

PETROLOGY AND TECTONIC SIGNIFICANCE OF GREENSCHISTS FROM THE MEDVEDNICA MTS. (SAVA UNIT, NW CROATIA)

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ABSTRACT

The Lower Cretaceous (123-115 Ma) low-grade metamorphic complex of the Medvednica Mts. is located within the southwestern edge of the Mid-Transdanubian shear zone. The SW-NE striking complex consists of metabasites overlain by metasediments, both affected by a single metamorphic event. Metamorphic parageneses and mineral compositions of the metabasites indicate greenschist facies conditions in the SE part and upper greenschist facies conditions in the NW one. Temperature estimates based on chlorite thermometry are consistent with temperatures derived from petrogenetic grids. Chemical compositions of the metabasites are likely controlled by pre- and syn-metamorphic modifications. Nevertheless, “immobile” element characteristics (HFSE, REE) indicate a subalkaline nature of the igneous precursors. Most probably, the protoliths were subduction-related low-K tholeiitic basalts. Structural analysis suggests that the greenschists of the Medvednica Mts. were formed during southwest-vergent obduction of Jurassic to Lower Cretaceous ophiolites onto the Dinaridic continental margin composed of Ordovician to Upper Triassic sedimentary and volcano-sedimentary successions. The petrological and geochemical investigations thus indicate that an island arc was involved in the obduction that formed the Medvednica Mts. low-grade metamorphic complex.

INTRODUCTION

Mineral assemblages of low- and very low-grade mafic rocks are controlled by changes in pressure-temperature (P - T) conditions. Thus, these rocks may yield tight constraints on (changing) metamorphic conditions. Furthermore, mafic rocks can be used to constrain the geodynamic setting of their protoliths, provided that metamorphism was not preceded or accompanied by significant changes in composition. In this paper, we present the results of a petrologic and geochemical study on low-grade metabasites occurring below an ophiolite mélangé in the Medvednica Mts. located to the north of Zagreb in Croatia. We will use our data to speculate on the geodynamic significance of these rocks during subduction and closure of the Tethyan oceanic realm.

GEOLOGIC AND TECTONIC SETTING

The Medvednica Mts. belong to the complex Sava Unit bordered by the Periadriatic Line in the north and the Zagorje - Mid-Transdanubian shear zone in the south (Fig. 1). Located in the border-area between the South Alpine, Tisia and Internal Dinaridic Units, the Medvednica Mts. include different tectonostratigraphic and tectonometamorphic slices of unclear origin (Pamić and Tomljenović, 1998; Herak, 1999; Haas et al., 2000; Tomljenović, 2002). The low-grade metamorphic Medvednica Unit (MU) is tectonically overlain by an ophiolite mélangé of Middle Jurassic to Hauterivian age (Kalnik Unit, KU), whereby in the NE, the thrust contact is reversed and refolded (Babić et al., 2002). Both MU and KU are covered by Cretaceous-Paleocene flysch (Fig. 2).

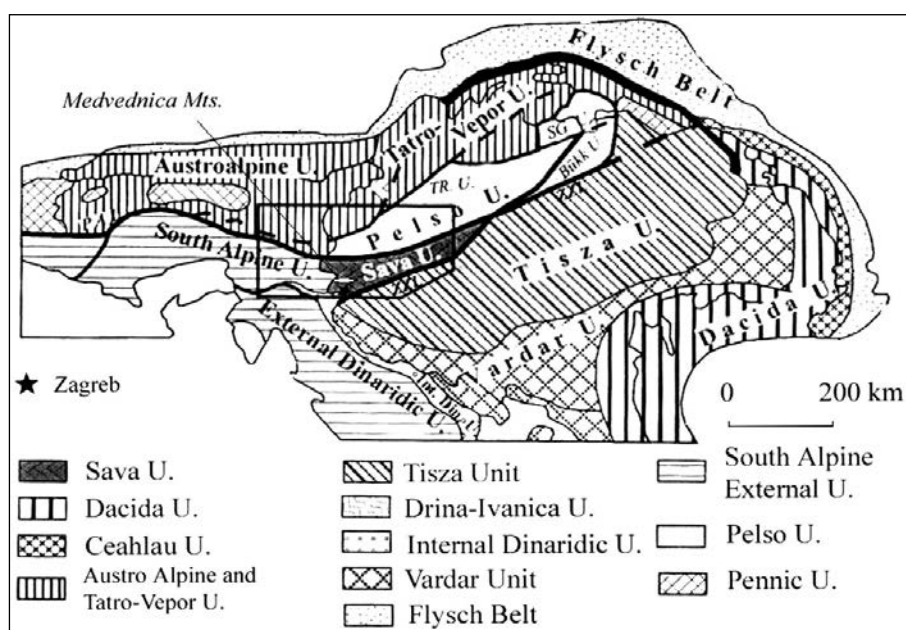


Fig. 1 - Pre-Tertiary tectonic units of the Pannonian Basin and surrounding regions (after Haas et al., 2000).

The Žumberak Nappe is made up of Triassic carbonates and clastics, and forms the uppermost tectonic unit (Šikić et al., 1979). All these basement units are transgressively covered by Miocene limestones, siliciclastics and marls.

The greenschist-facies MU crops out in the southern slopes of the Medvednica Mts. and consists of metabasites overlain by metasediments (metapelites, meta-arenites, marbles, metatuffites). Biostratigraphic data indicate Silurian to Early Carnian ages of the sedimentary precursors (Đurđanović, 1968; Kochansky-Devidé, 1981; Sremac and Mihajlović-Pavlović, 1983; Belak et al., 1995a). Locally, the metabasites contain relict gabbro and diabase protoliths (Kišpatić, 1918; Marić, 1959; Šikić et al., 1979; Pamić and Injuk, 1985/86; Belak et al., 1995a).

According to Jamičić (2000), the MU was affected by three deformational phases. Tomljanović (2002), however,

suggests four deformational phases. The oldest phase was synmetamorphic and produced a foliation showing SW-NE oriented stretching lineations. This phase is thought to be related to SW-vergent ophiolite obduction. Consistent K-Ar ages on two whole-rock samples from the metabasites (117.6 ± 4.0 and 120.0 ± 4.0 Ma) and three muscovite/phengite concentrates from the metasediments (115.4 ± 4.4 , 115.6 ± 4.4 , 122.8 ± 4.7 Ma) indicate an early Aptian age of metamorphism (Belak et al., 1995b). The second deformational phase affected the MU, KU and the overlying Cretaceous-Paleocene flysch and produced NW-vergent folds and thrusts (Fig. 2). The third and fourth deformational phases are related to Neogene to Quaternary tectonics and resulted in slight folding of the MU (Tomljanović, 2002).

