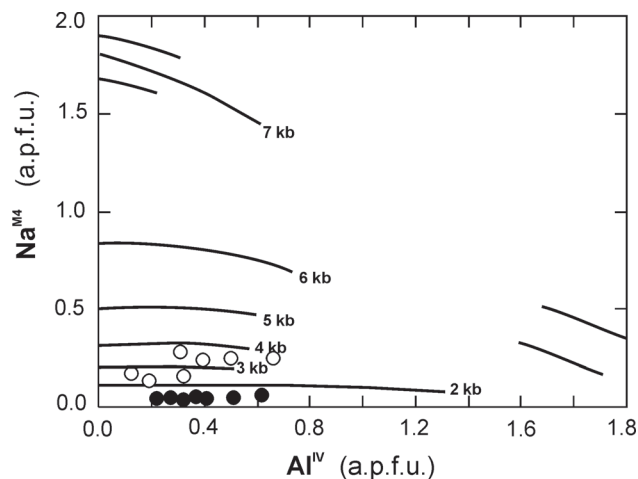


Fig. 11. Al^{IV} – Na^{M4} pressure discrimination diagram (Brown 1977; Laird et al. 1984) for amphiboles from ortho-greenschists from Mt. Medvednica metamorphic complex. White dot=prograde and retrograde phase (Sljeme Unit); black dot=prograde phase (Tusti Breg Unit).

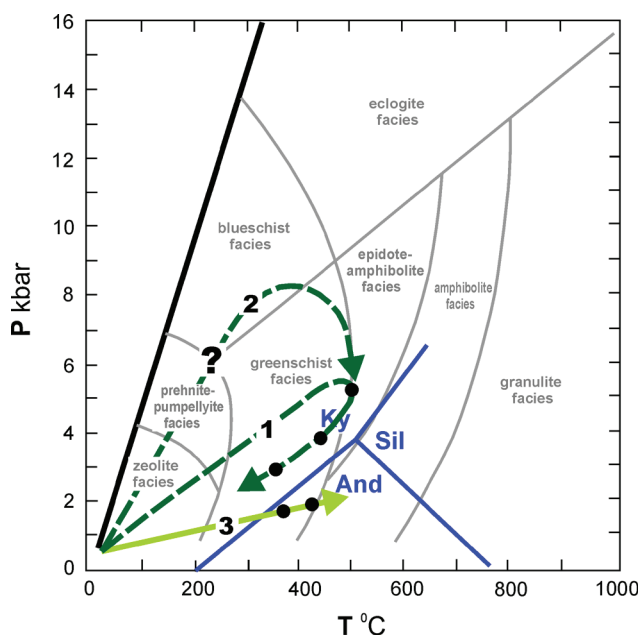


Fig. 12. P–T path (after Spear 1995) for ortho-greenschists from Mt. Medvednica metamorphic complex. Prograde and retrograde phase (Sljeme Unit: 1=metamorphic phase of epidote amphibolite facies, 2=possible retrograde reaction path of ortho-greenschists from the rocks of blueschists facies; Tusti Breg Unit: 3=prograde phase). And=andalusite; Ky=kyanite; Sil=sillimanite.

from which the studied rocks were generated. In the Th–Ta/16–Hf/3 discrimination diagram following Wood (1980), the most greenschists (dominant from Sljeme Unit) are plotted in the field of normal mid-ocean ridge basalts (N-MORB) with the tendency of enrichment to the E-MORB-type (Fig. 13A). Such characteristics may be indicative of transitional mid-ocean ridge basalts (T-MORB-type) affinity (e.g. Klein 2003;

Geshi et al. 2007) as shown in Figures 10A1,B1 and 13A,B. However, the greenschists that show evidence of prograde metamorphism, whose protoliths were Anisian basalts (Tusti Breg Unit; Fig. 2), indicate their possible connection with island arc tholeiites (IAT, Fig. 13A). These rocks appear as smaller basaltic bodies or as dykes. In the Ta/Yb vs. Th/Yb

discriminant diagram (following Pearce 1983; Fig. 13B) and in the SiO₂/100–Na₂O–TiO₂ diagram and Al^{IV}–Ti-diagram (following Beccaluva et al. 1989, Fig. 14A,B), where the chemical composition of the primary clinopyroxenes is considered, the studied rocks showed the same affinities. In short, it is clear that the protoliths of the studied greenschists from

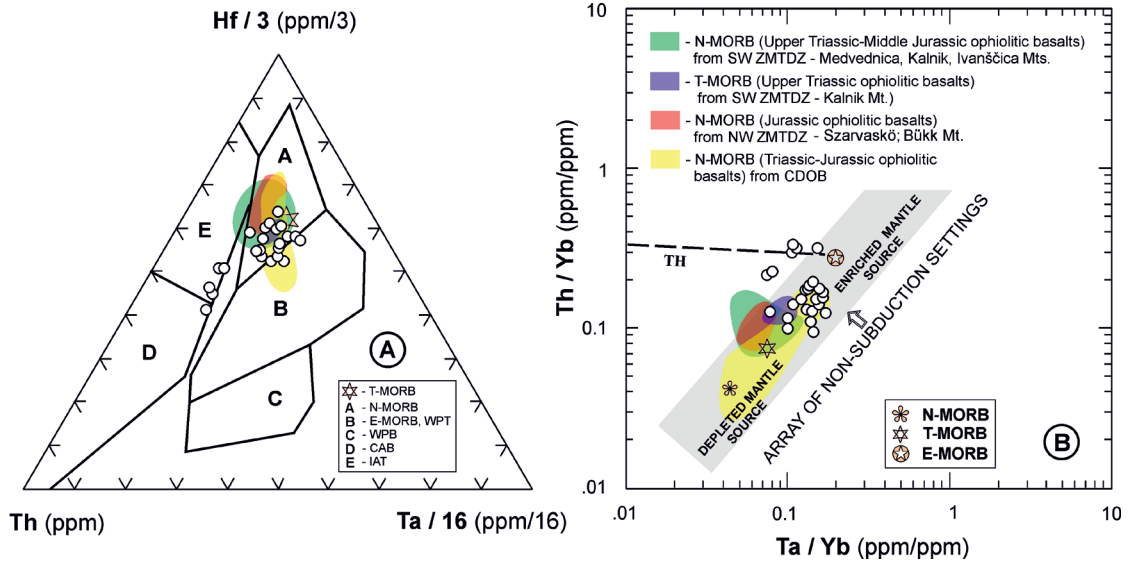


Fig. 13. Discrimination diagrams for the ortho-greenschists from Mt. Medvednica metamorphic complex. **A** — Th–Ta/16–Hf/3 diagram (Wood 1980). A – normal mid-ocean ridge basalts (N-MORB); B – enriched MORB (E-MORB) and within-plate tholeiites (WPT); C – alkaline within-plate basalts (AWPB); D – calc-alkali basalts (CAB); E – island-arc tholeiites (IAT). **B** — Ta/Yb–Th/Yb diagram (Pearce 1983). N-MORB and E-MORB are from Sun & McDonough (1989), T-MORB are from Klein (2003) and Geshi et al. (2007). Field for Jurassic extrusives from the northeastern part of ZMTDZ (Szarvaskő–Darnó complexes in Mt. Bükk; Downes et al. 1990; Harangi et al. 1996; Aigner-Torres & Koller 1999; Kiss et al. 2012) and basalts from CDOB (Lugović et al. 1991; Trubelja et al. 1995) are plotted for correlation constraints.

