Middle Triassic basaltic pyroclastic rocks from the Mt. Medvednica ophiolitic mélange (NW Croatia): petrology, geochemistry and tectono-magmatic setting

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Abstract

Hectometric blocks of Middle Triassic mafic pyroclastic rocks, represented by volcanic agglomerates/breccias and lapilli tuffs, form part of the ophiolitic mélange of Mt. Medvednica, situated in the southwestern segment of the Zagorje-Mid-Transdanubian Zone. These rocks share petrochemical characteristics with pyroclastic derivatives of alkali, within-plate basaltic lavas of Mts. Medvednica, Samoborska Gora, and Kalnik, indicating the occurrence of explosive events preceding the dominant effusive submarine volcanism during the Middle Triassic (Illyrian-Fassanian?) stages. The formation of these pre-ophiolitic pyroclastics is associated with an intracontinental rift setting and reflects melts derived from an OIB-type enriched mantle plume source. These pyroclastics represent uncontaminated melts that erupted through a highly thinned continental crust. In geodynamic terms, the formation of pyroclastites occurred during the Late Anisian-Early Ladinian along the continental margin of Palaeotethys through the proto back-arc rifting of continental lithosphere (Adria Plate), leading to the formation of the Maliak/Balkan Neotethys Rift, in the emerging northwestern segment of Neotethys. The investigated pyroclastic rocks of Mt. Medvednica document the extension in an evolved intracontinental rift basin, which immediately preceded the generation of the initial Neotethyan oceanic lithosphere during the Upper Triassic.

1. INTRODUCTION

The intra-Pannonian inselbergs in northwestern Croatia (Mts. Medvednica, Samoborska gora, Kalnik, and Ivanščica) consist of Palaeozoic and Mesozoic Dinaridic and Alpine tectono-stratigraphic/-metamorphic units (e.g. PAMIĆ & TOMLJE-NOVIĆ, 1998; TARI & PAMIĆ, 1998; PAMIĆ, 2002). The ancient Neotethyan oceanic lithosphere that predominantly outcrops in these mountains belongs to the westernmost part of the Western Vardar Ophiolitic Unit (sensu SCHMID et al., 2008, 2020; Fig. 1a), or more specifically, the southwest part of the Zagorje-Mid-Transdanubian Zone (ZMTDZ; sensu PAMIĆ & TOMLJENOVIĆ, 1998; Fig. 1b). It is preserved in metre-to-kilometre-scale fragments archived within the ophiolitic mélange (Figs. 1b-d). The largest manifestations of Triassic-Jurassic oceanic lithosphere, preserved as coherent thrust sheets, are found on the northern slopes of Mt. Medvednica (Figs. 1b-d). Research on the tectono-sedimentary ophiolitic mélange of the same mountain and the fragments of oceanic crust archived therein, conducted over the past three decades, has identified all components of a typical ophiolitic sequence (HALAMIĆ, 1998; HALAMIĆ et al., 1998, 1999; LUGOVIĆ et al., 2007; SLOVENEC & LUGOVIĆ, 2008, 2009; SLOVENEC et al., 2010; SLOVENEC & ŠEGVIĆ, 2023). Primarily, these are effusive branches of Triassic and Jurassic basaltic alkali and tholeiitic lavas with various geochemical affinities (WPAB, E-, T-, N-MORB, IAT, BARB, BON), formed in convergent and divergent geotectonic settings. However, the research presented here shows that, in

addition to effusive volcanism, exclusively represented by pillow and massive basalts, pyroclastic rocks also found (Figs. 1e, f), though they are rare. These rocks indicate the explosive character of volcanism generated during the Middle Triassic.

This study provides the initial mineralogical, petrological, and geochemical insights into Middle Triassic pyroclastites from the mélange of Mt. Medvednica. It offers evidence of a shared petrogenetic and tectonomagmatic evolution of ophiolitic pyroclastic rocks formed during the Middle Triassic period in the northwestern part of Neotethys.

2. GEOLOGICAL OUTLINES

Mt. Medvednica is located at the junction of the South-Eastern Alps, the Dinarides and the Tisza Mega-Unit (Fig. 1a) and forms part of the southwestern segment of the Zagorje-Mid-Transdanubian Zone (ZMTDZ) (PAMIĆ & TOMLJENOVIĆ, 1998; Fig. 1b). The ZMTDZ is bounded by the Periadriatic-Balaton lineament to the north and the Zagreb-Zemplin lineament to the south. It is characterized by mixed Alpine-Dinaridic lithologies. The ophiolitic mélange of the SW segment of the ZMTDZ crops out at multiple locations in NW Croatia's mountains. These mélange locations collectively make up what is known as the Kalnik Unit (KU) (HAAS et al., 2000; Fig. 1b). The age of accretion for the KU, which predominantly contains fragmented remnants and allochthonous blocks of the Neotethyan oceanic lithosphere, is estimated to range from the Callovian to the Late Valanginian (SLOVENEC & LUGOVIĆ, 2009). Different blocks/fragments of Triassic and Jurassic

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igneous and sedimentary rocks are largely incorporated within the mélange matrix through tectonic processes, making it challenging to discern their original geological context of formation (HALAMIĆ, 1998; SLOVENEC & PAMIĆ, 2002). The fragmented remnants of the ophiolitic sequence of oceanic crust on Mt. Medvednica actually form a distinct connection between the Vardar-Dinaridic ophiolites situated to the southwest and the Meliata-Maliak ophiolites to the northeast (SLOVENEC & LUGOVIĆ, 2009).

Mt. Medvednica is composed of Palaeozoic, Mesozoic-Palaeogene, and Neogene-Quaternary formations (SLOVENEC & PAMIĆ, 2002; BELAK et al., 2022). In the structural succession, the lowest tectonostratigraphic unit is the metamorphic Medvednica Unit (HAAS et al., 2000; Fig. 1b). This unit consists of greenschist facies para- and ortho-metamorphic Lower Aptian rocks the protoliths of which likely covered the Siluarian to Ladinian period (ŠIKIĆ et al., 1978, 1979; BASCH, 1981, 1983; BELAK et al., 1995, 2022), but also of an epidote-bearing albite granite of Middle Triassic age (BALEN et al., 2022). The Medvednica Unit was thrust over a Late Jurassic ophiolitic mélange and Lower Cretaceous turbidite deposited in peripheral foreland piggyback basins, i.e. the Kalnik Unit (Figs. 1c, d). These units were overlain by Upper Cretaceous-Palaeocene clastic-carbonates and turbidites (ŠIKIĆ et al., 1979). The Neogene and Quaternary rock succession either rest unconformably on Palaeozoic-Mesozoic rocks or are tectonically superimposed upon them (Fig. 1d).

The ophiolitic mélange of Mt. Medvednica exhibits a block-in-matrix fabric typical of subduction-related tectonic mélanges (FESTA et al., 2010). It is composed of a pervasively sheared and fine-grained shaly-silty matrix that incorporates metre to kilometre-sized fragments and slices of Mesozoic greywacke, shale, chert, limestone and igneous rocks (peridotite cumulate, gabbro, dolerite dyke, and basalt) (SLOVENEC & LUGOVIĆ, 2008, 2009; SLOVENEC et al., 2010). The magmatic components show distinct geochemical affinities in line with their geotectonic settings of origin (within-plate, mid-ocean ridge, island arc, back-arc), which existed from the Illyrian to the late Oxfordian (SLOVENEC & LUGOVIĆ, 2009; SLOVENEC et al., 2010).

