ACTA
Mineralogica
Petrographica

CORRENSITE IN METABASALTS AND METAGABBROS FROM MT. MEDVEDNICA, CROATIA

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ABSTRACT

Complex mineral paragenetic and mineral structural and -chemical studies were carried out on metabasite samples from the ophiolitic mélange unit of Mt. Medvednica, Croatia using petrographic microscopic, XRPD and EMP techniques. According to XRPD studies of the <2 μm and < 0.6 μm grain-size fractions, chlorite and corrensite (regularly interstratified chlorite/smectite) are the predominant phyllosilicate components. Randomly interstratified chlorite/smectite and discrete smectite are also found in minor amounts. On the basis of the EMP analyses chemical composition of "chloritic materials" from different textural positions reveals that they contain not only chlorite layers but certain amount of trioctahedral smectite (saponite) interlayers also occur being responsible for their relatively high Ca and/or Na contents, large excess of Al(VI) relative to Al(IV) and high octahedral vacancy. The formation temperature of the "chloritic materials" is suggested to be in the range of ca. 160-200 °C using the geothermometer of Cathelineau (1988). Metabasalt samples from the ophiolitic mélange could be affected by minimum alteration, and the appearance of corrensite, together with mixed-layered chlorite/smectite and discrete smectite suggest "intermediate" temperature conditions (Shau and Peacor, 1992). According to Proust (1982) and Proust et al. (1986) corrensite as chlorite/vermiculite forms as an intermediate product of the weathering but the occurrence of chlorite/smectite in the studied samples may indicate that rather the diagenetic-incipient metamorphic alteration is the process that may be the main mechanism responsible for its formation.
Key words: corrensite, smectite-to-chlorite transition, hydrothermal metamorphism, weathering.

INTRODUCTION

Corrensite is an R1 50/50 regularly interstratified chlorite/smectite or chlorite/vermiculite named after C. W. Correns whose former student, F. Lippmannn identified it first in 1954 (Lippman, 1954). The presence of corrensite in different rock types has recently been receiving much attention. Corrensite occurs in variable geological settings, e.g. in contact metamorphic zones of shales, carbonate sequences, Lake Superior iron ores, in metabasalts and metagabbros affected by hydrothermal metamorphic alteration or weathering. Corrensite forms during burial diagenesis or weathering of sedimentary rocks containing sufficient amount of Mg (Reynolds and Moore, 1997).

The conversion of trioctahedral smectite into chlorite is a well-known process during diagenesis and under very low-grade metamorphic conditions. It is a very common feature of phyllosilicate reaction progress (in the sense of Merriman and Peacor, 1999) during hydrothermal metamorphism of the ocean crust. A common path of the smectite to chlorite transition process starts with smectite and involves a continuous sequence of interstratified chlorite/smectite phases with increasing proportion of chloritic layers as the alteration proceeds, and reaches chlorite as a stable phase (Liou et al., 1985; Bettison-Varga et al., 1991; Schiffman and Fridleifsson, 1991; Robinson et al., 1993). The second way is considered to be discontinuous with steps from smectite to corrensite and from corrensite to chlorite without any continuous sequence of mixed-layering (Tribble, 1991; Shau

and Peacor, 1992; Schmidt and Robinson, 1997). In this model corrensite is considered to be a discrete phase and only smectite/corrensite and chlorite/corrensite interstratifications are suggested (Reynolds, 1988; Shau et al., 1990; Shau and Peacor, 1992). Recently, a third pathway has also been recognized, namely a direct transformation from smectite to chlorite (Robinson et al., 2002). Another debated consideration in connection to the smectite to chlorite transformation is whether this change represents equilibrium or disequilibrium processes. According to Robinson et al. (2002) the smectite to chlorite transition involving the above mentioned three pathways proves disequilibrium progression in which these pathways are interpreted as irreversible, episodic reactions that proceed in one or more steps with a minimization of free energy (Peacor, 1992; Essene and Peacor, 1995). Robinson et al. (2002) claim that there are several kinetic factors that control the smectite to chlorite transition besides the temperature, pressure and the whole rock composition. The fluid/rock ratio, the porosity and the permeability of the rock are proved to be the most important kinetic controls clearly affecting fluid transport and nutrient supply for recrystallization (Schiffman and Staudigel, 1995; Schmidt and Robinson, 1997).