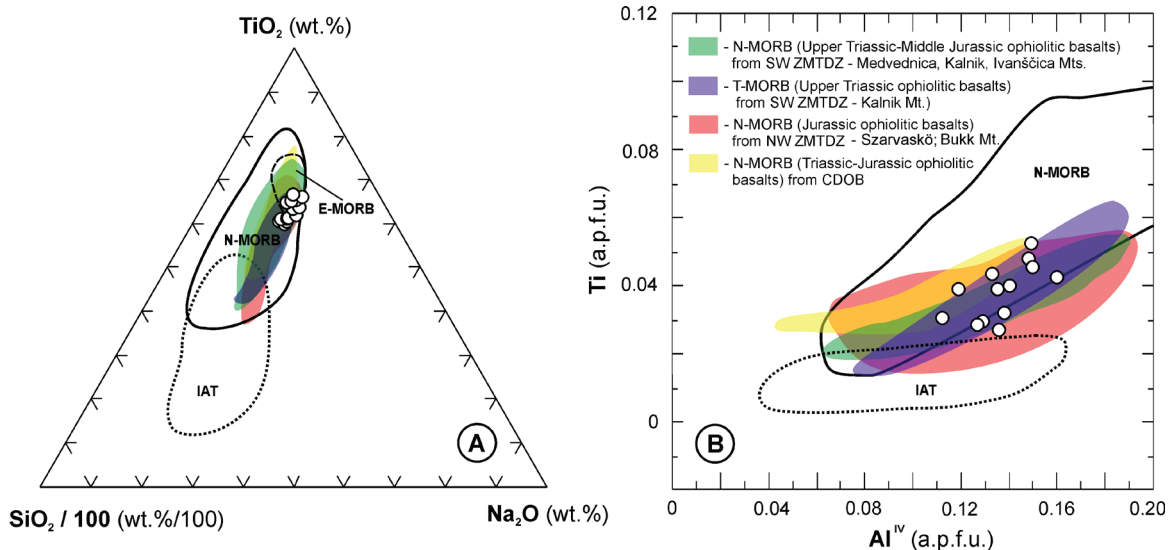


Fig. 14. Discriminant diagram SiO₂/100–Na₂O–TiO₂ (**A**) and Al^{IV}–Ti (**B**) (simplified after Beccaluva et al. 1989) for clinopyroxene from ortho-greenschists from Mt. Medvednica metamorphic complex. IAT= island-arc tholeiites, E-MORB= enriched mid-ocean ridge basalts, N-MORB= normal mid-ocean ridge basalts. Field of clinopyroxene composition of the Jurassic extrusives from the northeastern part of ZMTDZ (Szarvaskő complex in Mt. Bükk; Balla & Dobretsov 1984) and basalts from CDOB (Lugović et al. 1991) are plotted for correlation constraints.

the Sljeme Unit originated in a geotectonic setting corresponding to the transitional N-MORB- to E-MORB-type. Therefore, we suggest their origin in a geotectonic setting as having the characteristics of the transitional mid-ocean ridge type (T-MORB; Figs. 11A1, B1 and 14A, B). Their parent magma was likely just slightly contaminated with the components from the earlier subducted Paleotethyan (?) oceanic lithosphere and/or with injection of the E-MORB-type melt. Contamination with the subducted components is most prominent in the oldest (Anisian) metabasalts from the Tusti Breg Unit. These metabasalts crystallized first from the melt, which became more and more depleted in the subducted components during the Late Triassic, when extrusive rocks of the Sljeme Unit began to crystallize and later during the Jurassic gained the typical geochemical characteristics of MORB.

Although the studied greenschists occur in the Lower-Cretaceous, low-grade metamorphic complex of Mt. Medvednica, the geochemical features of their basaltic protoliths of the Middle and Upper Triassic to the Middle Jurassic(?) age are very similar to the analogous non-metamorphosed Upper-Triassic (Carnian) to Middle Jurassic (Bajocian) basalts, which have been found in the neighbouring magmatic-sedimentary complexes (ophiolite mélanges) of the Medvednica, Kalnik, and Ivanščica Mts. (Slovenec & Lugović 2009, 2012; Slovenec et al. 2010, 2011). This is clearly evidenced by: (a) almost ideally analogous spider and REE patterns, (b) the ratios of the discriminant elements of basalts from the mentioned ophiolite mélanges and those of greenschists from the Mt. Medvednica (Figs. 10A2, B2; 13A, B). In addition, similarities are evident in the chemical composition of clinopyroxene from the igneous and metamorphic complexes (Fig. 14A, B). A good positive correlation of the geochemical features of the low-grade metamorphic rocks of Mt. Medvednica and similar non-metamorphosed Jurassic extrusives from the northeastern part of ZMTDZ (Szarvaskő-Darnó complexes in Mt. Bükk; e.g., Harangi et al. 1996; Aigner-Torres & Koller 1999; Kiss et al. 2012), as well as those from Central Dinaric Ophiolite Belt (CDOB; Lugović et al. 1991; Trubelja et al. 1995) was indicated based on the same discriminatory criteria (Figs. 14A, B and 15A, B). It can be concluded that the basaltic protoliths of the Lower-Cretaceous low-grade metamorphic complex of Mt. Medvednica and the Upper Triassic to the Middle Jurassic extrusive non-metamorphosed ophiolite rocks from neighboring ophiolite mélanges (Medvednica, Kalnik, Ivanščica Mt.), as well as those from the Szarvaskő-Darnó complexes (NE ZMTDZ) and CDOB areas in the southeast, formed in a similar geotectonic setting and derived from a similar parental mantle, indicating their common magmatic origin possibly in the same oceanic domain (sensu Bortolotti et al. 2004, 2013; Schmid et al. 2008, 2020), which existed in the western part of the Tethys during the Mesozoic era.