3. MATERIALS AND ANALYTICAL TECHNIQUES

The research area includes three locations where rock samples were taken for further analytical procedures (Fig. 1d). Following the petrographic microscopy investigation, nine representative rock samples were chosen for further analysis (Table 1). The classification of the pyroclastic rocks was based on the scheme proposed by SCHMID (1981). Seven whole-rock samples were selected for chemical analysis wich were carried out by ICP-OES for major elements, and ICP-MS for trace elements at Actlab Laboratories (Ancaster ON, Canada).

Bulk-rock powders for chemical analyses were obtained from rock chips free of veins and amygdales. Samples with calcite-filled amygdals were dissolved in diluted HCl. The ICP-MS measurements were performed on 0.2 g of sample, which followed a lithium metaborate/tetraborate fusion and diluted nitric acid digestion. Loss on ignition (LOI) was acquired by weight difference, after ignition at 1000 °C.

Major and trace elements concentrations were measured using USGS BHVO-2, W-2 and BIR-1 reference materials with accuracy and precision better than ±1% and ±5%, respectively. It is 3σ at 10 times detection limit. Detection limit: TiO_2, MnO = 0.001 wt.%; SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, P_2O_5 = 0.01 wt.%; Lu = 0.002 ppm; Eu = 0.005 ppm; Ta, Pr, Sm, Gd, Ho, Er, Yb, U = 0.01 ppm; Th, La, Ce, Nd, Tm = 0.05 ppm; Cs, Hf = 0.1 ppm; Nb = 0.2 ppm; Y = 0.5 ppm; Sc, Rb, Zr = 1 ppm; Sr = 2 ppm; Ba = 3 ppm; V, Pb = 5 ppm; Cr, Ni = 20 ppm. The quality of the measurements was checked by replicating the analysis on ~12% of the samples.

X-ray diffraction (XRD) analyses were performed on a set of five representative samples. Sample preparation included an initial material powdering in an agate mortar prior to measurements. The measurements were undertaken at Texas Tech University's Geosciences Clay Laboratory (Lubbock TX, United States) using a Bruker D8 Advance diffractometer. The XRD procedure included a step scan in the Bragg-Brentano geometry with CuKα radiation (40 kV and 40 mA). Analyzed material was scanned for 1.8 s per 0.02°, from 3° to 70 °2θ. The interpretation of XRD traces was conducted using the Bruker EVA software coupled with the PDF4 database released by the International Centre for Diffraction Data.

4. RESULTS

4.1. Geology of the study area

The investigated pyroclastic rocks, which outcrop along the northern slopes of Mt. Medvednica in the area of the Podbreg locality, are incorporated as hectometre-sized blocks in the ophiolitic mélange (Fig. 1d). These rocks consist of lapilli tuffs (Figs. 1e, f) and predominantly volcanic agglomerates/breccias (Fig. 1g). The lapilli tuffs are characterized by a tuffaceous matrix containing angular to weakly rounded lithoclast fragments (basalt; Fig. 1f) up to 2 cm in size and subordinate crystal clasts (pyroxene and plagioclase). Weakly rounded volcanic fragments and well-rounded volcanic bombs, formed through rapid cooling during eruption, are composed of basaltic lava up to 20 cm in size and embedded in the tuffaceous matrix (Fig. 1g). The tuffaceous matrix has undergone significant post-consolidation alterations and surface weathering.

4.2. Petrography

The analyzed rocks are represented by lapilli tuffs and volcanic bombs. The latter are composed of basaltic lavas charac-

Table 1: Overview of the analyzed rock samples

Sample Rock type	PB-1 LT	PB-2 LT	PB-3 LT	PB-4 LT	PB-4A LT	PB-5 LT	PB-7 LT	PB-21 LT	PB-71 LT
XRD anal.	+	+	+	+		+			
ICP-OES/MS anal.		+			+	+	+	+	+

BA = basalt (clast in tuff), LT = lapilli tuff.

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terized by porphyritic structure and almond-shaped texture (Figs. 2a, b). The phenocrysts are magmatic, idiomorphic, homogeneous, prismatic, augitic, clinopyroxene, (shows yellow interference colour of the 2nd order, optically positive with 2V of about 60°, high relief, colourless and no pronounced pleochroism), and platy plagioclase, measuring up to 2.5 mm in size.
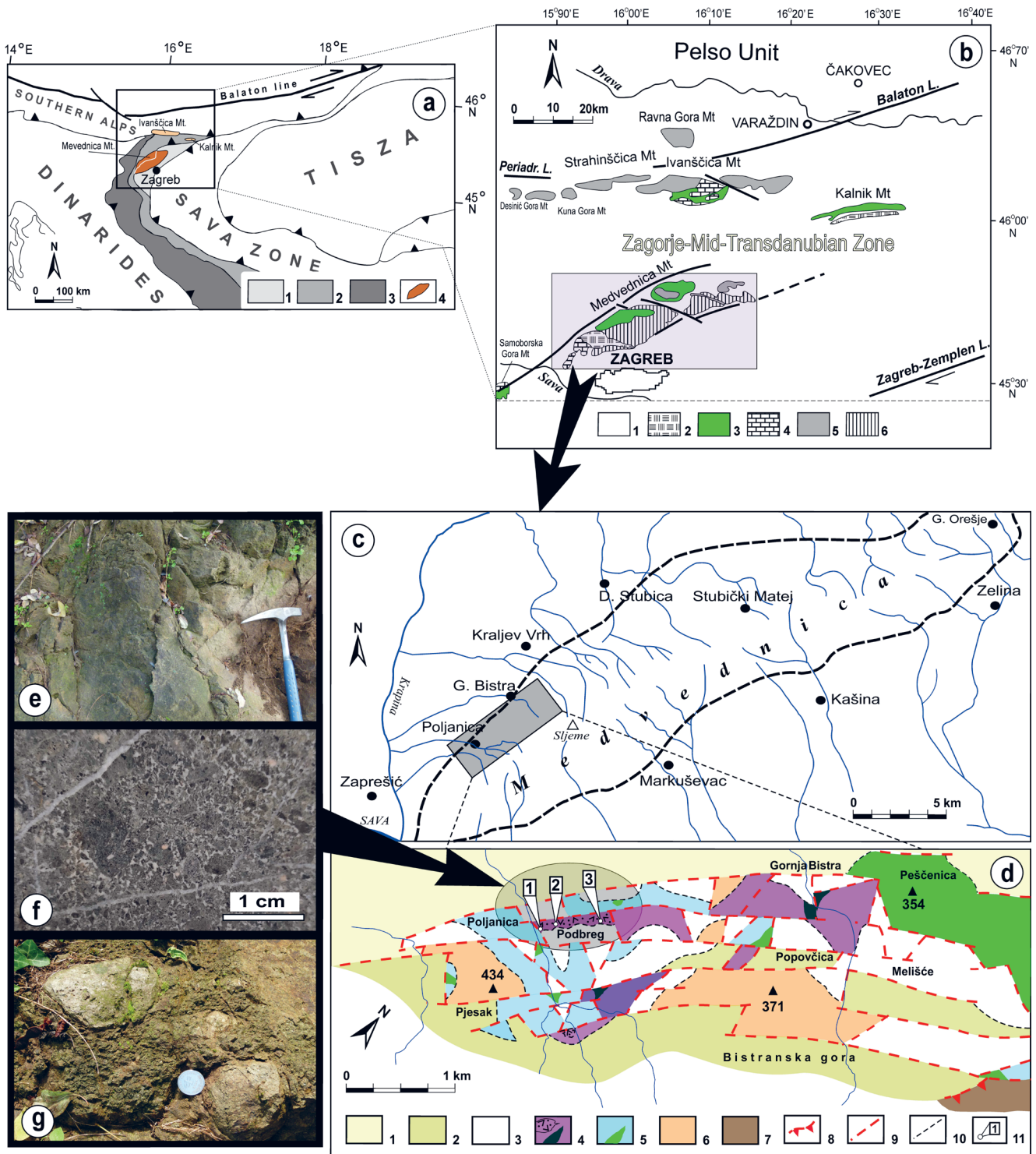
Figure 1: (a) Geotectonic sketch map of the major tectonic units (simplified after SCHMID et al., 2008, 2020). Legend: 1 = Bükk, Jadar, Kopaonik; 2 = Ophiolites oceanic accretionaly prism: Meliata, Darnó-Szarvaskö, Dinaric, Western Vardar, Mirdita; 3 = Pre-Karst & Bosnian Flysch; 4 = Mt. Medvednica. (b) Geological sketch map of the Croatian part of the Zagorje-Mid-Trandanubian Zone (slightly modified after PAMIĆ & TOMLJENOVIĆ, 1998). Legend: 1 = Quaternary and Neogene fill of the Pannonian Basin; 2 = Upper Cretaceous-Palaeocene flysch; 3 = Ophiolitic mélange (Kalnik Unit); 4 = Upper Triassic platform carbonates; 5 = Upper Palaeozoic and Triassic clastics and carbonates interlayered with volcanics and tuffs; 6 = Palaeozoic-Triassic metamorphic complex (Medvednica Unit). (c) Geographical location of the study area (gray shaded). (d) Simplified geological map of Mt. Medvednica (slightly modified after HALAMIĆ, 1998). Legend: 1 = Neogene and Quaternary sedimentary rocks; 2 = Late Cretaceous-Palaeocene flysch including Senonian carbonate breccias; 3 = ophiolitic mélange with blocks of: 4 = Middle Triassic radiolarites, shales, limestones, pyroclastites and basalts (black fields), 5 = Middle Jurassic radiolarites, shales and basalts (dark gray fields), 6 = Alb-Cenomanian limestones and clastic rocks (shale, siltite and sandstone); 7 = Lower Cretaceous metamorphic complex; 8 = reverse or thrust faults; 9 = normal faults; 10 = geological contact line; 11 = sample locations: 1 = PB-1, PB-2, PB-3, PB-4, PB-4A, PB-5; 2 = VS- 7, VS-21; 3 = VS-71. Field occurrence of the (e-f) basaltic lapilli tuff, (g) aglomerates from the Mt. Medvednica ophiolitic mélange (Location 1).