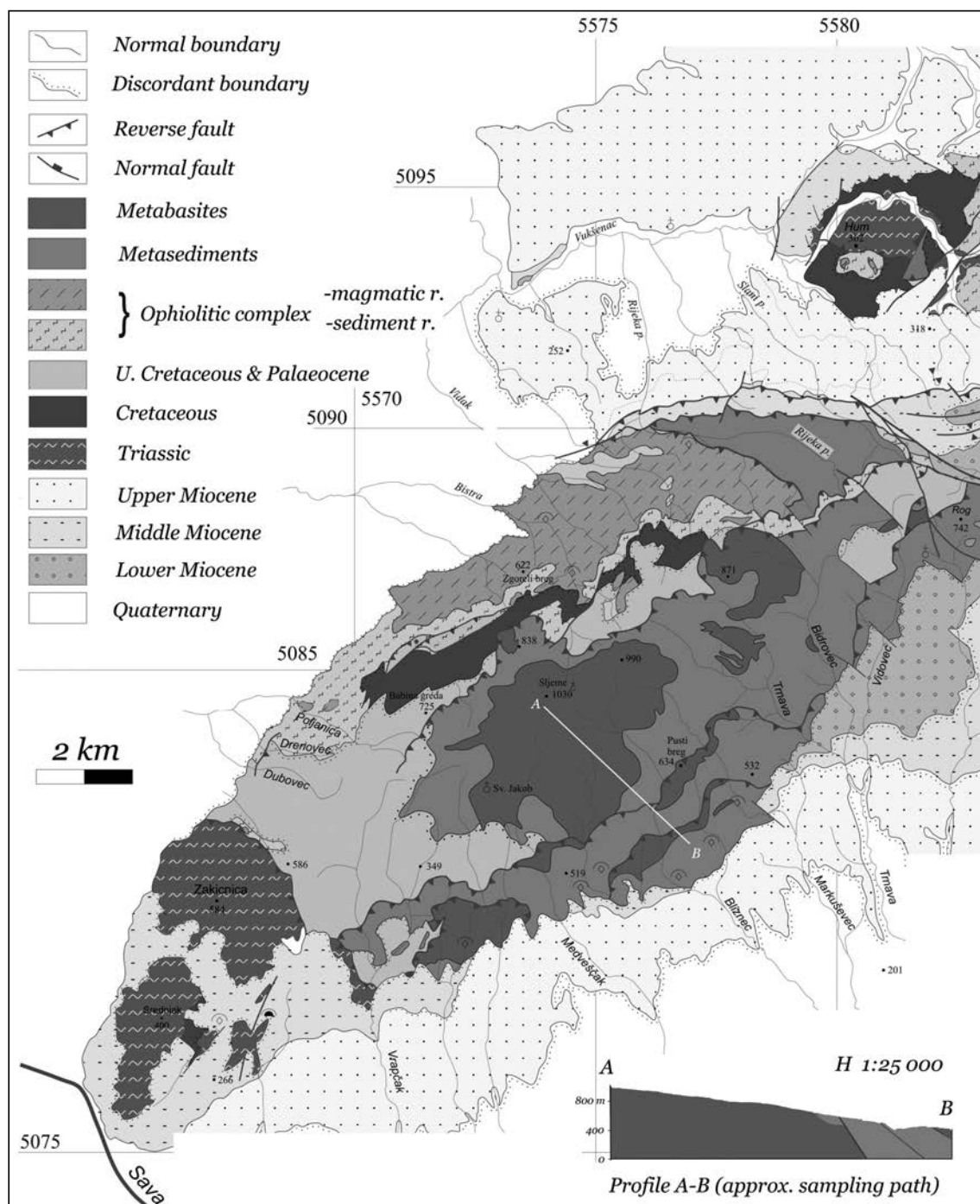


Fig. 2 - Geological map of the Medvednica Mts. (compiled by Tomljanović, 2002). A-B profile in the southwestern sector of the map approximately indicates the metabasite sampling path.

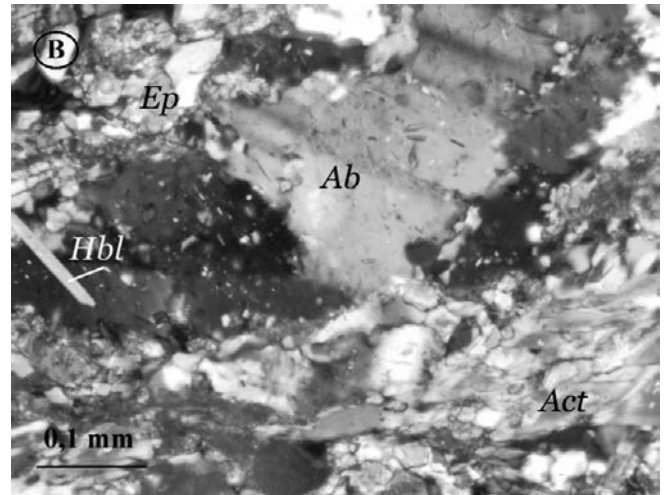
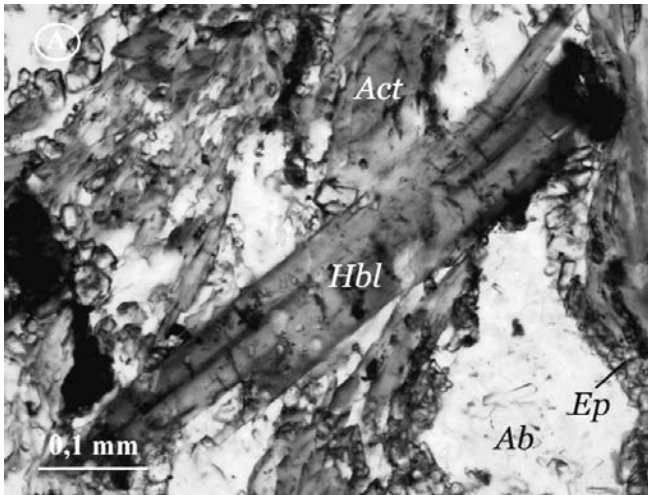


Fig. 3 - Microphotographs of sample GS. (A) 'Coexisting' actinolite (Act) and magnesiohornblende (Hbl), epidote (Ep) and albite (Ab). Black aggregates are leucoxene. Parallel polarizers. (B) Albite porphyroblast in a matrix of actinolite, epidote and acicular magnesiohornblende. Crossed polarizers.

ANALYTICAL TECHNIQUES

Mineral analyses from 9 representative samples were performed at the Mineralogisches Institut, Universität Heidelberg, using a CAMECA SX51 electron microprobe equipped

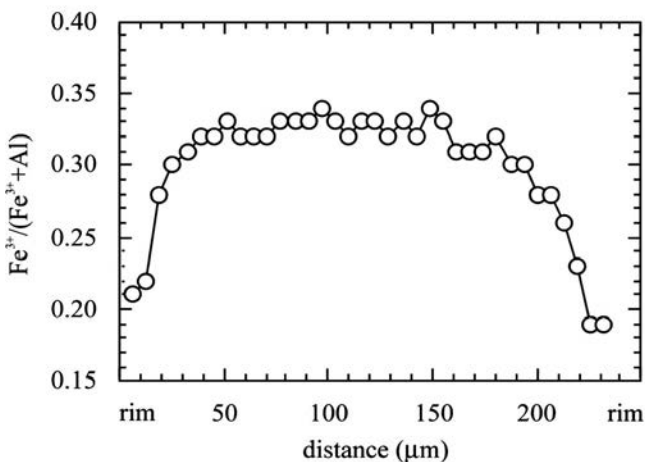
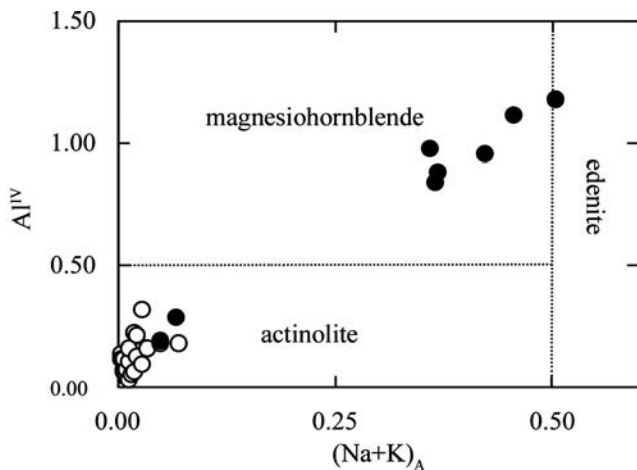


Fig. 4 - (Upper) Al^{IV} versus $(Na+K)_A$ classification diagram for amphiboles (Leake et al., 1997) from metabasites of the Medvednica Mts. Full circle = amphibole compositions in sample GS; open circles = actinolite from other samples. (Lower) Variation of $Fe^{3+}/(Fe^{3+}+Al)$ across an epidote porphyroblast in sample 8A interpreted as prograde metamorphic zoning pattern, i.e. decreasing pistacite content at grain rims.

with five wavelength-dispersive spectrometers. Operating parameters were of 15 kV accelerating voltage, 20 nA beam current, $\sim 1 \mu m$ beam size ($10 \mu m$ for albite) and 10 s counting time for all elements. Natural minerals, oxides (corundum, spinels, hematite and rutile) and silicates (albite, orthoclase, anorthite and wollastonite) were used for calibration. Raw data for all analyses were corrected for matrix effects with the PAP algorithm (Pouchou and Pichoir 1984; 1985) implemented by CAMECA. Formula calculations were done by using a software package designed by Hans-Peter Meyer (Mineralogisches Institut, Universität Heidelberg).