Geodynamic significance

In the geodynamical examination of the Dinarides, the geology of Mt. Medvednica and neighbouring Mt. Ivanščica and

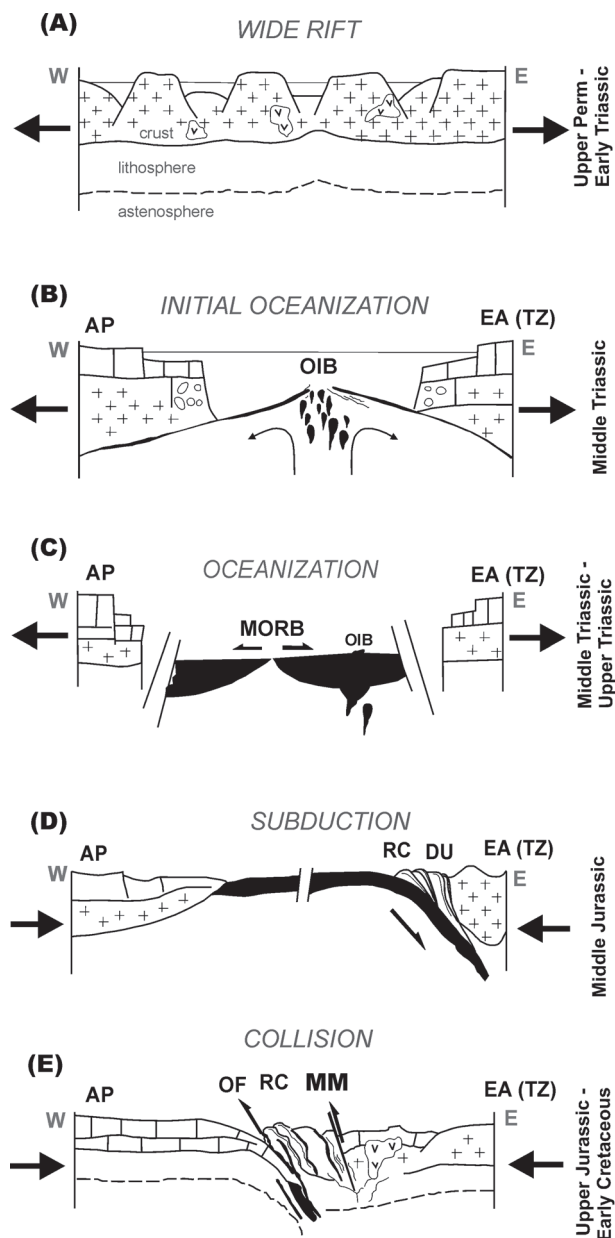


Fig. 15. Schematic geodynamic evolutionary model of the formation of protolithic rocks of Mt. Medvednica ortho-greenschists and their metamorphic geotectonic setting. **A** — Wide rift phase [Upper Permian–Early Triassic]; **B** — The beginning of the opening of the Tethys Ocean [oceanic island basalts (OIB)], the western side of the Adriatic Plate (AP) and the eastern side of Eurasia (EA)–(Tisza (TZ)) [Middle Triassic]; **C** — Intensive ocean extension (protolithic rocks of Mt. Medvednica ortho-greenschists: mid-ocean ridge basalt (MORB) and rarely oceanic island basalts OIB) [Middle–Upper Triassic]; **D** — Ocean subduction – east side active continental margin (accretion prism) with Repno Complex (RC) (Jurassic ophiolite mélangé) and Drenova Unit (DU) metamorphic rocks of accretion prism with high-pressure metamorphic rocks, blue- and jadeite-schists [Middle Jurassic]; **E** — Collision of the Adriatic Plate and Eurasia (Tisza (TZ)), formation of compression foreland basin Ostrc Formation (OF), rocks of Repno Complex (RC) and metamorphic rocks of Mt. Medvednica (MM); Jurassic units Drenova, and Sljeme (greenschists) exhumed and retrogradely metamorphosed during Early Cretaceous.

Mt. Kalnik plays an important role (Fig. 1 inset). The Central and Eastern Dinarides, which lie to the southeast of a broader area of the above-mentioned mountains, are clearly recognizable in the terms of lithofacies complexes that originated in the different geotectonic environments of the Dinaridic part of the Mesozoic Tethys (Pamić et al. 1998b). The Paleozoic complexes occur in these parts of the Dinarides in the form of masses that form the base of the Mesozoic carbonate platform (Pamić et al. 1998a,b). However, in Paleozoic rocks, in addition to locally present huge masses of metarhyolite (Jurković & Majer 1954), the occurrences of metabasalts are extremely rare (Pamić & Podubsky 1969). Westward, in the so-called Northwestern Dinarides, these great lithofacial complexes are completely lacking. This is the area of the so-called Sava Folds or Sava Nappe (Mioč 1982). This nappe is built up mostly of Triassic and subordinately Paleozoic rocks, where no occurrences of diabase rocks or ortho-greenschists have been observed. East of Mt. Medvednica, in the Mt. Moslavačka Gora and area of the Slavonian mountains (Psunj, Papuk, and Krndija Mts.), as well as in several deep boreholes, rocks of ortho-greenschist are completely lacking. The Slavonian Mountains are mostly built up of granitoid rocks, gneisses, migmatites, and amphibolites. Only in the Upper Paleozoic metasedimentary rocks on Mt. Papuk and Mt. Psunj can veins of metadiabases be found.

Penninian ophiolites are spatially associated with the so-called Bünderschiefer formation of Jurassic–Cretaceous age. However, the rocks of this formation are not found on Mt. Medvednica or neighbouring mountains. On the northern slopes of Mt. Medvednica, as well as on Mt. Kalnik, the rocks of ophiolite melange occur in a large area and can be correlated positively with the appropriate forms of the Dinaridic ophiolite zone (e.g., Pamić 1997; Babić et al. 2002; Slovenec & Pamić 2002; Schmid et al. 2008; Slovenec & Lugović 2009; Slovenec et al. 2011). The time of formation of the matrix of the ophiolite melange (so called Repno Complex) is determined as the Middle Jurassic (Babić et al. 2002), based on the palynomorphs. The blocks of the oceanic lithosphere (basalts, diabases, gabbros, serpentinites) and radiolarites of the Middle- to Upper-Triassic age (Ladinian-Norian) and the Middle- to Upper-Jurassic age are preserved in the ophiolite melange (e.g. Pamić 1997; Halamić 1998; Slovenec & Pamić 2002; Slovenec & Lugović 2009, 2012; Slovenec et al. 2011). The same span of the ages is obtained for the ophiolite rocks which form the Dinaridic ophiolite zone (DOZ – Pamić 1996). On the basis of the aforementioned and correlative geochemical characteristics of the rocks (Fig. 10A,B), as well as the primary mineral phases (Fig. 14A), it can be assumed that the studied ortho-greenschists from the Sljeme and Tusti Breg Units, which had metamorphosed during the Early Cretaceous (Belak et al. 1995; Judik et al. 2004, 2008; Borojević-Šoštarić et al. 2012; van Gelder et al. 2015), could have originated from the Middle–Upper-Triassic and Lower–Middle Jurassic basaltic rocks preserved in the ophiolite melange of Mt. Medvednica and Mt. Kalnik and therefore, most likely represent their protoliths.