The groundmass is composed of volcanic glass devitrified to varying degrees and needle-like microlites of plagioclase. The modal composition includes clinopyroxene (35–50 vol.%), plagioclase (35–45 vol.%) and volcanic glass (20–25 vol.%). The phenocrysts crystallized slowly at deeper levels, unlike the needle-like microlites in the groundmass, which belong to second-generation minerals and crystallized at shallower parts of the flows. Occasional clustering of phenocrysts in aggregates gives the structure a glomeroporphyritic characteristic. A typical feature of these lavas is the dominance of rounded to ellipsoidal monomineralic calcite and subordinate chlorite nodules, each up to 1.2 mm in size, which constitute the matrix filler of the rock (Figs. 2a, b).

The lapilli tuffs correspond to pyroclastics: (a) juvenile in origin, formed during lava eruption, consisting of fragments of cooled lava and phenocrysts formed prior to the eruption (Fig. 2c), and (b) cognate in origin, formed by crushing of older lavas during a new eruption (Fig. 1f). Lithoclastic-vitrophyric varieties of these basic tuffs with vitriclastic structures and homogeneous, occasionally fluidal textures are predominantly present (Figs. 2c, d). The content of crystal clasts within samples in the glassy groundmass is not uniform and is mostly represented by euhedral platy plagioclases up to 0.5 mm in size (Fig. 2c). Crystal clasts, as well as fragments of volcanic glass and fine ash powder from the groundmass, are the products of approximately simultaneous crystallization. The volcanic glass is significantly devitrified into chlorite, and calcitization of the tuffs is a common consequence of the alteration processes (Figs. 2c, d).

X-ray diffraction traces show the mineral composition of lapilli tuffs to be largely composed of albite, calcite, analcime, and minor titanite, chlorite, 10Å phyllosilicate, and other phases (Table 2). However, basaltic bombs, in addition to all the aforementioned phases feature the presence of clinopyroxene. Finally, chlorite-smectite (C-S) intermediates seem to be the major alteration products of the vitreous component in both studied lithotypes. While chlorite-rich C-S is clearly of hydrothermal origin (ŠEGVIĆ et al., 2023), relative intensities of the 002 reflection at ~7.1 Å and the 001 reflection at 14.1-14.3 Å of such C-S (WEAVER, 1956), are taken as evidence of chlorite vermiculitization which took place during oxidative dissolution (GU et al., 2020; KRZESIŃSKA et al., 2021), following the emplacement of the analyzed rocks. Further weathering likely led to C-S dissolution and emergence of illite and illite-smectite interlayers as documented in sample PB-1 (Table 2).
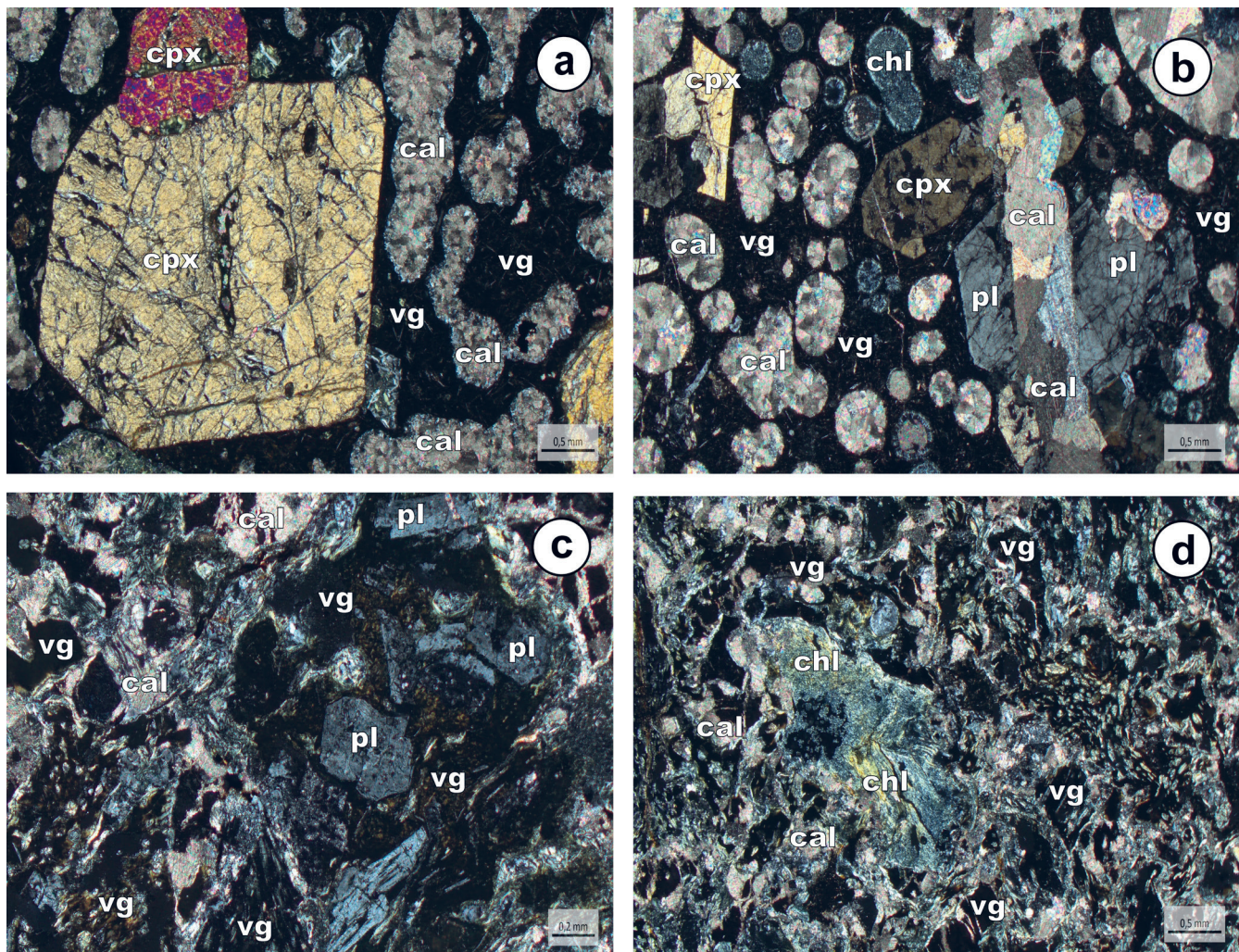
Figure 2. Photomicrographs of thin-sections of the Mt. Medvednica basaltic pyroclastic rocks: (a-b) lava from a volcanic bomb (sample PB-4A), (c) lapilli tuff (sample VS-7) and (d) tuff matrix (sample PB-5). Mineral abbrevations after WHITNEY & EVANS (2010): cpx = clinopyroxene; cal = calcite; chl = chlorite; pl = plagioclase; vg = volcanic glass.