Bulk-rock powders for chemical analyses of 15 samples were obtained from rock chips free of visible veins. Major element concentrations and trace element abundances (Rb, Ba, Th, Pb, Nb, Sr, Zr, Y, Cr and Ni) were measured by XRF using conventional techniques. Divalent Fe concentrations were obtained by volumetric titration with $KMnO_4$. H_2O contents were determined gravimetrically and CO_2 contents were measured by infrared spectrometry. Five selected samples were analysed by ICP-MS for rare earth elements (REE), Cs, Th, U, Ta and Hf at Actlab Laboratories in Toronto, Canada.

PETROGRAPHY

The investigated greenschist samples were collected along a profile through the southwestern part of the MU (Fig. 2). The common paragenesis of our samples includes albite, actinolite, epidote and chlorite, accompanied by accessory titanite, magnetite, apatite and zircon. Our samples do not contain stilpnomelane and biotite that were described by Belak et al. (1995b) in another area. Both magnesiohornblende and actinolite were detected in sample GS, taken at the NW end of the sampling profile. Rock textures do not allow for an unequivocal interpretation of the age relationship between the two types of amphibole (Fig. 3). Either hornblende may be younger than actinolite, or both amphiboles may coexist and testify to the well known miscibility gap between hornblende and actinolite (e.g. Smelik et al., 1991).

Sample 12A from the SE end of the profile lacks actinolite and epidote but contains prehnite. The lack of amphibole and epidote in the latter sample could be due to either an exceptionally low CaO content (2.71 wt%), or to a lower metamorphic grade. Ti-rich cryptocrystalline aggregates (leucoxene)

Table 1 - Selected microprobe analyses and formulae of albite, amphibole, epidote, chlorite and titanite in the greenschist-facies metabasites from the Medvednica Mts.

Mineral	Albite				Amphibole				Epidote				Chlorite				Titanite						
	6A	10A	GS	IB	3E	6C	GS	5A	8A	8A	20c	8A	21r	2-05,c	GS	3E	6A	7	GS	5A	10A	GS	
Analysis nr.	2-07,c	2-03,c	2-07,c	2-08,c	2-02,r	3-03,r	3-03,c	1-02,c	20c	21r	2-05,c	GS	3-06	14	1-08	1-01,c	2-10,c	2-04,c					
SiO ₂	68.62	68.11	67.72	54.91	55.11	53.78	45.22	38.25	37.52	37.99	37.07	26.08	28.68	27.18	26.16	30.65	30.78	30.77					
TiO ₂	n.a.	n.a.	n.a.	0.02	0.02	0.02	0.12	0.05	0.08	0.14	0.01	0.04	0.01	0.01	0.01	37.89	35.58	38.17					
Al ₂ O ₃	20.27	19.47	20.30	1.40	0.86	2.38	8.00	26.61	22.59	25.56	21.37	19.57	17.51	20.09	19.74	1.55	2.79	0.95					
Cr ₂ O ₃	n.a.	n.a.	n.a.	0.00	0.02	0.00	0.00	0.00	0.00	0.07	0.05	0.06	0.15	0.13	0.02	0.07	0.06	0.07					
Fe ₂ O ₃	0.11	0.12	0.12	0.11	0.40	0.00	5.86	8.42	13.82	9.58	15.47	0.00	0.00	0.00	0.00	0.46	1.00	1.36					
FeO	n.a.	n.a.	n.a.	11.27	12.69	14.33	14.22	0.00	0.00	0.00	0.00	26.14	24.39	20.97	23.89	0.00	0.00	0.00					
MnO	n.a.	n.a.	n.a.	0.32	0.26	0.38	0.47	0.12	0.13	0.08	0.14	0.33	0.38	0.32	0.45	0.00	0.03	0.04					
MgO	n.a.	n.a.	n.a.	16.09	15.49	13.59	9.88	0.00	0.00	0.00	0.00	15.03	15.96	18.83	17.30	0.00	0.02	0.00					
CaO	0.43	0.04	0.46	12.43	12.62	12.03	10.75	23.79	23.52	23.79	23.07	0.04	0.70	0.09	0.03	28.35	28.81	27.92					
Na ₂ O	11.64	11.42	11.75	0.32	0.19	0.48	2.28	0.04	0.00	0.02	0.00	0.03	0.03	0.01	0.00	0.00	0.01	0.01					
K ₂ O	0.09	0.05	0.04	0.11	0.03	0.11	0.52	0.02	0.00	0.00	0.00	0.03	0.01	0.01	0.01	0.01	0.02	0.00					
H ₂ O				2.08	2.08	2.06	1.99	1.90	1.87	1.89	1.85	11.27	11.46	11.65	11.43								
Total	101.16	99.20	100.39	99.05	99.77	99.14	99.31	99.20	99.52	99.12	99.03	98.63	99.29	99.29	99.04	98.99	99.10	99.29					
Si	2.967	2.995	2.954	7.902	7.927	7.839	6.821	3.012	3.006	3.009	3.004	2.776	3.001	2.798	2.745	1.008	1.012	1.011					
Al ^{IV}	1.033	1.009	1.044	0.098	0.073	0.161	1.179					1.224	0.999	1.202	1.255								
Al ^{VI}				0.139	0.074	0.249	0.244	2.469	2.133	2.386	2.040	1.231	1.160	1.234	1.186	0.060	0.108	0.037					
Ti				0.002	0.002	0.002	0.014	0.003	0.005	0.008	0.000	0.003	0.001	0.001	0.001	0.937	0.879	0.943					
Cr				0.000	0.002	0.000	0.000	0.000	0.000	0.004	0.003	0.005	0.013	0.010	0.002	0.002	0.002	0.002					
Fe ³⁺	0.004	0.004	0.004	0.012	0.043	0.000	0.666	0.499	0.833	0.571	0.943	0.000	0.000	0.000	0.000	0.011	0.025	0.034					
Fe ²⁺				1.356	1.526	1.747	1.794	0.000	0.000	0.000	0.000	2.327	2.134	1.805	2.096	0.000	0.000	0.000					
Mn				0.039	0.032	0.047	0.060	0.008	0.009	0.005	0.009	0.030	0.034	0.028	0.028	0.000	0.001	0.001					
Mg				3.451	3.321	2.953	2.222	0.000	0.000	0.000	0.000	2.385	2.489	2.889	2.706	0.000	0.001	0.000					
Ca	0.020	0.002	0.022	1.916	1.945	1.879	1.737	2.007	2.019	2.018	2.003	0.005	0.079	0.010	0.003	0.999	1.014	0.983					
Na	0.976	0.974	0.994	0.090	0.054	0.135	0.666	0.007	0.000	0.003	0.000	0.007	0.005	0.001	0.000	0.000	0.001	0.000					
K	0.005	0.003	0.002	0.020	0.005	0.020	0.100	0.002	0.000	0.000	0.000	0.004	0.002	0.001	0.001	0.000	0.001	0.000					
An	2.00	0.17	2.11																				
X _{Mg}				71.79	68.51	62.82	55.32					50.62	53.84	61.55	56.35								
Fe ³⁺ /(Fe ³⁺ +Al)								0.168	0.281	0.193	0.316					0.160	0.187	0.476					

Formulae of albite calculated on the basis of 8 oxygens and all Fe as Fe₂O₃; amphibole on the basis of 23 oxygens (2 OH) and 13 cations excluding Ca, Na and K; epidote on the basis of 12.5 oxygens (1 OH) and all Fe as Fe₂O₃; chlorite on the basis of 14 oxygens (8 OH) and all Fe as FeO; titanite on the basis of 5 oxygens and all Fe as Fe₂O₃; c- grain core.

are common; titanite was detected by microprobe as the most common phase in these aggregates. Chlorite sheets are oriented subparallel to foliation. Actinolite occurs as needle-like porphyroblasts surrounded by epidote and chlorite, and contains inclusions of epidote. Epidote often forms isolated subidiomorphic blasts or occurs in aggregates. Albite forms large porphyroblasts (up to 1 mm in diameter) containing inclusions of actinolite and chlorite (Fig. 3B).