Weathering is another important corrensite-forming process in basic rocks of the ocean crust, as first described by Johnson (1964). According to Proust (1982) and Proust et al. (1986) corrensite as an intermediate product of the

weathering is characterized as chlorite/vermiculite. This process involves loss of Fe and Mg to such an extent that the chlorite gradually loses its trioctahedral character transforming into the end-member vermiculite being strictly dioctaherdal, which may evolve into smectite.

The aim of the present paper is to provide a characterization of phyllosilicates of metabasite samples from the ophiolitic mélange unit of Mt. Medvednica, using petrographic microscopic, X-ray powder diffractometric and electron-microprobe techniques in order to give additional data on its metamorphic and/or post-metamorphic evolution.

GEOLOGICAL SETTING AND PREVIOUS DATA ON METAMORPHISM

The Zagorje–Mid-Transdanubian Zone (ZMTZ) is located in the triple junction of the Dinaridic, Alpine and Pannonian units (Fig. 1). In the north and northwest it is bordered by the Periadriatic-Balaton Lineament. The Zagreb-Zemplén Lineament is considered to be its southeastern boundary, while in the south it is bordered by the north-northeastern margin of Adriatic-Dinaridic carbonate platform, i.e. by the External Dinarides (Pamić and Tomljenović, 1998).

Mt. Medvednica is one of the few outcrops within ZMTZ composed of four pre-Neogene tectono-stratigraphic units. These are (1) the Middle Jurassic–Early Cretaceous ophiolitic mélange; (2) the Paleo–Mesozoic complex affected by Eoalpine (122-110 Ma) very low- to low-grade regional metamorphism; (3) the Late Cretaceous–Paleocéne overlying sequence and (4) the dominantly Triassic Medvednica-Žumberak nappe.

Field work coupled with collection of representative samples was carried out on the Middle Jurassic–Early Cretaceous ophiolitic mélange characterized mainly by sheared pelitic-silty matrix, containing fragments of ophiolites (predominantly metabasalt and metagabbro), graywackes, radiolarites, shales and limestones. On the basis of the radiolarite biostratigraphy the ages of the radiolarite fragments are considered to be Late Ladinian – Late Carnian (Halamić and Goričan, 1995) and Jurassic (Halamić et al., 2000). Diabase and gabbro samples gave Early to Middle Jurassic (189-185 Ma) and Early to Late Cretaceous (110-66 Ma) K/Ar whole rock apparent ages (Pamić, 1997a, b).