Table 2: XRD analyses of the basaltic pyroclastic rocks from the Mt. Medvednica ophiolite mélange

Sample	Rock Type	Ab	Cpx	Chl	C-S	Cal	Tit	Anl	Ms/Ill	I-S	Qtz	Fe-oxide	Ap
PB-1	Lapilli tuff	++		+			+		++	+		+	+
PB-2	Lapilli tuff	++			+	++			+				
PB-3	Lapilli tuff	++			++	++	+	+				+	
PB-4	Basalt	++	++		++	++	+	++	+				
PB-5	Lapilli tuff	++	+		++	++	++	++	+		+		

Abbreviations after WHITNEY & EVANS (2010): LT – lapilli tuff; BA – basalt; Qtz – quartz; Ab – albite; Chl – chlorite; Cal – calcite; Anl – analcime; Ms – muscovite; Ill – illite; Ap – apatite; C-S – chlorite-smectite; I-S – illite-smectite; ++ – indicates major phases, + – indicates minor phases

4.3. Bulk rock chemistry

The chemical composition of the studied rocks samples is detailed in Table 3. The examined rocks are characterized by a high content of TiO_2 (1.85-2.28 wt.%) and CaO (> 7.5 wt.%) and also high loss on ignition (LOI = 6.02-13.30 wt.%), moderately low content of Al_2O_3 (10.22-13.01 wt.%), and a relatively stable Mg# in the range of 55-67 wt.%, corresponding to analogous effusive rocks of Mts. Medvednica, Samoborska Gora, and Kalnik (SLOVENEC et al., 2010, 2011). The mobility of the analyzed elements in the investigated rocks of Mt. Medvednica was assessed by plotting their concentrations against Zr as a differentiation index (Fig. 3). Except for TiO_2, K_2O and P_2O_5, which positively correlate with Zr, other major elements, as well as large ion lithophile elements (LILE; Cs, Rb, Ba, Sr), and transitional metals (V, Cr, Ni), show no correlation, indicating significant mobilization during deuteric alteration. This renders these elements unreliable for petrogenetic constraints. However, high field strength elements (HFSE) such as Ti, Th, Hf, Nb, Ta, P, and Y, and rare earth elements (REE) exhibit a good magmatic correlation with the differentiation index. They were, therefore, used for geochemical and petrogenetic interpretation, a method successfully applied to similar mafic rocks (e.g. PEARCE & NORRY, 1979). On the Zr/TiO_2 vs. Nb/Y diagram, utilized for the classification of altered extrusive rocks, the analyzed rocks correspond to alkali basalts (Fig. 4).

Figure 5a illustrates the element spider diagram normalized to N-MORB values for the Middle Triassic pyroclastic rocks of Mt. Medvednica. Overall, these patterns exhibit a smooth profile characterized by a gradual enrichment in the Th to Lu segment, as well as slightly positive P anomalies. These characteristics of the studied pyroclastic rocks closely resemble the patterns observed in the rift related within-plate alkali basalts (WPAB), and they bear a striking resemblance to the patterns of average ocean island basalts (OIB) (Fig. 5a). However, Cs, Ba, Rb, K and Sr show selective mobilization of these elements.

Chondrite normalized REE patterns of the studied rocks are displayed in Figure 5b. The REE patterns show a higher enrichment of LREE/HREE [$(La/Lu)_{cn}$ = 13.9-16.1] compared to the rift related alkali basalts, as well as to the alkaline basalts of the nearby Medvednica, Samoborska Gora and Kalnik mountains [$(La/Lu)_{cn}$ = 5.3-12.8; SLOVENEC et al., 2010, 2011; Fig. 5b]. These rocks are characterized by either the absence of, or presence of an extremely small positive Eu anomaly (Eu/Eu* = 1.00-1.06) typical for fractionation of plagioclase or its low accumulation. All samples have Lu_{cn} < 10 which may indicate residual garnet (SPATH et al., 2001).

Table 3: Chemical analyses of basaltic pyroclastic rocks from the Mt. Medvednica ophiolite mélange

Sample	PB-2	PB-4A	PB-5	VS-7	VS-21	VS-71
Rock type	LT	BA	LT	LT	LT	LT
SiO_2	49.89	47.52	46.56	50.21	47.34	47.82
TiO_2	1.96	2.28	2.18	1.85	2.31	2.18
Al_2O_3	10.52	11.65	12.14	10.22	12.96	13.01
Fe_2O_3 total	6.88	8.34	8.45	6.23	8.81	8.24
MnO	0.18	0.15	0.15	0.18	0.15	0.16
MgO	4.11	7.87	7.68	4.05	7.14	7.43
CaO	8.29	8.80	7.87	11.36	10.22	8.66
Na_2O	2.95	2.11	2.01	3.05	3.21	2.91
K_2O	0.86	1.38	1.33	0.88	1.06	0.99
P_2O_5	0.45	0.47	0.54	0.44	0.48	0.51
LOI	13.30	8.80	10.00	10.06	6.02	7.95
Total	99.39	99.37	98.91	98.53	99.70	99.86
Mg#	54.9	66.7	66.2	59.1	64.5	65.4
Cs	0.6	5.6	6.2	0.7	4.6	6.4
Rb	21	38	32	24	34	38
Ba	104	266	247	128	286	261
Th	4.99	5.39	5.78	4.93	5.21	5.77
Ta	3.00	3.29	3.29	3.01	3.24	3.28
Nb	41.5	53.0	52.1	45.3	49.4	52.6
Sr	197	181	161	202	214	173
Zr	207	247	238	198	221	217
Hf	5.0	5.6	5.7	5.1	5.3	5.5
Y	23.2	24.1	24.5	22.1	23.9	25.2
Sc	12	23	23	14	16	24
V	144	197	208	141	152	210
Cr	40	340	300	41	162	296
Ni	30	130	140	29	98	122
La	30.4	33.3	34.7	31.1	33.7	34.8
Ce	71.6	76.8	80.2	72.4	75.6	79.7
Pr	8.24	9.09	9.71	8.12	8.98	9.21
Nd	32.3	34.3	37.1	32.1	33.9	36.2
Sm	6.15	6.66	6.93	6.01	6.31	6.68
Eu	1.96	2.07	2.09	1.99	2.01	2.06
Gd	5.27	5.14	5.43	5.20	5.19	5.37
Tb	0.79	0.74	0.78	0.81	0.77	0.79
Dy	4.06	4.30	4.53	4.01	4.20	4.51
Ho	0.75	0.75	0.82	0.74	0.76	0.80
Er	1.91	2.02	2.15	1.94	1.99	2.09
Tm	0.251	0.268	0.276	0.258	0.261	0.273
Yb	1.47	1.60	1.52	1.49	1.51	1.56
Lu	0.227	0.243	0.240	0.231	0.238	0.236