MINERAL CHEMISTRY

Albite compositions correspond to $Ab_{97.5-99.6}Or_{0.2-1.5}An_{0.2-2.1}$. Fe_2O_3 contents are generally below 0.12 wt%, provided that tiny inclusions of chlorite and/or actinolite were not part of the activated volume during EMPA analysis.

Actinolite shows limited compositional variations with X_{Mg} ranging from ~ 0.55 to 0.74 and Al_2O_3 contents between 0.53 and 2.38 wt% (Table 1). Amphibole grains from sample GS, however, show bimodal compositions in terms of Al_2O_3 contents with 'coexisting' actinolite and magnesiohornblende (Fig. 4A).

Epidote analyses are highly variable with X_{Fe} [= $Fe^{3+}/(Fe^{3+}+Al)$] ranging from 0.12 to 0.35. Individual grains show homogeneous cores and a rimward decrease of X_{Fe} in their outermost zones (Fig. 4B). This kind of zoning is a characteristic feature of prograde epidote growth under low-grade metamorphic conditions (Coombs et al., 1976; Liou et al., 1985; Beiersdorf and Day, 1995). High whole-rock Fe contents (total $Fe_2O_3 = 8.41 - 14.38$ wt%) in conjunction with relatively low X_{Fe} of epidote suggest low oxygen fugacity during metamorphism.

Chlorite compositions show limited chemical variations. 'Uncontaminated' analyses with $(Na+K+Ca) < 0.09$ cations per formula unit (cpfu), calculated on the basis of 14 oxygens and total Fe as Fe^{2+} (Table 1) have a total number of cations between 9.85 and 10.03, suggesting low interlayer vacancy and low Fe^{3+} . Al_{total} varies between 2.16 and 2.57 cpfu, suggesting a lack of smectite inter-layers (Bettison and Schiffman, 1988). According to the classification of trioctahedral chlorite accepted by the CMS Committee (Bailey,

1988), the investigated chlorites belong to the group defined by clinocllore and chamosite end-members. In the classification scheme of Hey (1954), the chlorites correspond to ripidolite and pycnochlorite compositions (Fig. 5). There is a slight positive correlation between Al^{IV} and Fe^{VI} in the analysed chlorites ($r^2 = 0.610$) indicating that chlorite chemistry may be used as a geothermometer (Cathelineau and Nieva, 1985; Cathelineau, 1988).

Titanite is generally Al-rich (up to 2.25 wt% Al_2O_3) and Fe-poor (total Fe as $Fe_2O_3 < 1.39$ wt%). Ti varies from 0.88 to 0.99 cpfu (based on 5 oxygens and all iron as Fe^{3+}) indicating variable substitution according to $(Al, Fe^{3+}) + (OH, F) \Leftrightarrow Ti^{4+} + O^{2-}$ (Higgins and Ribbe, 1976).

Other minerals. Quartz and calcite are rare in primary parageneses but are common as filling in veins and lenses. A pure TiO_2 phase was detected in the leucoxene aggregates, associated with rare pyrite (sample 6A) and pyrrhotite (6C). Accessory apatite was found in samples 6C, 8A and 10A.

WHOLE-ROCK COMPOSITIONS

Major and trace element compositions are given in Table 2. Volatile components (H_2O+CO_2) range from ~ 2.0 to 9.0 wt%. Most samples are characterized by relatively low contents of CaO (≤ 11.2 wt%), P_2O_5 (≤ 0.28 wt%; sample 6C has 0.48 wt% P_2O_5), TiO_2 (≤ 1.83 wt%); except for samples 2B and 12A) and K_2O (≤ 0.30 wt%, apart from samples 1B and 12A).

In most samples, the abundances of large ion lithophile trace elements are relatively low (Table 2). Sample 7, however, is characterized by exceptionally high abundances of Ba and Pb that are most probably due to secondary mineralization. Indeed, galena- and sphalerite-bearing veins have been found in the metasedimentary subunit of the MU and baryte boulders have been described from the metabasite subunit (Marič, 1959; Šinkovec et al., 1988). Primitive mantle-normalized element abundance patterns and chondrite-normalized REE patterns for some of the samples are presented in Figs. 6 and 7, respectively.

DISCUSSION

Geochemical nature and geotectonic setting of precursor rocks

In most cases, chemical compositions of metabasic rocks are different from those of their igneous precursors. This is due to the effects of weathering, hydrothermal alteration, prograde dehydration and, eventually, retrograde rehydration. In particular, large ion lithophile elements (LILE), such as Cs, Rb, K, Na, Ba, Pb and U can easily be transported by hydrous fluids, and mafic igneous rocks may become enriched or depleted in these elements during weathering and metamorphism. Furthermore, significant changes in Fe/Mg ratios or in the oxidation ratio of Fe may occur during hydrothermal alteration and Si may become mobilized during low-grade metamorphism. Despite these limitations, some constraints on the nature of the igneous protoliths of metabasic rocks can be obtained from elements that are commonly regarded as relatively immobile, such as the HFSE and the REE.

The investigated metabasites are characterized by high contents of (H_2O+CO_2) (Table 2), indicating an extensive influx by fluids, if the primary igneous assemblage was nearly anhydrous. This implies that many chemical features

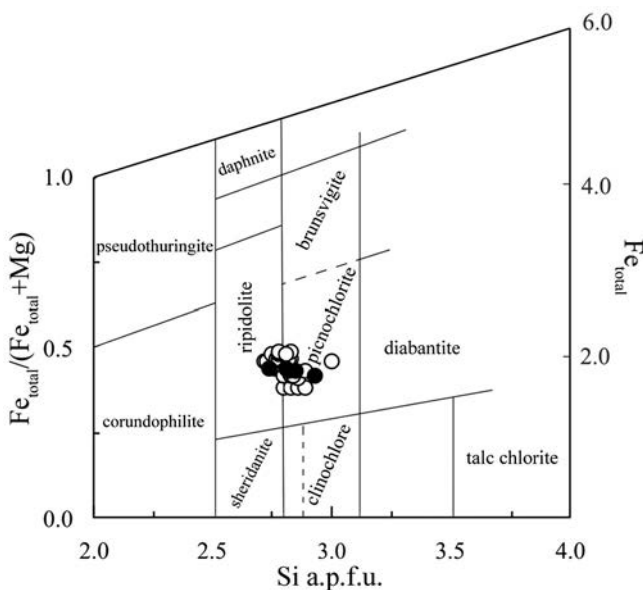


Fig. 5 - $Fe_{total}/(Fe_{total}+Mg)$ versus Si classification scheme of Hey (1954) with compositions of chlorite from metabasites of the Medvednica Mts. Symbols as in Fig. 4A.

Table 2 - Whole rock compositions of greenschist-facies metabasites from Medvednica Mts.