METHODS

X-ray powder diffraction patterns were obtained using a Philips PW-1730 diffractometer (with computerized APD system) with the following instrumental and measuring conditions: Cu K_α radiation, 45 kV/35 mA, proportional counter, graphite monochromator, divergence and detector slit of 1°, and collection of data with 0.02° 2Θ steps, using time intervals of 5 s.
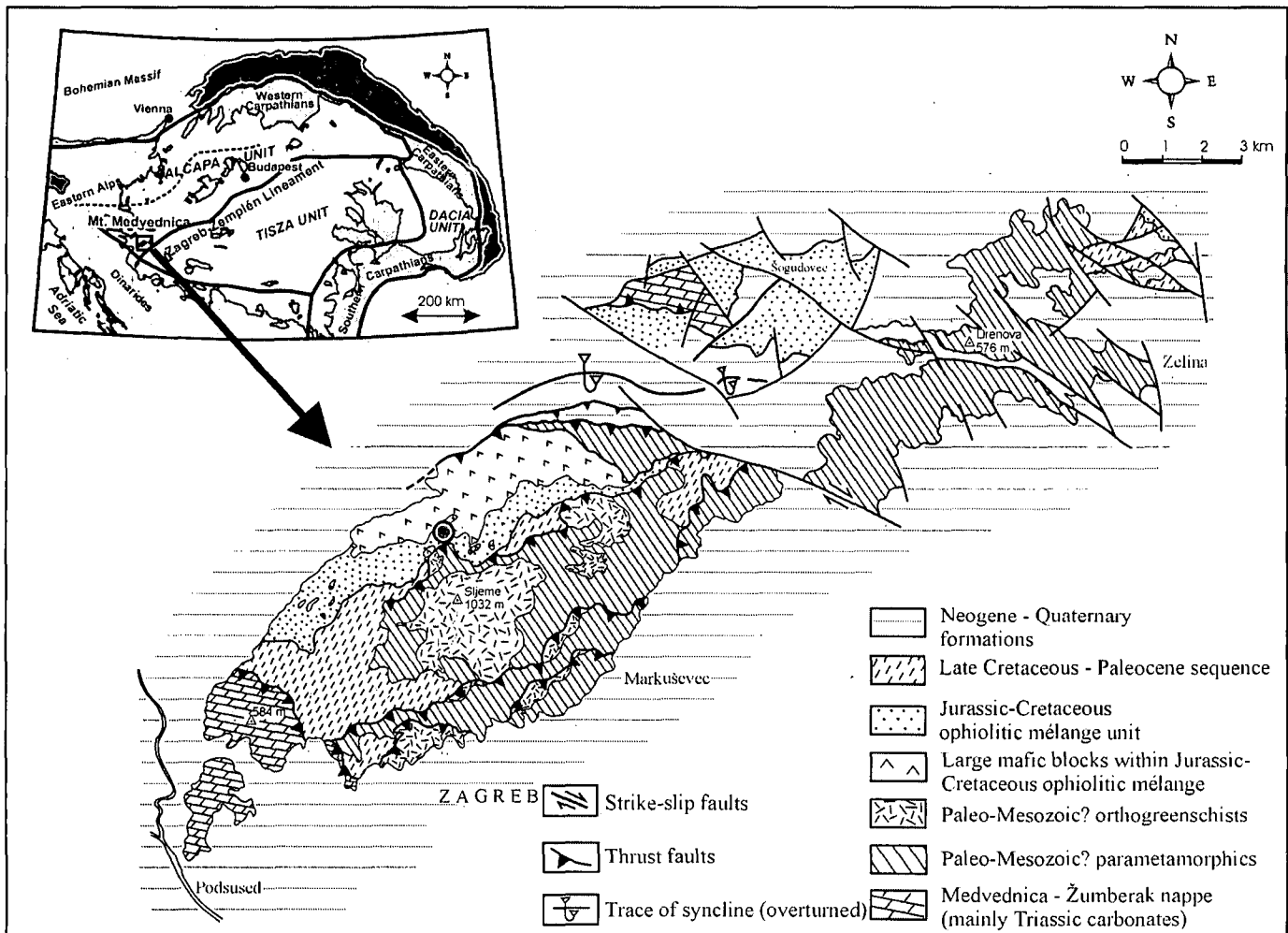