In the broader continental area of Godwana, the synrift phase of the Neotethys began during the Late Permian (e.g. Pamić 1984; von Raumer et al. 2015; Fig. 15A). The “wide-rift” is, according to Buck (1991), the consequence of extension and thinning of the continental lithosphere. The Permian–Triassic magmatic activity in the broader area of the Dinarides varied from neutral-acid to basic magmatism (e.g. Pamić 1996; Harangi et al. 1996 and reference therein). The acid magmatic activity in the central parts of the crust points to the “wide-rift” phase (Wernicke 1992), which is in contrast to the “narrow-rift” phase, where there was no acid fluid in the central parts of the crust and basic magmatic activity characterized the entire rift history (e.g., Baldrige et al. 1984; Ingersoll et al. 1990). The “narrow-rift” model corresponds to the passive continental rift according to Morgan & Baker (1983) and Ramberg & Morgan (1984).

During the Middle Triassic, in the area of limited-rift (“narrow-rift”) of the westernmost part of the Tethys, oceanization began (Fig. 15B). Intense oceanization of this environment happened during the Late Triassic (e.g., Halamić 1998; Slovenec & Lugović 2009; Slovenec et al. 2010, 2011; Fig. 15C). The chemistry of the studied basic extrusive protoliths of the greenschists of the Sljeme Unit from the metamorphic complexes of Mt. Medvednica points to the origin in a geotectonic environment, which corresponds to the transitional mid-ocean-ridge (T-MOR) during the Middle and Late Triassic. This is why the mentioned basalt protoliths from this unit can be positively correlated with the Upper-Triassic basalts from the Jurassic ophiolitic melange on Mt. Medvednica and Mt. Kalnik (Slovenec & Lugović 2009; Slovenec et al. 2011). Subduction processes began in the Middle-Jurassic (by the end of the Bajocian; Slovenec & Lugović 2012; Fig. 15D) and the convergence lasted to the end of the Bathonian (Babić et al. 2002), that is, up to the Oxfordian (Slovenec et al. 2011) according to paleontological data from the matrix of the Jurassic ophiolite melange (the so-called Repno Complex). The same authors share the opinion that the final closing of the ocean took part during the middle part of the Late Jurassic. Under the subduction processes, the following formations took place: (a) the so-called Repno Complex, that is, ophiolite melange (Babić et al. 2002; Slovenec & Pamić 2002), which is thermally altered under conditions of high diagenesis at a temperature of 100–240°C (Judik et al. 2008), (b) prograde metamorphism of the ortho-greenschists of the Sljeme Unit, (c) prograde metamorphism of the Stari Potok Unit (evidenced through monacite dating of 153±6.9 Ma, Mišur et al. 2022 in press); (d) the Drenova Unit which contains high pressure-low temperature lithons of blueschists of the Middle to Upper-Jurassic, based on Ar–Ar amphibole age (160–165 Ma) and phengite age (155 Ma; Belak et al. 2022 in press). The amphibole grains and phengite leaves from the blueschists (Drenova Unit) have a weakly pronounced retrograde metamorphic phase pointing to the fast exhumation of high pressure rocks. The fast exhumation of the rocks means fast sinking of the slope basin or forearc basin through the extension along normal faults (Platt 1986, 1987) and/or by reverse thrusting

(e.g. Scholl et al. 1980). The same authors include the slope sediments on the accretionary prism into the subduction complex as structurally chaotic accretionary rock mass (tectonic mixture).

The time of collision of the Adriatic continental plate and Euroasian continent (Tisza(?)) is associated with the Upper Jurassic–Lower Cretaceous period, when the foreland basin of the Oštrc Formation was built (Babić et al. 2002; Fig. 15E). The exhumation of the greenschists of the Sljeme Unit and their retrograde metamorphose from epidote–amphibolite facies or blueschist facies is assumed on the basis of isotopic ages from 125 Ma to 110 Ma (Belak et al. 1995; Judik et al. 2006; Borojević-Šošarić et al. 2012; van Gelder et al. 2015), which correspond to the period of the Lower Cretaceous (Aptian–Albian).

Conclusions

- Based on petrographic, mineralogical, paleontological, and field investigations in the low-grade metamorphic rocks of Mt. Medvednica the following lithostratigraphic units are recognized: (a) The Stari Potok Unit (Lower Triassic), (b) The Adolfovac Unit (Middle Triassic), (c) The Tusti Breg Unit (Middle Triassic); (d) The Bliznec Unit (Middle–Upper Triassic), (e) The Mrzljak Unit (Upper Triassic), (f) The Sljeme Unit (Upper Triassic–Middle Jurassic(?)), (g) The Risnjak Unit (Jurassic(?)).
- Both petrographic composition of the rocks and chemistry of the mineral phases point to the different types of the metamorphism of the ortho-greenschists from the metamorphic complex of Mt. Medvednica. The ortho-greenschists of the Sljeme Unit have a prograde and retrograde metamorphic phase (*metamorphic overprint*), but greenschists from the Tusti Breg and Bliznec Units show only prograde metamorphism.
- The following metamorphic zones can be distinguished in the ortho-greenschists showing retrograde metamorphism (the Sljeme Unit): (a) epidote–amphibolite facies, with metamorphic zone: Mg–hornblende+oligoclase_{an18.2}; (b) upper greenschist facies, with metamorphic zone: actinolite (high Al content)+albite+Fe–Mg chlorite+epidote_{ps33}+biotite+phengite; (c) the “central” parts of the greenschist facies with metamorphic zone: actinolite (middle Al content)+albite±K–feldspar+clinochlore_{xMg0.55–0.59}+epidote_{ps33}+biotite characterized by interlayer charge deficit ±stilpnomelane+phengite; (d) lower greenschist facies with metamorphic zone: actinolite (low Al content)+albite±ortoclase+clinochlore_{xMg0.52–0.54}+epidote_{ps32}+phengite+stilpnomelane at a temperature between 350 and 400 °C and pressure of 2–5 kbar.
- The protoliths of ortho-greenschists from the metamorphic complex of Mt. Medvednica have mostly the characteristics of tholeiitic basalts and diabases that originated in a geotectonic environment corresponding to the transitional mid-ocean ridge (T-MORB-type). The melts from which the protoliths were generated are slightly contaminated with

the components from possibly earlier subducted (Paleotethyan?) oceanic lithosphere. The intensity of the contamination with the subducted components clearly decreases from the oldest (Anisian) protolith basalts from the Tusti Breg Unit toward younger (Upper Triassic–Middle Jurassic(?)) basalts of the Sljeme Unit.