Sample	1B	2B	3A	3E ^a	4B ^a	4C	5A	6A ^a	6C ^a	7	8A	10A	10B2	12A	GS ^a
SiO ₂	48.40	47.20	48.60	50.32	49.30	49.30	48.30	46.38	48.62	47.00	47.10	46.10	46.40	50.30	49.98
TiO ₂	1.52	2.37	1.83	1.71	1.54	1.73	1.46	1.31	1.39	1.39	1.68	1.34	1.33	2.70	1.71
Al ₂ O ₃	15.60	14.40	15.20	13.51	14.00	15.30	16.40	12.78	15.24	15.10	15.20	16.10	16.20	18.40	14.99
Fe ₂ O ₃	3.12	1.85	3.45	4.01	3.31	3.23	3.48	5.36	3.91	2.95	3.59	1.11	1.20	2.56	11.46
FeO	5.83	8.22	6.53	6.12	6.56	6.18	5.47	7.91	6.64	5.63	6.33	6.57	6.67	6.73	n.a.
MnO	0.15	0.14	0.16	0.16	0.19	0.15	0.15	0.24	0.19	0.15	0.14	0.11	0.11	0.26	0.19
MgO	6.47	3.71	5.28	7.26	7.90	6.47	6.70	9.91	6.76	5.91	6.15	4.76	4.91	4.45	5.80
CaO	8.53	8.07	8.80	8.40	9.30	10.50	11.20	7.42	6.81	9.57	10.30	8.21	7.87	2.71	8.45
Na ₂ O	3.74	4.54	4.72	4.04	3.25	3.31	2.93	3.03	4.45	2.80	3.25	5.50	5.54	5.85	4.76
K ₂ O	1.15	0.30	0.17	0.17	0.31	0.26	0.15	0.23	0.29	0.29	0.06	0.08	0.07	1.00	0.13
P ₂ O ₅	0.19	0.28	0.21	0.20	0.23	0.20	0.18	0.26	0.48	0.16	0.21	0.14	0.15	0.31	0.27
H ₂ O	3.16	3.67	3.03	2.62	2.94	2.69	2.90	3.50	3.32	3.95	3.40	3.43	3.52	3.75	n.a.
CO ₂	1.10	4.90	1.42	<0.05	<0.05	<0.05	<0.05	0.21	1.09	4.1	1.85	5.60	5.52	<0.05	n.a.
LOI	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.96
Total	98.96	99.65	99.40	98.52	98.83	99.32	99.32	98.54	99.19	99.00	99.26	99.05	99.49	99.02	99.70
Cs	n.a.	n.a.	n.a.	0.2	0.6	n.a.	n.a.	0.2	0.2	n.a.	n.a.	n.a.	n.a.	n.a.	0.3
Rb	19	3	2	1	6	4	3	3	3	6	0	1	1	22	<1
Ba	173	106	50	21	38	86	95	15	17	719	89	72	65	148	19
Th	3	2	<1	1.01	0.44	<1	<1	0.51	1.24	3	1	3	1	<1	1.11
U	n.a.	n.a.	n.a.	0.25	0.11	n.a.	n.a.	0.16	0.42	n.a.	n.a.	n.a.	n.a.	n.a.	0.42
Pb	7	6	6	<5	<5	8	7	<5	<5	105	4	7	5	6	<5
Ta	n.a.	n.a.	n.a.	0.24	0.18	n.a.	n.a.	0.19	0.54	n.a.	n.a.	n.a.	n.a.	n.a.	0.60
Nb	4	6	3	4.9	3.6	3	3	3.60	7.7	2	4	4	4	5	5.50
Sr	379	79	365	139	190	325	270	75	139	258	312	100	98	65	189
Zr	163	232	227	196	146	151	121	153	342	114	165	132	132	230	274
Hf	n.a.	n.a.	n.a.	3.8	3.2	n.a.	n.a.	3.2	7.4	n.a.	n.a.	n.a.	n.a.	n.a.	5.2
Y	37	55	53	34.2	33.0	42	34	34	66.5	31	41	33	33	56	53
Cr	218	180	168	155	190	263	280	226	127	253	236	272	305	200	140
Ni	260	435	40	55	79	374	73	62	46	70	58	299	426	319	37
La	n.a.	n.a.	n.a.	5.07	5.57	n.a.	n.a.	5.72	15.1	n.a.	n.a.	n.a.	n.a.	n.a.	10.6
Ce	n.a.	n.a.	n.a.	14.0	17.0	n.a.	n.a.	16.4	40.0	n.a.	n.a.	n.a.	n.a.	n.a.	28.2
Pr	n.a.	n.a.	n.a.	2.33	2.58	n.a.	n.a.	2.68	6.19	n.a.	n.a.	n.a.	n.a.	n.a.	4.47
Nd	n.a.	n.a.	n.a.	11.7	13.1	n.a.	n.a.	13.7	29.5	n.a.	n.a.	n.a.	n.a.	n.a.	21.2
Sm	n.a.	n.a.	n.a.	3.75	4.10	n.a.	n.a.	4.26	8.42	n.a.	n.a.	n.a.	n.a.	n.a.	6.36
Eu	n.a.	n.a.	n.a.	1.20	1.45	n.a.	n.a.	1.37	2.65	n.a.	n.a.	n.a.	n.a.	n.a.	2.08
Gd	n.a.	n.a.	n.a.	4.72	5.16	n.a.	n.a.	5.32	10.2	n.a.	n.a.	n.a.	n.a.	n.a.	7.89
Tb	n.a.	n.a.	n.a.	0.96	1.00	n.a.	n.a.	1.04	1.98	n.a.	n.a.	n.a.	n.a.	n.a.	1.56
Dy	n.a.	n.a.	n.a.	5.80	5.87	n.a.	n.a.	5.98	11.7	n.a.	n.a.	n.a.	n.a.	n.a.	9.33
Ho	n.a.	n.a.	n.a.	1.31	1.28	n.a.	n.a.	1.28	2.56	n.a.	n.a.	n.a.	n.a.	n.a.	2.04
Er	n.a.	n.a.	n.a.	3.87	3.64	n.a.	n.a.	3.69	7.40	n.a.	n.a.	n.a.	n.a.	n.a.	5.83
Tm	n.a.	n.a.	n.a.	0.634	0.570	n.a.	n.a.	0.568	1.20	n.a.	n.a.	n.a.	n.a.	n.a.	0.914
Yb	n.a.	n.a.	n.a.	3.96	3.48	n.a.	n.a.	3.47	7.25	n.a.	n.a.	n.a.	n.a.	n.a.	5.34
Lu	n.a.	n.a.	n.a.	0.577	0.520	n.a.	n.a.	0.524	1.06	n.a.	n.a.	n.a.	n.a.	n.a.	0.765
Mg#	59.7	42.6	52.1	59.7	62.1	58.5	60.8	60.7	56.9	58.6	56.0	55.5	55.7	49.4	51.8

Mg# = 100*molar MgO/(MgO+0.9*FeO_{total}); ^a = trace element analyses performed by ICP-MS. Oxides in wt%, trace elements in ppm

of the samples may not be primary. Indeed, Harker variation diagrams for major and trace elements show a relatively large scatter, even when recalculated on an anhydrous basis (not shown). The same holds true, if MgO or Mg# are used instead of SiO₂.

Ni vs Mg# relationships reveal two groups of samples (Fig. 8): samples of the first group (3A, 3E, 4B, 5A, 6A, 6C, 7, 8A, GS) are characterized by low abundances of Ni that are positively correlated with Mg#. In marked contrast, samples of the second group (1B, 2B, 4C, 10A, 10B2, 12A) are characterised by high abundances of Ni that are not correlated with Mg#. Ni-Mg# systematics similar to those defined by samples of the first group are expected for a magma series produced by variable amounts of olivine fractionation. On the other hand, the unsystematic behaviour of Ni and Mg# in samples of the second group reflects the effects of some non-igneous process, such as weathering, hydrothermal alteration and/or addition of sedimentary components. These samples will therefore be excluded in the following discussion of the origin of the magmatic precursors.

Relatively low contents of TiO₂, CaO, P₂O₅, K₂O, Rb and Ba in samples of the second group (apart from sample 7, see above) suggest a subalkaline nature of the protoliths. This hypothesis is supported by “immobile” trace element

characteristics, such as low values of Nb/Y (0.06 to 0.12), high values of Zr/Nb (33 to 76) (Fig. 9a) and flat chondrite-normalized REE patterns with (La/Yb)_{cn} ≈ 1 (Fig. 7).