Fig. 1. *(A)* Geological sketch map of the Pannonian Basin and *(B)* simplified geological map of Mt. Medvednica modified after Šikić (1978), grey circle shows the sample locality.
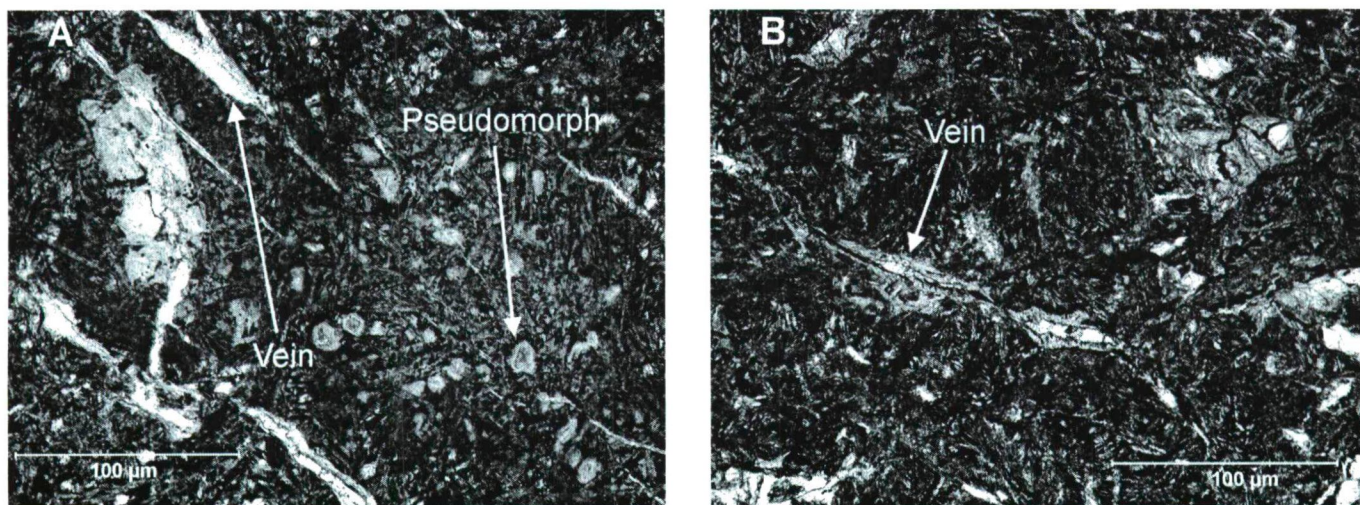
Fig. 2. Pseudomorphs presumably after clinopyroxenes consisting of chlorite, *(A)* prehnite and pumpellyite and *(B)* veins and aggregates containing dominantly chlorite and calcite in metabasalt sample PA 2/C.

Diffraction patterns were performed from non-oriented and highly oriented powder mounts of whole rock, <2 and <0.6 µm spherical equivalent diameter (SED) size fractions. The <2 and <0.6 µm grain-size fraction samples were obtained using the following procedure. Rock samples were disaggregated under standard conditions using a jaw crusher followed by crushing in a mortar mill (type Pulverisette 2, Fritsch) for 3 min. Final disaggregation was achieved by repeated shaking in deionized water. The <2 and <0.6 µm grain-size fractions were separated from aqueous suspension based on the differential settling of grains of different diameters. Following the technique of Kübler (1975), aqueous suspensions of the given fraction were pipetted onto glass slides and dried at room temperature to produce thin-layer, highly orientated preparates with a density of 3 mg/cm^2. Portions of air-dried <2 and <0.6 µm grain-size fraction were saturated with 1 mol/l MgCl$_2$, 1 mol/l KCl and LiCl solutions. Air-dried (AD), Mg-saturated and air-dried (Mg+AD), K-saturated and air-dried (K+AD) and Li-saturated and air-dried (Li+AD) mounts were obtained. Ethylene glycol (EG) and glycerol solvation (60 °C and 95 °C/ overnight) of AD mounts, as well as glycerol solvation of the Mg+AD samples, and heating of the Li+AD mounts at 250°C/16 h followed by glycerol solvation (Green-Kelly test) were carried out. AD samples were heat treated at 350 and 550 °C in order to complete the sample preparation procedure.

Electron microprobe analyses were carried out with a JEOL JXCA-733 instrument equipped with Oxford INCA 200 energy dispersive spectrometer (EDS) using periclase (Mg), corundum (Al), orthoclase (K), quartz (Si), albite (Na), hematite (Fe) and wollastonite (Ca) (C. M. Taylor Corporation) standards and PAP correction procedure (Pouchou and Pichoir, 1984). The measuring conditions were the followings: 15 keV acceleration voltage, 4 nA sample current 100 s measuring time and electron beam with a diameter of ca. 5-10 µm.