Major elements in wt.%, trace elements in ppm. LOI = loss on ignition at 1100 °C. BA = basalt (clast in tuff), LT = lapilli tuff. Mg# = 100*molar MgO/(MgO + FeOtotal).
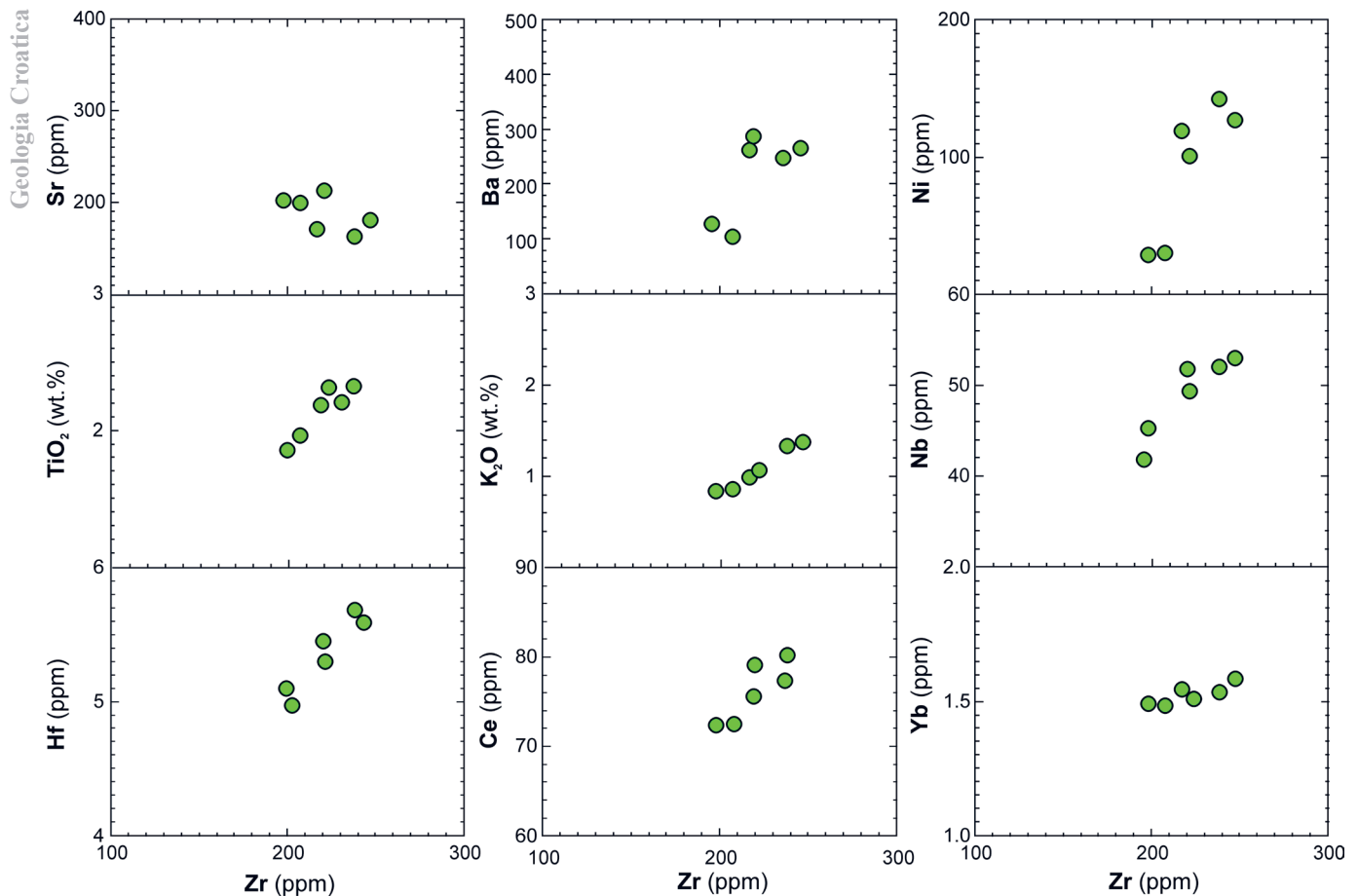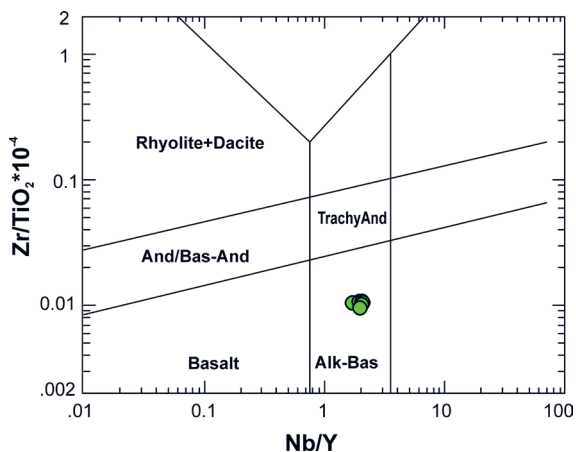
Figure 3. Variation diagrams for selected elements with Zr s index of differentiation for the basaltic pyroclastic rocks from the Mt. Medvednica ophiolite mélange.

5. DISCUSSION

The hectometre-scale blocks of the investigated volcaniclastic rocks included into the mélanges of Mt. Medvednica represent the sole known pyroclastic derivatives of the Middle Triassic alkali volcanic activity in the southwestern part of the Zagorje-Mid-Transdanubian Zone. This event has primarily produced basaltic pillow lavas, indicating its effusive submarine nature during the Late Anisian to Early Ladinian period (HALAMIĆ et al., 1998; SLOVENEC et al., 2010, 2011; KISS et al., 2012). However, the presence of alkali volcanic agglomerates and

Figure 4. Nb/Y – Zr/TiO₂*10⁻⁴ classification diagram (PEARCE, 1996) for the basaltic pyroclastic rocks from the Mt. Medvednica ophiolitic mélange.