The tectonic setting of the subalkaline protoliths (i.e. subduction-related vs mid-ocean ridge) is difficult to decipher, due to secondary changes of bulk-rock compositions. For example, primitive mantle-normalized element concentration patterns of Medvednica metabasites are characterized by depletions of Rb, Ba and K relative to Ta and Nb (Fig. 6), a feature that is observed in most mid-ocean ridge basalts. However, given the mobility of LILE elements in hydrous fluids relative to HFSE, low LILE/Nb ratios may result from dehydration-induced depletion of LILE. Therefore, we will confine the following discussion to the abundances of relatively immobile high-field strength elements (HFSE) and REE.

Medvednica metabasites are characterized by flat REE patterns with minor negative Eu anomalies (Fig. 7). Such patterns are shown by many low-K tholeiitic basalts from modern mid-ocean ridges, back-arc basins and immature intra-oceanic island arcs. On the other hand, primitive mantle-normalized element concentration diagrams are characterized by modest negative Ti anomalies (relative to Zr and Tb; Fig. 6), a feature typical for subduction-related magmas.

Furthermore, in the Th-Hf/3-Ta diagram of Wood (1980), four out of five samples fall into the field of primitive arc tholeiites characterized by $Hf/Th > 3$ and one sample plots very near to this subfield (Fig. 9b). A 'mild' arc-tholeiitic character of the igneous precursors is also suggested by their Th/Yb-Ta/Yb signatures (Fig. 10).

METAMORPHIC CONDITIONS

To constrain peak metamorphic conditions for the investigated metabasites, we used a schematic petrogenetic grid that was originally calculated in the Na_2O -CaO-MgO- Al_2O_3 - SiO_2 - H_2O (NCMASH) system by Liou et al. (1985) and later modified by including the effects of FeO and Fe_2O_3 (Schiffman and Day, 1999). In this system, the lower

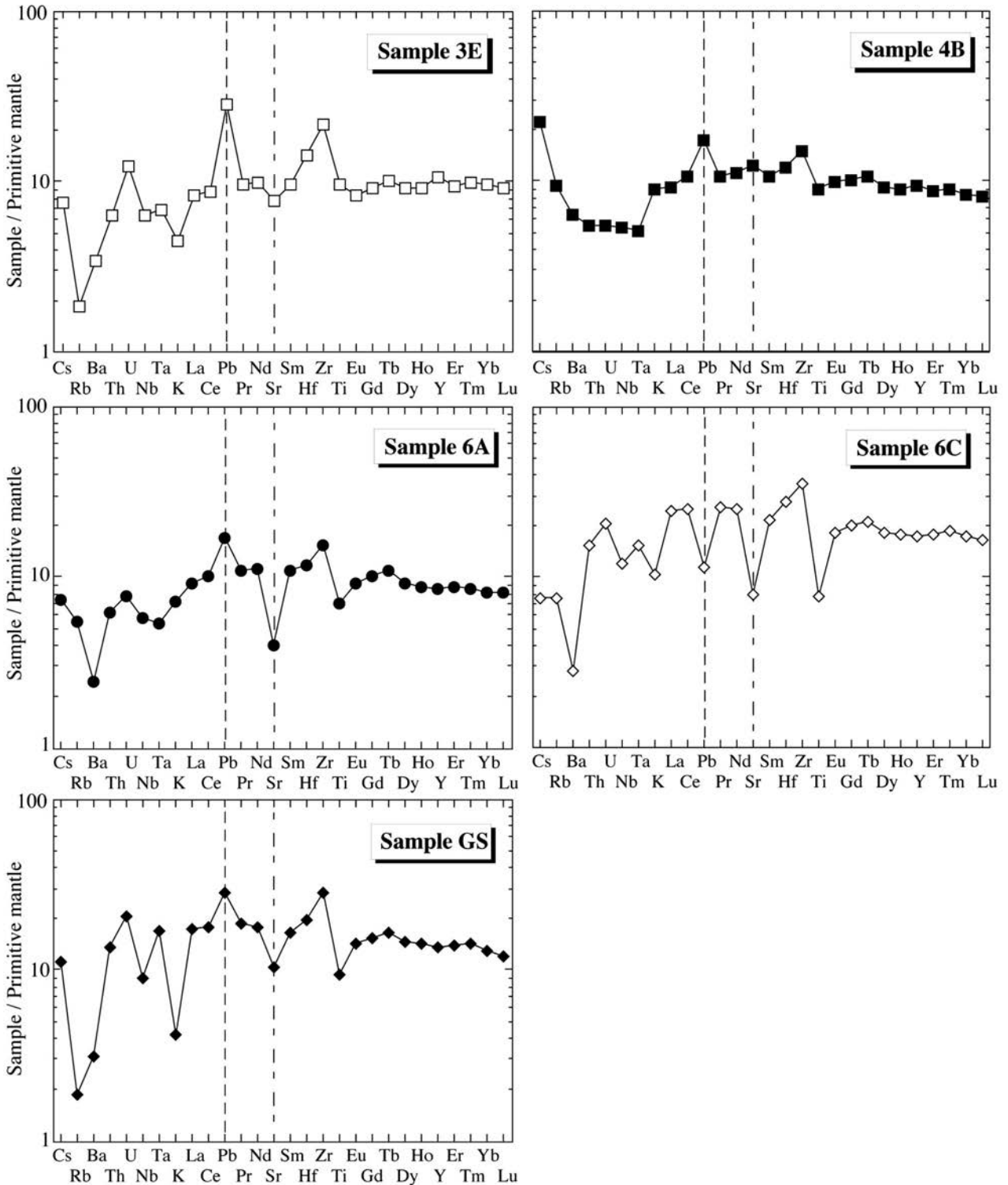


Fig. 6 - Primitive mantle-normalized element concentration diagram for selected samples of metabasites from the Medvednica Mts. (normalization values from Hofmann, 1988).