RESULTS
Petrographic microscopic features

Metagabbro fragments contain strongly chloritized clinopyroxene relics rimmed by actinolite needles, plagioclase grains completely altered into K-white mica, albite and quartz, as well as 3-4 mm thick veins containing prehnite and calcite. In the metabasalt samples chloritic pseudomorphs, presumably after clinopyroxene are the most abundant mafic constituents (Fig. 2A). Veins built up by chlorite, calcite, quartz and subordinate albite are recognized in these samples (Fig. 2B). Fibrous or rosette-like arrays of "chloritic materials" occur in veins and amygdules. In some metabasalts two separate domains can be distinguished; one is composed of mainly calcite, albite and "chloritic materials", whereas the other domain contains predominantly pseudomorphs presumably after clinopyroxenes, as well as albite and "chloritic materials".

XRPD characterizations

On the basis of the XRPD studies carried out on the <2 µm and < 0.6 µm grain-size fractions of metabasalt and metagabbro samples, chlorite and corrensite (regularly interstratified chlorite/smectite) are the predominant phyllosilicate phases. Additionally, randomly interstratified chlorite/smectite and discrete smectite can also be found. Corrensite was first identified by its 29 Å peak which shifted to 31 Å after ethylene glycol solvation. Mg-saturation and glycerol solvation confirm rather the smectitic nature of its swelling component than vermiculitic on the basis of the expansion of the 29 Å peak to 31-32 Å (Fig. 3). The appearance of the reflection at 18 Å after the same treatment proves the presence of a small amount of discrete smectite phase. Ethylene glycol solvation and Mg-saturation coupled with glycerol solvation suggest that irregularly interstratified chlorite/smectite is also present in the samples because of the slight broadening of the 14 Å peak and its shift towards the low angle values. After Li-saturation and heat treatment at 250 °C for 16 h (Green-Kelly test) of the <0.6 µm grain-size fractions, corrensite, irregularly interstratified chlorite/smectite and the minor smectite all keep their expansion capacity suggesting tetrahedral origin of the layer charge of their smectitic component (Fig. 4). Slight collapse of the 29 Å peak to 26 Å after K-saturation probably indicate the low layer charge of the expanding component(s). The 060 reflection at about 1.545 Å reveals the trioctahedral type of both the chlorite and smectite components.

EMP data

EMP analyses were carried out on "chloritic materials" situated in different textural positions and mineral parageneses in metabasalt sample PA 2/C. It was selected because of the highest amount of corrensite suggested by the XRPD measurements. On the basis of petrographic results "chloritic materials" from both the calcite-rich and the pseudomorph-rich domains were analyzed (Table 1).

Figure 5A shows that all the analyzed "chloritic materials" are classed as diabantite. All these "chloritic materials" contain Ca and/or Na, show large excess of Al(VI) relative to Al(IV) and have significant apparent octahedral vacancy (Figs. 5B, C and 6). These facts prove that analyses were in part contaminated by "inclusions" of materials other than ideal chlorite layers within the volume of interaction of the electron beam and sample (Árkai et al., 2000). Considering the electron beam diameter (5-10 μm) and the energy of the electron bombardment, the volume of the analyzed material may be ca. 100-800 μm³.