- Prograde metamorphism took part during Jurassic oceanic subduction by the closing of the Western Tethys with the metamorphic temperature peak in the period from 165 Ma to 150 Ma, whereas retrograde metamorphism occurred during the collision of the Adriatic Plate and Eurasian plate in the Lower Cretaceous (125–110 Ma).
- Identical geochemical characteristics and the same Middle-to Upper-Triassic age of the basalt protoliths of the ortho-greenschists from the low-grade metamorphic complex of Mt. Medvednica, as well as analogous non-metamorphosed basalts preserved in the neighbouring magmatic–sedimentary complex (ophiolite mélange) of Mt. Kalnik may point to its common magmatic source and origin in the single oceanic environment that existed in the western part of the Tethys during the Lower Mesozoic period.

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Supplement

Table S1: Representative chemical compositions and calculated mineral formulae of amphibole from ortho-greenschists from Mt. Medvednica metamorphic complex.

Sample	Md-4	Md-4	J-898	Slj-6	Želj-23	Želj-26
Anal. No.	50; c	52; r	16; c	147; c	67; c	104; c
Mineral	act	Mg-hbl	Mg-hbl	act	act	act
Oxides (wt. %)						
SiO ₂	53.99	51.59	49.65	52.64	53.15	54.45
TiO ₂	0.24	0.03	0.03	0.06	0.08	0.01
Al ₂ O ₃	1.88	3.88	4.19	2.06	1.95	0.81
FeO	12.98	13.47	19.55	16.15	16.55	13.84
Cr ₂ O ₃	0.3	0.16	0.02	0.04	0.02	0.01
MnO	0.24	0.3	0.4	0.28	0.55	0.29
MgO	15.01	14.52	10.74	13.15	13.3	15.08
CaO	12.56	12.3	10.82	11.35	9.71	12.15
Na ₂ O	0.34	0.64	1.41	0.76	1.63	0.1
K ₂ O	0.09	0.18	0.28	0.13	0.11	0.05
Total	97.33	96.91	97.07	96.58	97.03	97.13
Calculated mineral formulae (a.p.f.u.)						
TSi	7.812	7.496	7.392	7.733	7.707	7.89
TAl	0.188	0.504	0.608	0.267	0.293	0.11
Sum T	8	8	8	8	8	8
CAI	0.133	0.16	0.126	0.09	0.04	0.028
CCr	0.003	0.018	0.002	0.005	0.002	0
CFe ³⁺	0	0.276	0.561	0.345	0.738	0.16
CTi	0.026	0.003	0.003	0.007	0.009	0.001
CMg	3.238	3.145	2.384	2.88	2.675	3.258
CFe ²⁺	1.571	1.36	1.873	1.639	1.269	1.517
CMn	0.029	0.037	0.05	0.035	0.068	0.036
Sum C	5	5	5	5	5	5
BCa	1.947	1.915	1.726	1.787	1.508	1.941
BNa	0.053	0.85	0.274	0.213	0.458	0.028
Sum B	2	2	2	2	1.967	1.969
ACa	0	0	0	0	0	0
ANa	0.043	0.095	0.133	0.003	0	0
AK	0.017	0.33	0.053	0.024	0.02	0.009
Sum A	0.059	0.128	0.186	0.027	0.02	0.009
Sum cat	15.059	15.128	15.186	15.027	14.987	14.978
Sum O	23.003	23	23	23	23	23
Mg#	0.67	0.7	0.56	0.64	0.69	0.68
T (°C)*	470	430	500	450	400	350
P (kbar)**	1.8	2	5.1	3.8	3.8	3.1

Mg# = Mg/(Mg+Fe²⁺); act = actinolite; Mg-hbl; c = core; r = rim

*Plyusina 1982, Gerya et al. 1997; **Brown 1977, Laird et al. 1984

Table S2: Representative chemical compositions and calculated mineral formulae of feldspar from ortho-greenschists from Mt. Medvednica metamorphic complex.

Sample	Md-4	Md-4	Md-4	J-898	J-898	J-898
Anal. No.	78	93	16	1	18	126
Mineral	ab	ab	or	ab	ab	olg
Oxides (wt. %)						
SiO ₂	68.23	68.19	64.43	68.44	68.47	61.3
TiO ₂	0.01	0.02	0.03	0	0	0
Al ₂ O ₃	19.55	19.71	18	19.92	19.52	19.64
FeO	0.55	0.28	0.12	0.02	0.035	1.85
MnO	0.01	0.01	0.01	0	0	0
MgO	0.01	0.01	0.01	0	0	0
CaO	0.11	0.33	0.01	0.11	0.18	3.93
Na ₂ O	12.04	11.92	0.1	12	12.21	9.7
K ₂ O	0.06	0.08	16.51	0.16	0.04	0.05
Total	100.55	100.6	99.19	100.64	100.77	96.47
Calculated mineral formulae (a.p.f.u.)						
Si	11.93	11.889	12.025	11.9	11.92	11.371
Al	4.03	4.047	3.956	4.08	4.002	4.289
Ti	0.001	0.003	0.004	0	0	0
Fe ²⁺	0.038	0.041	0.019	0.001	0.051	0.287
Mn	0	0	0	0	0	0
Mg	0	0.003	0	0	0	0
Ca	0.052	0.073	0	0.02	0.034	0.781
Na	3.977	4.03	0.036	4.049	4.122	3.49
K	0.013	0.018	3.931	0.035	0.009	0.012
Sum cat	20.041	20.104	19.971	20.092	20.138	20.23
Ab	98.4	97.8	0.9	98.7	99	81.5
An	1.3	1.8	0	0.5	0.8	18.2
Or	0.3	0.4	99.1	0.9	0.2	0.3

ab = albite, olg = oligoclase, or = orthoclase

Table S3: Representative chemical compositions and calculated mineral formulae of pyroxene from ortho-greenschists from Mt. Medvednica metamorphic complex.