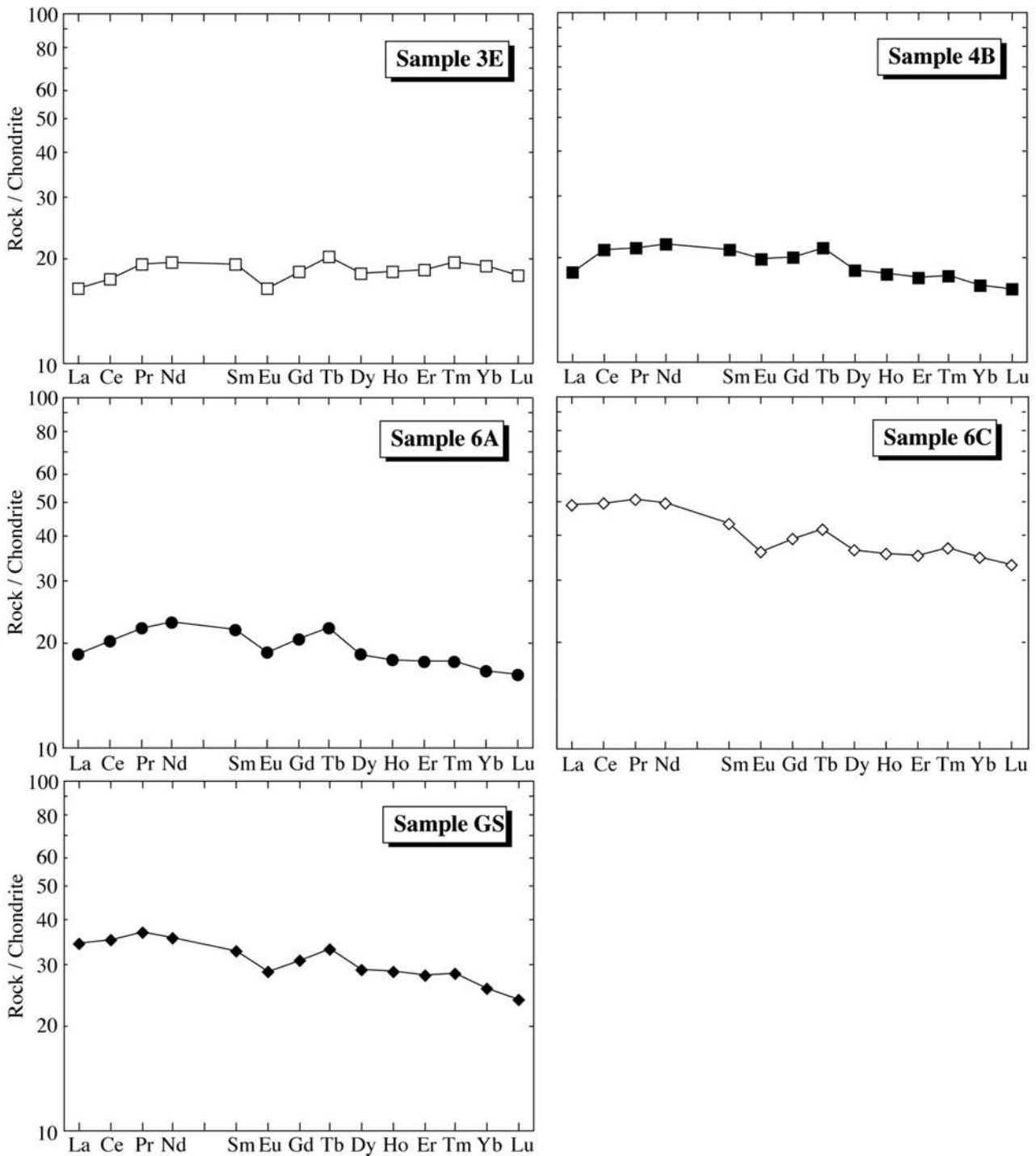


Fig. 7 - Chondrite-normalised REE patterns (values for chondrites from Boynton, 1984). Symbols as in Fig. 6.

thermal stability of clinozoisite/epidote at pressures between 0.15 and 0.3 GPa is restricted to temperatures above 250°C and the paragenesis actinolite + epidote indicating the lower limit of the greenschist facies is stable above 270°C, as compared to 330°C in the Fe-free system. At these temperatures, prehnite may still be stable, with or without actinolite + epidote (Schiffman and Day, 1999). However, higher metamorphic conditions may be inferred for sample GS (Fig. 3). Although the textures of this sample do not allow for an unequivocal interpretation of actinolite-hornblende relationships, there are no indications for a polyphase metamorphic evolution of this sample.

Critical evaluations of the potential of chlorite geother-

mometry came to the conclusion that previously proposed chlorite geothermometers may be unreliable, in part because neither activity-composition relations nor the exchange reactions or the influence of effective bulk compositions are accurately known (e.g. Essene and Peacor, 1995; Zane et al., 1996; Xie et al., 1997; Topuz and Altherr, 2004). Nevertheless, a test of the empirical chlorite thermometer formulation of Cathelineau (1988) on chlorites from regionally metamorphosed metabasites yielded reasonable results (Bevins et al., 1991). We thus applied this formulation to chlorites from the MU metabasites and obtained temperatures between 260 and 350°C with 85% of the data lying in the interval between 305 and 350°C. No

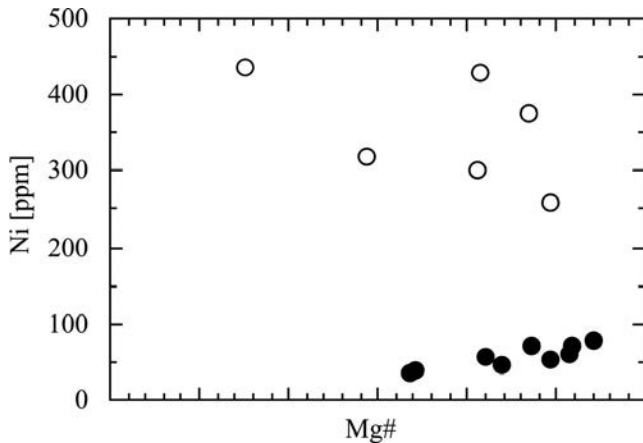


Fig. 8 - Variation of Ni with Mg# in metabasites from the Medvednica Mts. Two groups of samples can be identified. The first group (solid symbols) is characterized by a positive correlation between both parameters, indicating igneous fractionation, while the second group of samples (open symbols) shows unsystematic variations suggesting pre- or synmetamorphic chemical modifications. See text for further explanation.

correlation between temperature and sample location was found.

In F-poor very low- to low-grade metabasic systems, titanite tends to achieve stoichiometric purity, i.e. high Ti is allocated at the expense of $(Al+Fe^{3+})$ and the abundance of Ti versus $(Al+Fe^{3+})$ may be used as a relative geothermometer (Schmidt et al., 1977). Titanium contents higher than 0.88 cpfu, as observed in the MU titanites, may reflect conditions of the upper greenschist facies. Low Fe^{3+} contents in titanite confirm low oxygen fugacity as it can also be inferred from epidote compositions (Table 1).

Metapelites from the MU were studied by Judik et al. (2004). Phyllosilicate crystallinity index measurements, apparent crystallite thickness and lattice strain calculations,

K-white mica b_0 measurements, chlorite thermometry (Cathelineau, 1988) and chlorite-phengite geothermobarometry (Vidal and Parra, 2000) suggest peak metamorphic conditions of 350-400 °C and 0.35-0.40 GPa. These conditions are roughly similar to those obtained for the MU greenschist samples taken in the southeastern part of the sampling profile.

Tectonostratigraphic and tectonometamorphic correlations

For magmatic rocks found in the Hauterivian to Albian clastic deposits of the Repno Formation in the Ivanščica Mts. (located 35 km to the north of the Medvednica Mts.) an island-arc source has been suggested (Babić et al., 1979). Further to the NE, in the Zagorje-Mid-Transdanubian Zone of Hungary, an ophiolitic mélangé crops out at the Bükk Mts. (Balla et al., 1983), where meta-igneous rocks with an arc to back-arc origin has been recognised (Balla, 1984). The rocks were metamorphosed between the Eo-Hellenic (160-120 Ma) and the Austrian (100-95 Ma) orogenic phases at conditions of upper pumpellyite-actinolite to lower greenschist facies (Árkai, 1973; 1983; Árkai et al., 1995; Lelkes-Felvári et al., 1996). In addition, late Early Cretaceous ages (120-100 Ma) have been reported for very low- to low-grade metamorphic clastic sediments and volcanic rocks from the Uppony and Szendrő Mts., NE Hungary (Árkai et al., 1995). Furthermore, Balogh et al. (1990) reported similar Cretaceous metamorphic ages on various rock types from boreholes in the Barcs-West area.