As it is shown in Figures 5B and 6 the composition of the "chloritic mineral" suggests trioctahedral smectitic (saponitic) "contamination". Comparing to data obtained on "chloritic materials" from the matrix of the calcite–rich part (Fig. 7A) to data from the matrix of the pseudomorph-rich part (Fig. 7B) it is clear that "chloritic materials" from the carbonate enriched part contain more Si and Fe, and less Al(IV) and Mg, whereas they have the highest interlayer cation content. "Chloritic materials" from veins (Fig. 7C) have
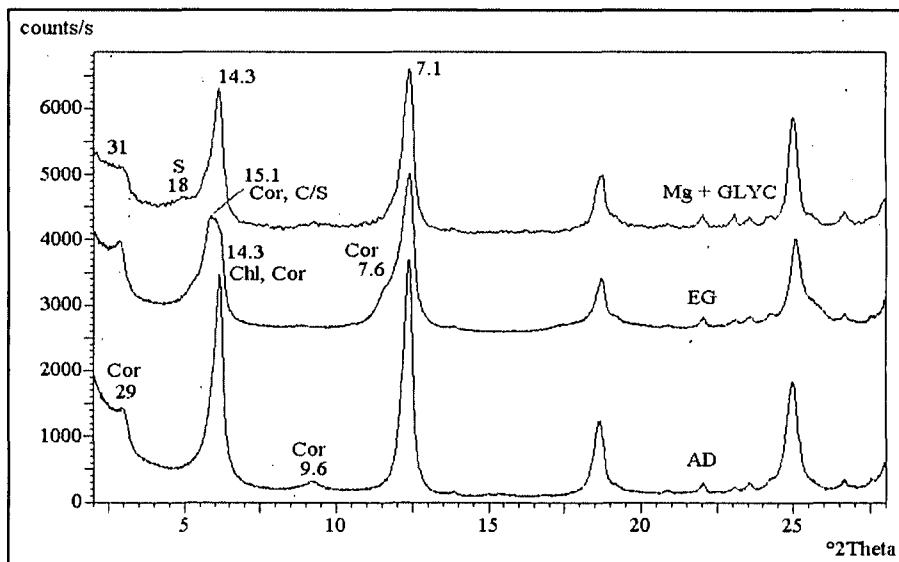

Fig. 3. X-ray powder diffraction patterns obtained on <2 μm grain size fraction of metabasalt sample PA 2/C. Air-dried (AD), ethylene glycol solvated (EG), Mg-saturated and glycerol solvated (Mg+GLYC) mounts. Abbreviation of mineral names are: Chl: chlorite, Cor: corrensite, C/S: irregularly interstratified chlorite/smectite, S: smectite. d values are in Ångstroms.
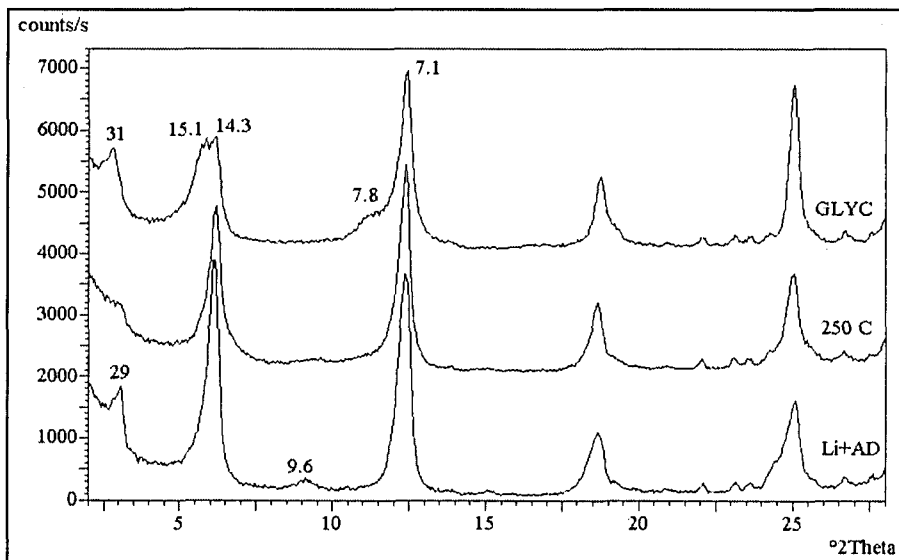