Sample	Md-4	Md-4	Md-4	Md-4
Anal. No.	7	38	66	104
Mineral	aug	aug	aug	aug
Oxides (wt. %)				
SiO ₂	50.11	49.01	49.34	49.32
TiO ₂	1.51	1.98	1.72	1.83
Al ₂ O ₃	3.22	3.33	3.31	3.66
FeO	8.73	10.23	9.79	9.84
Cr ₂ O ₃	0.1	0.05	0.04	0.09
MnO	0.23	0.31	0.2	0.2
MgO	14.49	13	13.47	14.05
CaO	21.05	20.91	20.66	20.4
Na ₂ O	0.45	0.49	0.49	0.47
K ₂ O	0.01	0.01	0.01	0.01
Total	99.9	99.31	99.02	99.87
Calculated mineral formulae (a.p.f.u.)				
TSi	1.862	1.849	1.86	1.84
TAl	0.138	0.148	0.14	0.16
TFe ³⁺	0	0.003	0	0
M1Al	0.003	0	0.007	0.001
M1Ti	0.042	0.056	0.049	0.051
M1Fe ³⁺	0.08	0.072	0.069	0.087
M1Fe ²⁺	0.069	0.139	0.117	0.076
M1Cr	0.003	0.001	0.001	0.003
M1Mg	0.803	0.731	0.755	0.762
M2Fe ²⁺	0.122	0.109	0.123	0.144
M2Mn	0.007	0.01	0.006	0.006
M2Ca	0.838	0.845	0.635	0.816
M2Na	0.032	0.036	0.036	0.034
M2K	0	0	0	0
Sum cat	4	4	4	4
Wo	43.66	44.27	43.77	42.69
En	41.82	38.28	39.71	40.91
Fs	14.51	17.43	16.52	16.4

aug = augite

Table S4: Representative chemical compositions and calculated mineral formulae of epidote from ortho-greenschists from Mt. Medvednica metamorphic complex.

Sample	Md-4	Md-4	Md-4	J-898	J-898	J-898
Anal. No.	45; c	47; r	80; r	29; r	41; c	42; r
Oxides (wt. %)						
SiO ₂	36.97	37.47	37.99	36.54	36.76	36.79
TiO ₂	0.06	0.13	0.32	0.13	0.05	0.05
Al ₂ O ₃	21.28	25.46	26.39	20.71	20.58	20.32
FeO	14.07	8.89	7.9	14.71	14.94	15.56
Cr ₂ O ₃	0.03	0.07	0.03	0.02	0.01	0.01
MnO	0.07	0.16	0.09	0.02	0.18	0.11
MgO	0.22	0.26	0	0.01	0.02	0.18
CaO	21.86	23.33	23.79	22.94	22.03	22.38
Na ₂ O	0.01	0.01	0.01	0.02	0.01	0.01
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.01
Total	94.57	95.77	96.52	85.09	94.57	95.41
Calculated mineral formulae (a.p.f.u.)						
Si	3.017	2.985	2.993	2.986	3.013	2.997
Al ^{IV}	4	0.015	0.007	0.014	0	0.003
Sum T	3.017	3	3	3	3.013	3
Al ^{VI}	2.045	2.374	2.442	1.979	1.986	1.946
Ti	0.004	0.008	0.019	0.008	0.003	0.003
Cr	0.002	0.004	0.002	0.001	0	0.001
Fe ³⁺	0.96	0.59	0.52	1	1.02	1.06
Mn	0.005	0.011	0.006	0.001	0.012	0.008
Sum M1	3.016	2.987	2.989	2.989	3.021	3.018
Mg	0.027	0.031	0	0	0.002	0.22
Ca	1.912	1.991	2.008	2.008	1.935	1.953
Na	0.002	0	0.002	0.003	0	0.002
K	0	0	0	0	0.001	0
Sum M2	1.941	2.022	2.01	2.011	1.938	1.977
Sum O	12.5	12.5	12.5	12.5	12.5	12.5
Ps	0.32	0.2	0.17	33.41	33.93	35.23
% AlFeEp	83.55	52.79	46.91	87.35	88.72	92.4

c = core; r = rim

Table S5: Representative chemical compositions and calculated mineral formulae of chlorite from ortho-greenschists from Mt. Medvednica metamorphic complex.

Sample	Md-4	Md-4	Md-4	J-898	J-898	J-898
Anal. No.	59; c	60; r	87	7	11	14
Oxides (wt. %)						
SiO ₂	27.17	30.39	26.51	26.09	25.86	25.94
TiO ₂	0.04	0.03	0.25	0.04	0.13	0.01
Al ₂ O ₃	19.36	16.37	19.74	18.84	18.69	18.4
FeO	0.01	0.01	0.01	0.01	0.01	0.01
Cr ₂ O ₃	22.85	22.37	23.21	26.51	26.31	26.31
MnO	0.4	0.3	0.35	0.6	0.59	0.59
MgO	17.28	16.54	16.95	15.02	14.87	15.15
CaO	0.09	0.32	0.15	0.04	0.09	0.05
Na ₂ O	0.01	0.02	0.01	0.02	0.01	0.04
K ₂ O	0.05	0.26	0.03	0.02	0.01	0.01
Total	87.24	86.61	87.19	87.19	86.56	86.57
Calculated mineral formulae (a.p.f.u.)						
Si	5.679	6.353	5.562	5.589	5.581	5.598
Al ^{IV}	2.321	1.547	2.438	2.411	2.419	2.408
Sum T	8	8	8	8	8	8
Al ^{VI}	2.444	2.383	2.439	2.342	2.331	2.292
Ti	0.006	0.005	0.039	0.006	0.021	0.002
Fe ³⁺	0	0	0	0.055	0.044	0.106
Fe ²⁺	3.994	3.911	4.072	4.694	4.704	4.643
Cr	0	0.002	0	0.002	0.002	0
Mn	0.071	0.053	0.062	0.109	0.108	0.108
Mg	5.384	5.155	5.301	4.797	4.784	4.874
Sum Ok	11.899	11.509	11.913	12.005	11.994	12.025
Ca	0.02	0.072	0.034	0.009	0.021	0.012
Na	0	0.008	0	0.008	0	0.017
K	0.13	0.069	0.008	0.005	0.003	0.003
Sum cat	19.932	19.658	19.955	20.027	20.018	20.057
Sum O	28	28	28	28	28	28
Fe#	0.43	0.43	0.43	0.5	0.5	0.49

Fe# = Fe/(Fe+Mg); c = core; r = rim

Table S6: Representative chemical compositions and calculated mineral formulae of biotite from ortho-greenschists from Mt. Medvednica metamorphic complex.