lapilli tuffs on Mt. Medvednica, which outcrop in the same studied area together with the geochemically identical alkali basaltic pillow lavas of known Middle Triassic (Illyrian-Fassanian?) age (HALAMIĆ et al., 1998), suggests the occurrence of explosive submarine events during the Late Anisian--Early Ladinian? stages. This is further supported by the abundance of rounded vesicles in the investigated basaltic volcanic bombs, suggesting rapid submarine crystallization due to the sudden cooling of magma as pressure decreased during its ascent and arrival at the surface, exposing the lava to significant gas expansion (BLOOMER, 1994).
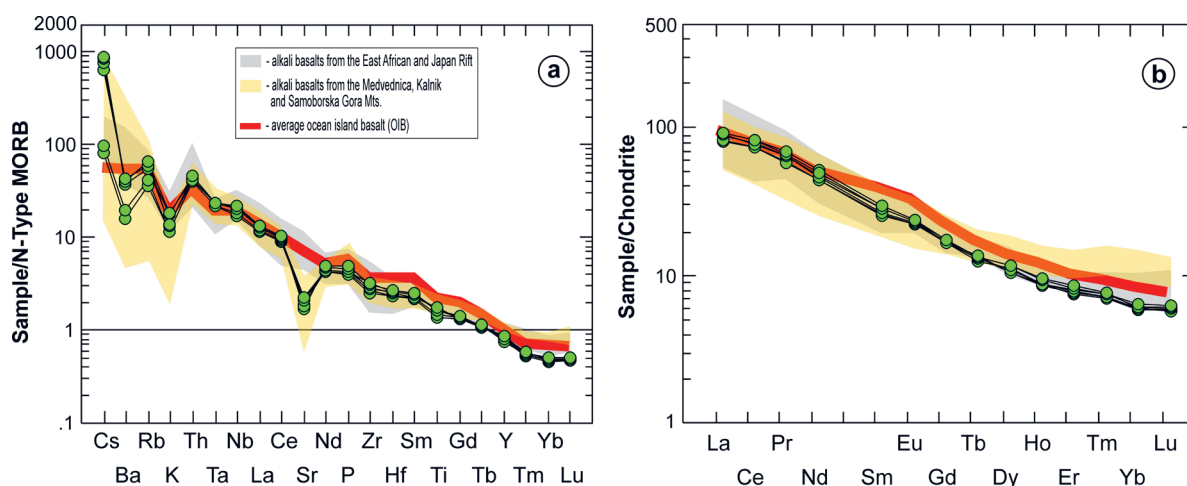
5.1. Petrogenetic and tectonomagmatic significance

Mesozoic alkali basalts, commonly found today as blocks preserved in ophiolitic mélanges across the broader Mediterranean region, are seen as remnants of either (a) intraoceanic islands (OI) and seamounts (e.g. SACCANI & PHOTIADES, 2005; MONJOIE et al., 2008; SAYIT & GÖNCÜOGLU, 2009), or (b) continental rifts (CR) (e.g. FITTON, 2007). The composition of continental rift basalts is akin to OI basalts; however, these rocks result from the continental break-up which preceded the formation of the nascent oceanic crust (BORTOLOTTI et al., 2009; KOGLIN et al., 2009).

Petrographic, XRD and geochemical analysis revealed significant sea-floor hydrothermal alterations in the rocks, confirmed by high loss on ignition and selective mobilisation

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Figure 5. (a) N-MORB normalized multielement patterns (SUN & McDONOUGH, 1989); (b) Chondrite normalized REE patterns (TAYLOR & McLENNAN, 1985) for the basaltic pyroclastic rocks from the Mt. Medvednica ophiolite mélange. Fields for alkali basalts from the Mts. Medvednica, Kalnik and Samoborska Gora ophiolitic mélange (SLOVENEC et al., 2010, 2011), and for the average composition of within-plate alkali basalts (WPAB; WILSON, 1989) and ocean island basalts (OIB; SUN & McDONOUGH, 1989) plotted for correlation constraints.

of LILE (Table 3; POLAT et al., 2002; POLAT & HOFMANN, 2003). Here reported post-magmatic parageneses (Table 2) are in line with those of similar hydrothermally altered mafic rocks from the area (SLOVENEC et al., 2012; ŠEGVIĆ et al., 2023). The formation of the investigated pyroclastic rocks is associated with alkali suites (Nb/ > 1 and high Ti/V = 62-91; SHERVAIS, 2023) formed in divergent within-plate settings (Fig. 6a). However, to reliably distinguish tectonomagmatic settings of origin for basaltic rocks where their geochemical characteristics exhibit features of continental ridge basalt (CRB) and ocean island basalt (OIB), the La/10 vs. Nb/8 vs. Y/15 diagram (CABANIS & LECOLLE, 1989) and the multi-element ratios discriminate function analysis proposed by AGRAWAL et al. (2008) were successfully utilized. Based on these criteria, the analyzed pyroclastics from Mt. Medvednica, along with their volcanic equivalents represented by the basaltic lavas of Mts. Medvednica, Samoborska Gora, and Kalnik, unequivocally originated in the same geotectonic area of an intracratonic rift (Figs. 6b, c). Therefore, it seems more fitting to interpret these rocks as volcanic or volcaniclastic deposits in a pre-ophiolitic continental rift basin, rather than considering them as the remains of an intraoceanic island or seamounts.

Although the investigated alkali pyroclastic rocks share the same geochemical characteristics with Illyrian-Fassanian basaltic lavas of Mts. Medvednica, Samoborska Gora, and Kalnik, there are certain minor differences in their source composition. Specifically, higher values of key discriminative ratios [(Th/Yb)$_{pm}$ = 19-22, (Ta/Yb)$_{pm}$ = 24-26, and La/Yb = 21-23], along with a lesser degree of partial melting (Fig. 7) in the pyroclastic rocks of Mt. Medvednica compared to basaltic lavas [(Th/Yb)$_{pm}$ = 7-16, (Ta/Yb)$_{pm}$ = 10-18, and La/Yb = 8-13; SLOVENEC et al., 2010, 2011], indicate their more primitive nature and suggest the generation of pyroclastics immediately preceding the formation of basaltic lavas. Consequently, it can be inferred that explosive volcanism recorded on Mt. Medvednica directly preceded the dominant effusive volcanism that resulted in the formation of basaltic lavas on Mts.

Medvednica, Samoborska Gora, and Kalnik, during the Late Anisian-Early Ladinian stages.

The very low La/Ta ratio (< 10.5) observed in the investigated pyroclastics, which is significantly lower than the values for uncontaminated Continental Rift Basalt (CRB) (La/Ta < 22; e.g. FITTON et al., 1988; HART et al., 1989), suggests that these pyroclastics represent uncontaminated melts erupted through highly thinned continental crust. The diminished relative abundance of HREE in these alkali pyroclastic rocks indicates residual garnet in the mantle source (e.g. SPATH et al., 1996). The analyzed pyroclastic rocks reflect melts derived from a primitive OIB-type mantle plume source, which experienced around 4-4.5% of partial melting (Fig. 7). This percentage is slightly lower than that of the mantle source for Mts. Medvednica, Samoborska Gora, and Kalnik alkali basaltic lavas.

5.2. Geodynamic significance

The origin of the investigated pyroclastic rocks of Mt. Medvednica can be explained by two geodynamic models based on two distinct Palaeogeographic reconstructions of geological events in the wider Mediterranean area during the Middle Triassic. The first model was introduced by STAMPFLI & BOREL (2002, 2004) and STAMPFLI & HOCHARD (2009), whilst the second one was presented by van HINSBERGEN et al. (2020).