The Aptian metamorphism and regional-scale crustal shearing of the MU can be regarded as the consequence of subduction of Tethyan oceanic crust along the Tisia margins (Pamić, 1998). This hypothesis is confirmed by the presence of blueschists cropping out on the NE part of the Medvednica Mts. (Belak and Tibljaš, 1998). Both greenschist-facies rocks of the MU and blueschist unit are probably correlated with metamorphic associations of similar grade and age ex-

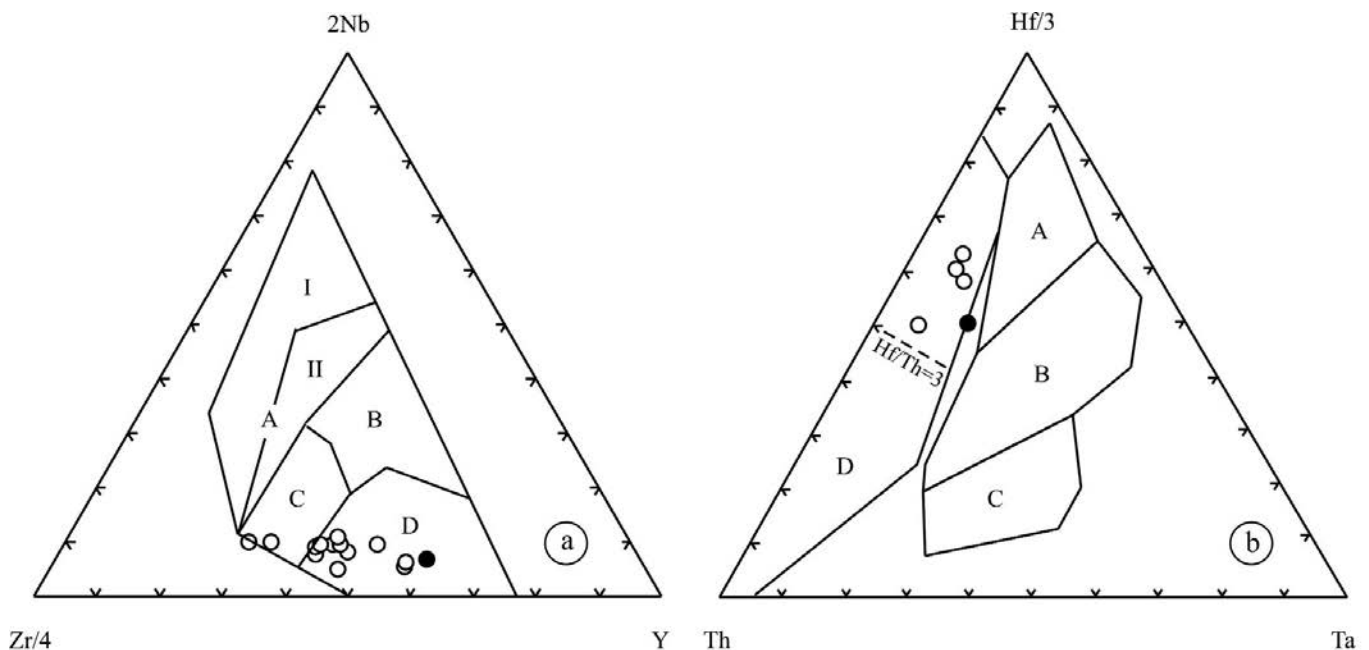


Fig. 9 - Trace element-based discrimination diagrams showing fields for basalts/andesites from various tectonic settings. (a) Zr/4-2Nb-Y diagram after Meschede (1986): A = within-plate basalts, B = E-type MORB, C = within-plate basalts, D = N-type MORB and volcanic-arc basalts. Samples from the MU plot into or near to field D. (b) Th-Hf/3-Ta diagram after Wood (1980): A = N-type MORB; B = E-type MORB and within-plate tholeiites, C = alkaline within-plate basalts, D = calc-alkaline basalts. Mu samples fall into the upper part of field D, representing island-arc tholeiites with $Hf/Th > 3$. Symbols as in Fig. 8.

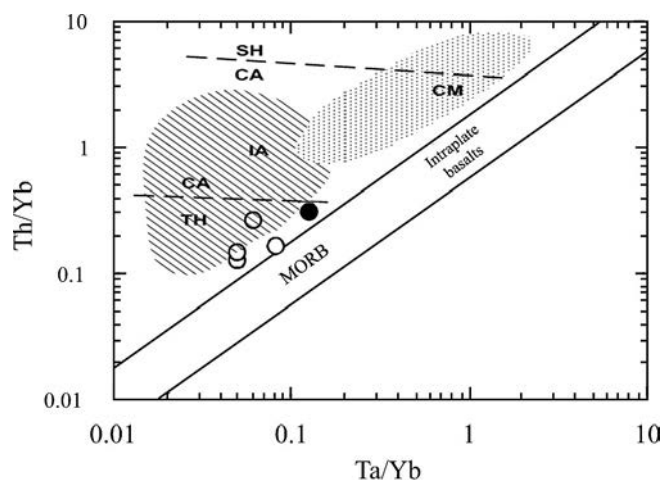


Fig. 10 - Th/Yb versus Ta/Yb discrimination diagram (Pearce, 1982). In contrast to MORB and intraplate basalts, mafic volcanic rocks from subduction settings are characterized by elevated Th/Yb ratios. Symbols as in Fig. 8. Metabasites from the Medvednica Mts. plot in the field of tholeiitic (TH) island-arc basalts (IA). CM = basalts from active continental margins, CA = calc-alkaline basalts, SH = basalts of shoshonitic series.

isting in the Motajica Mts. in N Bosnia (Varićak, 1966) and in the Fruška Gora Mts. in NW Serbia (Majer and Lugović, 1991; Milovanović et al., 1995).

The structural analysis suggests that metamorphism of the MU metabasites took place during SW-vergent obduction of the Jurassic to Lower Cretaceous ophiolites onto the Adria continental margin composed of Ordovician to Upper Triassic sedimentary and volcano-sedimentary successions (Tomljenović, 2002). The Mesozoic closure of this part of the Tethyan Ocean realm caused weak metamorphism in the underlying Mesozoic carbonate platform and its basement. Petrological and geochemical analyses presented in this study revealed that an intra-oceanic island arc might have been involved in these tectonics. Triassic volcanic rocks throughout the Dinarides have calc-alkaline affinity in general (Pamić, 1984) and in the Zagorje-Mid-Transdanubian Zone, in particular (Goričan et al., 2005). We thus suggest a Jurassic age of the island arc evolved in the obduction.

Spinel compositions in the Berrriasian to lower Albian clastic succession in the Gerecse Mts. (northern Transdanubian Mid-Mountains, Árgyelán, 1996) suggest an origin from harzburgite tectonite and ultramafic cumulates from the Medvednica Mts. (Slovenec and Lugović, 2000; Lugović and Slovenec, 2004) and from other peridotite occurrences in the SW Zagorje-Mid-Transdanubian Zone (Lugović et al., submitted). A possible explanation for this feature is the exposition and the weathering of the harzburgites and accumulation of spinels in the sediments from this clastic succession. If this holds true, the former position of the MU must have been somewhere to the north, between the Southern Alps and the Inner Dinarides, as it was inferred by the structural analysis of Tomljenović (2000), before the large-scale Alpine dextral displacements along the Periadriatic-Balaton fault system (Haas et al., 2000) late Paleogene to Oligocene (Early Miocene) 110° counter-clockwise rotation and large scale SE transportation of the Medvednica Mts. are responsible for its present-day position (Márton et al., 2002).

We interpret the domain where these rocks were derived as located in the Meliata-Maliac segment of the Tethys in the sense of Stampfli and Borer (2002), and not to the Dinaric/Vardar strand. This statement may be deduced from

the similar metamorphic ages obtained for the MU metabasites (Belak et al., 1995b) and for the high-grade mafic metamorphic sole of the Kalnik Unit (Šegvić et al., 2005). These ages are fairly similar (126-110 Ma), and different than the Sm-Nd isochron age of 171 Ma obtained for the time of MORB-oceanic crust metamorphism in the Central Dinaric Ophiolite Belt (Olker et al., 2001).

CONCLUSIONS

Metabasites from the Medvednica Unit in the Zagorje - Mid-Transdanubian shear zone were metamorphosed at greenschist facies conditions. Metamorphic temperatures based on chlorite geothermometry indicate values of 300-350°C, consistent with the minimum temperatures derived from petrogenetic grids. However, the occurrence of 'coexisting' actinolite and magnesiohornblende in one sample from the northern end of the sampling profile suggests slightly higher temperature conditions. Microstructures and textures point to synkinematic growth of metamorphic minerals during ductile deformation. Chemical compositions of the MU greenschists suggest an origin from primitive intra-oceanic arc basalts and andesites. The MU is genetically linked to the consumption of the Dinaric oceanic segment of Tethys during the Early Cretaceous. During closure of this oceanic realm, ophiolites were obducted onto the Dinaric carbonate platform and onto marginal (volcano-) sedimentary complexes of Ordovician to Late Triassic age.

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