Sample	Slj-6	Slj-6	Slj-6	Želj-23	Želj-23	Želj-23
Anal. No.	121	127	129	53	60	73
Oxides (wt. %)						
SiO ₂	37.41	37.59	36.33	35.96	36.14	36.05
TiO ₂	0.98	1.21	1.14	1.06	1.07	0.97
Al ₂ O ₃	14.16	13.77	14.33	14.02	13.94	14.12
FeO	0.02	0.03	0.02	0.01	0.11	0.03
Cr ₂ O ₃	21.48	21.25	21.97	20.2	19.85	20.86
MnO	0.21	0.26	0.26	0.19	0.16	0.25
MgO	10.69	10.65	10.04	11.45	11.7	12.09
CaO	0.11	0.03	0.16	0.67	0.39	0.24
Na ₂ O	0.05	0.04	0.08	0.03	0.05	0.08
K ₂ O	9.34	8.86	9.12	6.06	6.99	7.84
Total	94.45	93.69	93.45	89.64	90.4	92.53
Calculated mineral formulae (a.p.f.u.)						
Si	5.814	5.88	5.735	5.773	5.771	5.682
Al ^{IV}	2.186	2.134	2.265	2.227	2.229	2.318
Al ^{VI}	0.406	0.397	0.399	0.424	0.392	0.303
Ti	0.115	0.142	0.135	0.128	0.129	0.115
Fe ²⁺	2.792	2.773	2.9	2.712	2.651	2.75
Cr	0.002	0.004	0.002	0	0.014	0.004
Mn	0.028	0.034	0.036	0.026	0.022	0.033
Mg	2.477	2.478	2.383	2.74	2.785	2.841
M p.f.u.	2.91	2.914	2.917	3.015	2.997	3.023
Ca	0.018	0.005	0.027	0.115	0.067	0.041
Na	0.015	0.012	0.024	0.009	0.015	0.024
K	1.852	1.764	1.837	1.241	1.424	1.576
I p.f.u.	0.94	0.89	0.94	0.68	0.75	0.82
Sum cat	15.705	15.609	15.722	15.395	15.499	15.687
Sum O	22	22	22	22	22	22
Fe#	0.53	0.53	0.55	0.5	0.49	0.49
Mg#	0.47	0.47	0.45	0.5	0.51	0.51

Fe# = Fe²⁺/(Fe²⁺+Mg); Mg# = Mg/(Mg+Fe²⁺)

Table S7: Representative chemical compositions and calculated mineral formulae of stilpnomelane from ortho-greenschists from Mt. Medvednica metamorphic complex

Sample	Run-1	Run-1	Run-1	Run-1	Run-1	Run-1
Anal. No.	19	44	51	62	63	64
Oxides (wt. %)						
SiO ₂	47.1	46.75	45.4	45.97	45.84	46.6
TiO ₂	0.04	0.08	0.01	0.01	0.01	0.01
Al ₂ O ₃	7.07	6.54	5.78	5.98	6.04	6.1
Cr ₂ O ₃	0.01	0.02	0.01	0.01	0.01	0.01
FeO	23.97	25.31	26.55	26.67	26.96	26.62
MnO	0.99	1.1	1.08	1.33	1.3	1.03
MgO	6.77	6.3	6.65	6.8	6.52	6.82
CaO	0.34	0.3	0.7	0.54	0.41	0.51
Na ₂ O	0.97	0.67	0.08	0.09	0.06	0.09
K ₂ O	0.82	1.02	1	0.92	0.88	0.83
Total	88.07	88.09	87.25	88.32	88.02	88.6
Calculated mineral formulae (a.p.f.u.)						
Si	8	8	8	8	8	8
Al ^{IV}	1	1	1	1	1	1
Al ^{VI}	0.414	0.318	0.199	0.226	0.241	0.233
Ti	0.005	0.01	0	0.001	0.001	0
Fe _{total}	3.405	3.622	3.912	3.882	3.935	3.822
Cr	0	0.003	0.001	0.001	0	0
Mn	0.142	0.159	0.161	0.196	0.192	0.15
Mg	1.714	1.607	1.747	1.764	1.696	1.745
M	5.68	5.719	6.02	6.07	6.065	5.95
Ca	0.062	0.055	0.132	0.101	0.077	0.094
Na	0.319	0.222	0.027	0.03	0.02	0.03
K	0.178	0.223	0.225	0.204	0.196	0.182
l	0.559	0.5	0.384	0.335	0.293	0.306
Sum cat	15.239	15.219	15.404	15.405	15.358	15.256

Table S8: Representative chemical compositions and calculated mineral formulae of white mica from ortho-greenschists from Mt. Medvednica metamorphic complex

Sample	M-710	M-710	M-710	Slj-1/6	Slj-1/6	Slj-1/6
Anal. No.	39	72	121	12	141	177
Oxides (wt. %)						
SiO ₂	48.38	51.81	48.17	50.38	50.76	49.49
TiO ₂	0.05	0.04	0.03	0.03	0.04	0.03
Al ₂ O ₃	28.6	24.61	29.43	27.67	24.68	26.2
FeO	0.01	0.05	0.02	0.03	0.05	0.01
Cr ₂ O ₃	3.73	3.03	3.71	5.49	6.77	6.53
MnO	0.05	0.02	0.02	0.01	0.01	0.08
MgO	2.64	3.63	1.66	2.3	3.24	2.15
CaO	0.05	0.05	0.01	0.01	0.01	0.01
Na ₂ O	0.15	0.05	0.11	0.13	0.09	8.06
K ₂ O	10.72	10.58	11.07	10.21	10.34	10.33
Total	94.37	93.87	94.22	96.25	95.98	94.89
Calculated mineral formulae (a.p.f.u.)						
Si	6.589	7.033	6.574	6.74	6.874	6.773
Al ^{IV}	1.411	0.967	1.426	1.26	1.126	1.227
Sum T	8	8	8	8	8	8
Al ^{VI}	3.176	2.967	3.304	3.1	2.81	2.996
Ti	0.005	0.004	0.003	0.003	0.004	0.003
Fe ²⁺	0.052	0.3	0.237	0.284	0.223	0.328
Fe ³⁺	0.373	0.044	0.186	0.33	0.544	0.419
Cr	0	0.005	0.002	0.003	0.005	0.001
Mn	0.006	0.002	0.002	0	0.001	0.009
Mg	0.536	0.735	0.338	0.459	0.654	0.439
Sum M p.f.u.	2.074	2.028	2.036	2.089	2.12	2.097
Ca	0.007	0.007	0	0.001	0	0.001
Na	0.04	0.013	0.029	0.034	0.024	0.016
K	1.863	1.832	1.927	1.743	1.786	1.804
Sum I p.f.u.	0.955	0.926	1.956	0.889	0.905	0.91
O	22	22	22	22	22	22

Table S9: Chemical analyses of ortho-greenschists from Mt. Medvednica metamorphic complex.