The geodynamic model based on the Palaeogeographic reconstructions of STAMPFLI & BOREL (2002, 2004) and STAMPFLI & HOCHARD (2009) involves the Palaeotethyan Middle Triassic northward subduction under an active margin of Laurentia (Fig. 8a). Along the Palaeotethyan nortwestern margin, extensional tectonism occurred as a result of asthenospheric passive upwelling. This, in turn, caused the emergence of an OIB-type mantle plume within the ensialic back-arc lithosphere. The rise of this primitive mantle dome was attributed to adiabatic decompression along a network of subparallel faults, as outlined by SLOVENEC & ŠEGVIĆ (2021). This process was further facilitated by the substantial northeast-
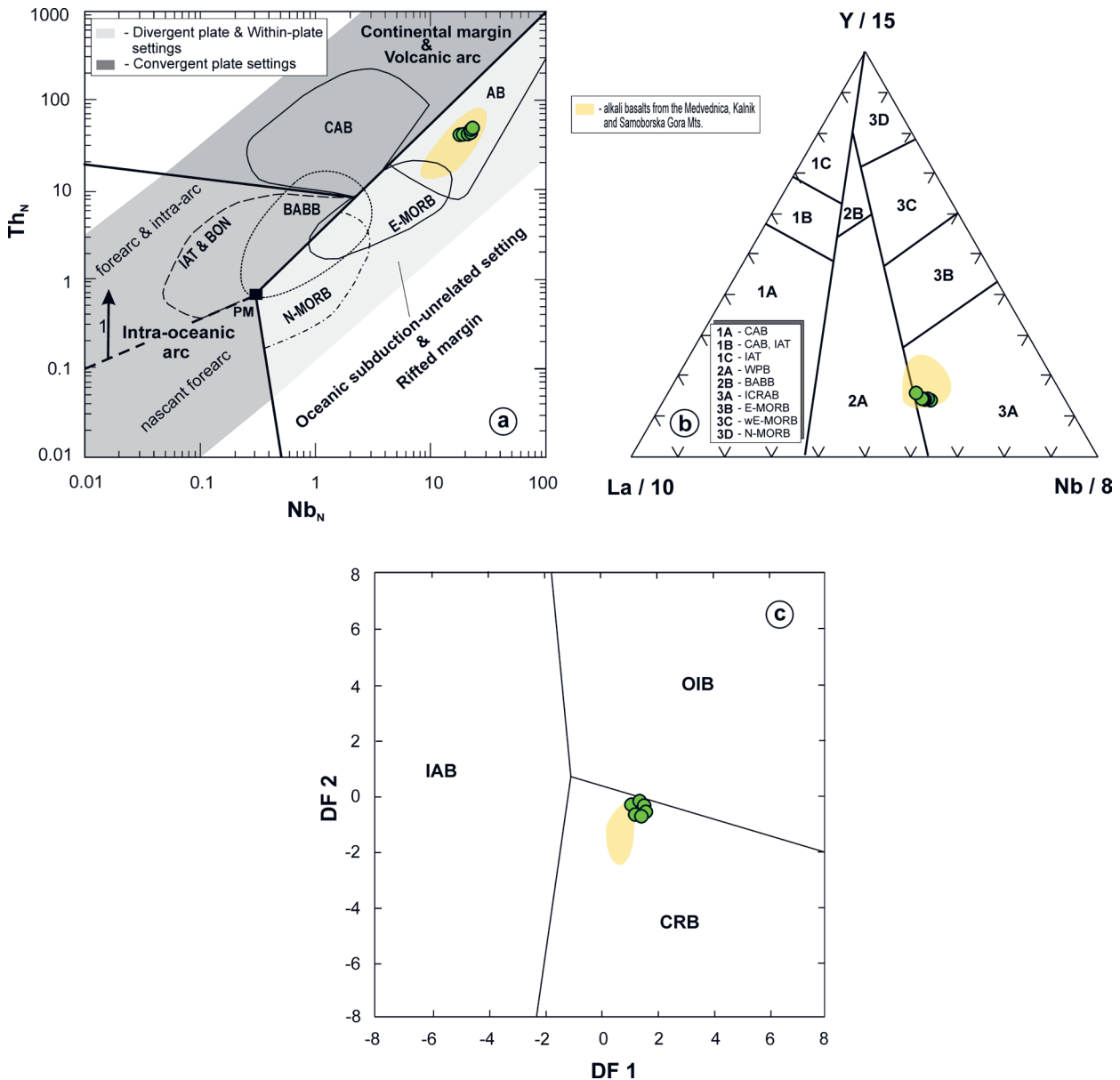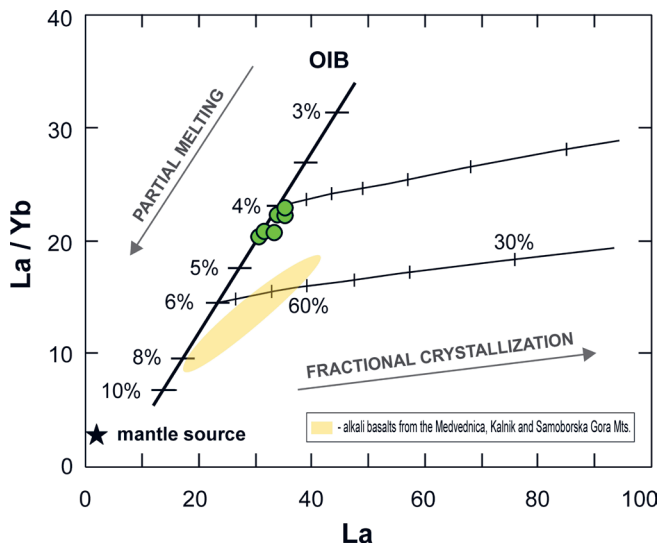
Figure 6. Discrimination diagrams for the basaltic pyroclastic rocks from the Mt. Medvednica ophiolitic mélange. (a) Simplified Th_N – Nb_N diagram (SAC-CANI, 2015). PM = primitive mantle. Th and Nb normalized to the N-MORB composition (SUN & McDONOUGH 1989). AB = alkali basalts, BABB = back-arc basin basalts, BON = boninites, CAB = calc-alkali basalts, IAT = island-arc tholeiites, N-MORB = normal mid-ocean ridge basalts, E-MORB = enriched MORB. (b) La/10 – Nb/8 – Y/15 diagram (CABANIS & LECOLLE, 1989). 1 = volcanic arc basalts; 2 = continental basalts; 3 = oceanic basalts; 1A = calc-alkali basalts (CAB); 1B = calc-alkali basalts and island-arc tholeiites (CAB, IAT); 1C = island-arc tholeiites (IAT); 2A = within-plate basalts (WPB); 2B = back-arc basin basalts (BABB); 3A = intracontinental rift alkali basalts (ICRAB); 3B = enriched MORB (E-MORB); 3C = weakly enriched MORB (E-MORB); 3D = normal mid-ocean ridge basalts (N-MORB). **(c)** DF_1 – DF_2 diagram (AGRAWAL et al., 2008; $DF_1 = 0.5533 \log_e (La/Th) + 0.2173 \log_e (Sm/Th) – 0.0969 \log_e (Yb/Th)$ $+ 2.0454 \log_e (Nb/Th) – 5.6305$; $DF_2 = -2.4498 \log_e (La/Th) + 4.8562 \log_e (Sm/Th) – 2.1240 \log_e (Yb/Th) – 0.1567 \log_e (Nb/Th) + 0.94$. IAB – island-arc basalts; OIB – ocean-island basalts; CRB – continental rift basalts. Fields for alkali basalts from the Mts. Medvednica, Kalnik and Samoborska Gora ophiolitic mélange (SLOVENEC et al., 2010, 2011) plotted for correlation constraints.

ward roll-back and retreat of the Palaeotethyan subducted slab (SLOVENEC et al., 2010). Ultimately, this sequence of events resulted in proto back-arc rifting within the continental crustal stable mass. This most likely happened behind the pericontinental volcanic arc thus giving rise to the Maliak back-arc rift within the emerging northwestern segment of Neotethys. (Fig. 8a). In this region, the phenomenon of back-arc rifting resulted in the formation of uncontaminated alkali basaltic lavas and pyroclastites, ranging from primitive to moderately evolved (OIB-type). These volcanic materials are characterized by their absence of subduction components and crustal contami-

nation. Therefore, the investigated pyroclastic rocks of Mt. Medvednica, along with their volcanic outflows from the southwest segment of the ZMTDZ, likely represent the last stage of spreading in a mature intracontinental rift basin. However, these alkali rocks, not qualifying strictly as ophiolitic rocks, also mark the initial (proto) phase of the opening of the future northwestern part of Neotethys, (the Meliata-Maliak-Pindos ocean system), as well as epidote-bearing albite granite from Mt. Medvednica (BALEN et al., 2022). This likely occurred before the formation of the nascent oceanic crust during the Upper Triassic (SLOVENEC et al., 2011).

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Figure 7. Petrogenic model for the basaltic pyroclastic rocks from the Mt. Medvednica ophiolitic mélange. Partial melting line for moderately enriched mantle source (OIB-like) (La = 1.5 ppm, Yb = 0.5 ppm). Model parameters = garnet-lherzolite source ($ol_{60.1}$-$opx_{18.9}$-$cpx_{13.7}$-$gt_{7.3}$), melting proportion = $ol_{1.3}$-$opx_{8.7}$-cpx_{36}-gt_{54}, distribution coefficients are from KOSTOPOULOS & JAMES (1992). Fractional crystallization lines: initial magma = 4% and 6% melting of the moderately enriched mantle source, fractionated mineral assemblage = ol_{30}-cpx_{40}-pl_{30}, distribution coefficients are from CHEN et al. (1990). Fields for alkali basalts from the Mts. Medvednica, Kalnik and Samoborska Gora ophiolitic mélange (SLOVENEC et al., 2010, 2011) plotted for correlation constraints.

According to the geodynamic model relying on the Palaeogeographic reconstruction presented by van HINSBERGEN et al. (2020), the initiation of the Balkan Neotethys Ocean can be attributed to the west-oriented subduction of the Balkan Palaeotethys Ocean under the northeastern margin of Greater Adria/Dacia. During this process, there was a successively northeastward roll-back and retreat of the subducted sinking slab of the Balkan Palaeotethys (Fig. 8b). These intense processes of slab retreat freed up significant space in the asthenosphere, allowing for uninterrupted upwelling of asthenospheric mantle during the Upper Anisian. This upwelling mantle was characterized by OIB-type mantle plumes, leading

to the formation of the proto back-arc Balkan Neotethys Rift accompanied by intense volcanism. Similar to the previous geodynamic model, this volcanism is marked by eruptions and effusions of primitive to moderately evolved (OIB-type) uncontaminated alkali basaltic pyroclastites and lavas (Fig. 8b), now archived in the ophiolitic mélange of the southwest segment of the ZMTDZ (Figs. 1b-d). Subsequent extensional events during the Upper Triassic and Middle Jurassic were followed by continuous magmatism and generation of the oceanic lithosphere within the Balkan Neotethys Ocean (SLOVENEC & ŠEGVIĆ, 2023).

However, apart from the two geodynamic models proposed for events on the northeastern margin of Adria (i.e. Dinarides, Southern Alps and Alcapa) during the Middle Triassic, it is also possible to assume the one proposed by LUSTRINO et al. (2019), CASSETA et al. (2019), DE MIN et al. (2020) and VELICOGNA et al. (2023) is credible. They associate magmatism with complex mantle heterogeneities or as an inheritance from previous tectonic events, discarding the hypothesis that an active subduction occurred in Adria during the Triassic. In this sense, the mantle source was variably metasomatized, and the magmatism was probably triggered by the extensional and transtensional tectonics related to the rifting system. The subduction signatures of the magmas were probably inherited from the subduction events that occurred during the Variscan or even older orogenic cycles.

6. CONCLUSIONS

• In the ophiolitic mélange of Medvednica Mt., situated in the southwestern segment of the Zagorje-Mid-Transdanubian Zone, hectometre blocks of Middle Triassic (Late Anisian-Early Ladinian?) mafic pyroclastic rocks (volcanic agglomerates/breccias and lapilli tuffs) were discovered for the first time.

• These pyroclastic derivatives of alkali within-plate basaltic lavas, which outcrop in the same studied area, indicate the occurrence of explosive events preceding the dominant effusive submarine volcanism.

• The mineral composition and chemistry of the rocks reflects significant sea-floor hydrothermal alterations.
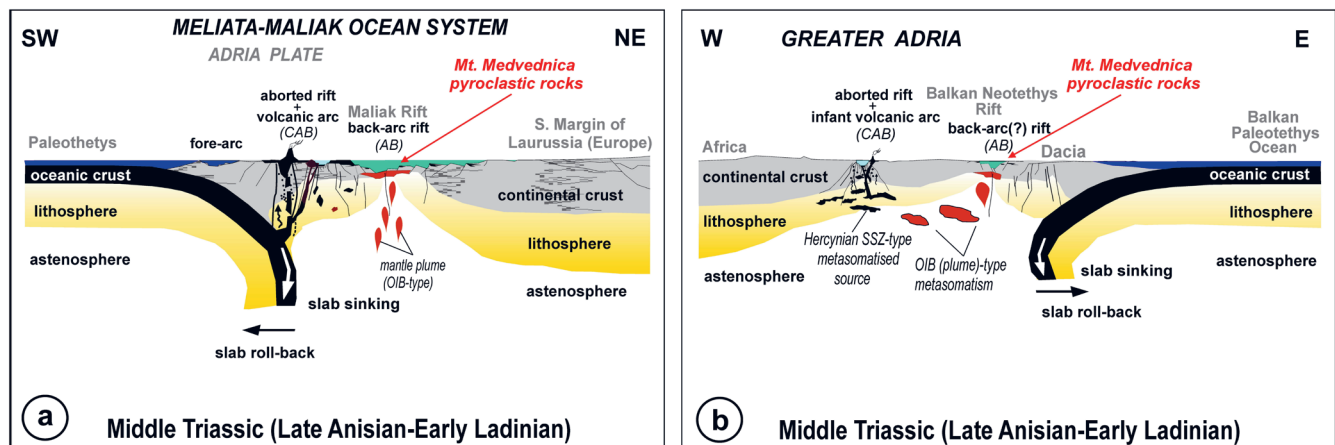
Figure 8. Schematic geodynamic sketch model of the tectonic setting of the investigated Mt. Medvednica basaltic pyroclastic rocks and formation of the back-arc rift in accordance with the Palaeogeographic reconstruction: (a) STAMPFLI & BOREL (2002, 2004) and STAMPFLI & HOCHARD (2009) and (b) van HINSBERGEN et al. (2020) (slightly modified after SLOVENEC & ŠEGVIĆ, 2023). AB = alkaline basalts/pyroclastites, CAB = calc-alkaline and shoshonitic basalts/volcaniclastites, OIB = ocean island basalts.

• The formation of studied pre-ophiolitic pyroclastics is associated with an intracontinental rift setting and reflects melts derived from an OIB-type enriched mantle plume source, which experienced around 4-4.5% of partial melting.

• The investigated pyroclastites were most likely generated during the Late Anisian-Early Ladinian? along the continental margin of Palaeotethys through the proto back-arc rifting of continental lithosphere (Adria Plate), leading to the formation of the Maliak/Balkan Neotethys Rift in the emerging northwestern segment of Neotethys. These events, which do not indicate the existence of active subduction in the Adria Plate, immediately preceded the generation of the initial Neotethyan oceanic lithosphere during the Upper Triassic.

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