Sample	Ms-1B	Ms-2	Bd-1C	Bd-2	Me-1	Tb-1A	Tb-2A	S-1/1	S-1/2	S-1/2A	S-13/1A	S-22/2	S-26	S-27/2
Rock type	MB	MB	MB	MB	MB	MB	MB	MB	MB	MB	MB	MB	MB	MB
Unit	SLJ	SLJ	MR	MR	TB	TB	TB	SLJ	SLJ	SLJ	SLJ	SLJ	SLJ	SLJ
SiO ₂	49.02	47.8	46.11	45.22	48.74	49.19	47.03	44.28	47.27	46.74	44.34	47.6	49.61	47.82
TiO ₂	1.53	1.93	2.19	2.89	1.65	1.98	1.93	2.36	2.63	2.19	1.76	2.48	1.78	1.83
Al ₂ O ₃	15.75	18.61	16.53	14.67	15.42	14.8	13.35	15.37	15.37	15.14	15.62	14.99	15.24	15.99
Fe ₂ O _{3total}	10.22	9.93	16.13	9.78	10.53	11.8	10.02	10.21	14.09	12.42	9.99	12.36	10.92	11.76
MnO	0.16	0.14	0.14	0.11	0.15	0.16	0.16	0.77	0.22	0.19	0.19	0.14	0.19	0.16
MgO	5.93	3.86	2.64	4.55	5.57	5.21	3.56	5.65	5.08	6.02	2.88	4.06	6.22	6.86
CaO	11.24	7.53	8.91	9.72	5.75	8.55	11.51	6.8	6.86	9.86	9.88	9.26	8.98	7.8
Na ₂ O	3.55	5.35	4.57	5.14	5.09	2.73	3.01	4.5	3.71	2.29	6.23	3.69	3.71	3.79
K ₂ O	0.07	0.35	0.5	0.1	0.36	0.07	0.16	0.05	0.37	0.24	0.09	1.32	0.64	0.23
P ₂ O ₅	0.18	0.28	0.34	0.42	0.19	0.23	0.22	0.28	0.34	0.27	0.25	0.31	0.21	0.23
LOI	2.23	3.91	2.57	7.03	6.47	3.86	8.11	9.26	3.91	3.58	8.58	3.48	2.32	3.28
Total	99.9	99.69	100.6	99.63	99.93	98.55	99.08	99.54	99.85	98.94	99.73	99.75	99.82	99.75
Cs	0.1	0.4	0.6	0.7	4	0.2	1.1	8	-	-	-	17	40.2	-
Rb	1	6	8	2	7	1	3	4	11	4	4	36	10	6
Ba	15	13	27	42	89	11	25	30	54	27	38	46	60	27
Th	0.62	0.68	0.5	0.78	1.4	0.91	1.15	0.61	0.91	0.46	0.4	0.5	0.58	0.55
Ta	0.41	0.49	0.43	0.59	0.4	0.32	0.36	0.66	0.8	0.7	0.5	0.5	0.6	0.6
Nb	3.7	5.3	4.9	6.8	3.6	1.8	2.7	4.9	7	6.1	3.6	4.9	4.4	4.6
Sr	276	242	132	143	138	685	392	170	142	193	146	173	258	187
Zr	149	165	186	246	177	156	190	200	235	186	137	193	163	178
Hf	3.7	4.3	4.4	5.6	4.7	4	4.7	5.8	5.7	4.6	3.7	5.2	4.4	3.8
Y	33.3	36.2	39.2	52	34	44.9	42.2	55.9	62.9	53.8	36.2	59.9	43.4	42.8
Sc	32	30	36	40	37	35	33	39	37	39	41	40	40	43
V	242	243	382	328	269	306	288	238	319	297	247	332	248	276
Cr	220	229	90	30	110	140	100	125	71	134	105	82	152	161
Ni	60	65	40	40	30	40	20	33	36	45	83	53	63	51
La	7.3	7.5	7.9	10.9	8.6	7.8	8.9	16.4	12.1	10.5	6.5	8.7	7.9	8.5
Ce	20.6	20.8	24.5	30.7	24.4	22.8	26.1	33.2	30.8	28.2	17.2	26.7	21.2	23
Pr	2.8	3.5	3.5	4.6	3.2	3.1	3.9	5.4	5.4	4.7	2.8	4.5	3.4	3.5
Nd	14.2	17	17.9	24	15.9	17.5	17.8	22.7	22.3	20.7	13.3	18.5	16.8	18.8
Sm	4.2	5.1	5.4	7.1	4.4	5.5	5.6	7.2	7	6.4	4.5	6.3	5.1	5.4
Eu	1.36	1.82	1.86	2.41	1.42	2.01	1.86	2.4	2.3	2.13	1.75	2.07	1.98	1.96
Gd	5.3	6.3	6.6	8.9	5.5	7.3	6.9	7.3	7.4	6.8	4.7	6.6	5.1	5.6
Tb	0.99	1.06	1.22	1.64	1.05	1.31	1.26	1.22	1.25	1.15	0.85	1.19	0.94	1.01
Dy	6.3	6.7	7.8	10.4	6.5	8.3	7.7	8.6	9.2	8.2	6	8.7	6.9	7.1
Ho	1.33	1.37	1.57	2.1	1.34	1.69	1.62	1.7	1.83	1.58	1.19	1.72	1.4	1.44
Er	3.75	3.9	4.38	5.77	3.8	4.8	4.57	4.73	5.44	4.71	3.63	5.4	3.92	4.31
Tm	0.55	0.58	0.64	0.82	0.56	0.68	0.68	0.72	0.8	0.65	0.54	0.8	0.59	0.64
Yb	3.77	3.56	4.32	5.55	3.83	4.35	4.62	4.74	5.31	4.86	3.65	5	3.66	3.86
Lu	0.61	0.57	0.69	0.91	0.62	0.71	0.75	0.74	0.8	0.69	0.53	0.78	0.59	0.58

Major elements in wt.%, trace elements in ppm. LOI = loss on ignition at 1100°C. MB = metabasalt. MR = Mrzljak Unit, SLJ = Sljeme Unit, TB = Tusti Breg Unit