Fig. 4. X-ray powder diffraction patterns obtained on <0.6 μm size fraction of metabasalt sample PA 2/C. Li-saturated (Li+AD), Li-saturated and heated at 250 C (250 °C), and Li-saturated, heated and glycerol solvated (GLYC) sample mounts.
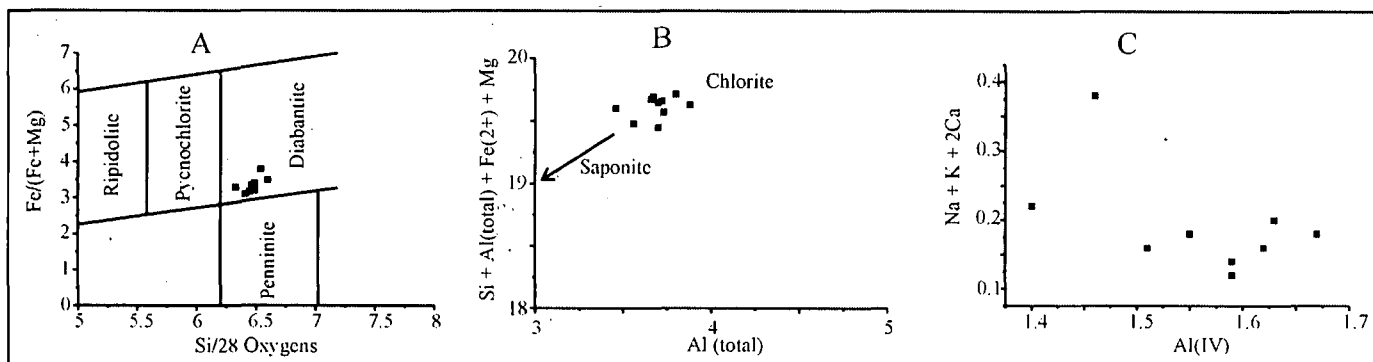

Fig. 5. (A) Fe/(Fe+Mg) vs. Si compositional variations of chlorites from metabasites modified after Hey (1954), (B) chlorites in metabasites as plotted after Schiffman and Fridleifsson (1991) and (C) relations between the Al(IV) content and the total interlayer charge expressed by Na+K+2Ca values (c). Cation numbers on the basis of 28 oxygens.

homogenous chemical composition, they contain more Al but their Fe content is lower than the matrix "chloritic materials" from the carbonate-rich part.

DISCUSSION

According to XRPD studies of the <2 μm and < 0.6 μm grain-size fractions of the metabasalt and metagabbro samples the predominant phyllosilicate components are chlorite and corrensite (regularly interstratified chlorite/smectite) with minor amounts of irregulary interstratified chlorite/smectite and discrete smectite. On the basis of the EMP analyses chemical composition of all "chloritic materials" ("chlorites" in Table 1) from different textural positions reveals that they contain not only chlorite layers, but certain amounts of trioctahedral smectite (saponite) layers also occur causing relatively high Ca and/or Na contents, large excess of Al(VI) relative to Al(IV) and high octahedral vacancy.

Using the chlorite-Al(IV) geothermometer of Cathelineau (1988) the temperature of the formation of the "chloritic materials" analyzed by EMP ranges between ca. 160-200 °C. This range is in agreement with the data obtained by Kristmanndóttir (1975, 1979) and Evarts and Schiffman (1983) who claimed that the temperature of the disappearance of corrensite is ca. 230-250 °C in the Islandic geothermal fields and 225 °C in the Del Puerto Ophiolite, respectively. Cathelineau and Nieva (1985) and Cathelineau and Izquierdo (1988) suggest 220-260 °C for the disappearance of corrensite in the Los Azufres geothermal system.

Shau and Peacor (1992) give additional information to the formation conditions of corrensite. They claim that intense alteration of basalts with high fluid/rock ratio and high permeability is characterized by pervasive albitization and zeolitization. By contrast, minimal alteration in basalts with low permeability and low fluid/rock ratio results in sporadic albitization and zeolitization accompanied by the occurrence of saponite±mixed-layered chlorite/smectite in low-temperature alteration zone and mixed-layered chlorite/corrensite or mixed-layered talc/chlorite in the high-temperature alteration zone. According to the above mentioned observations metabasalt samples from the
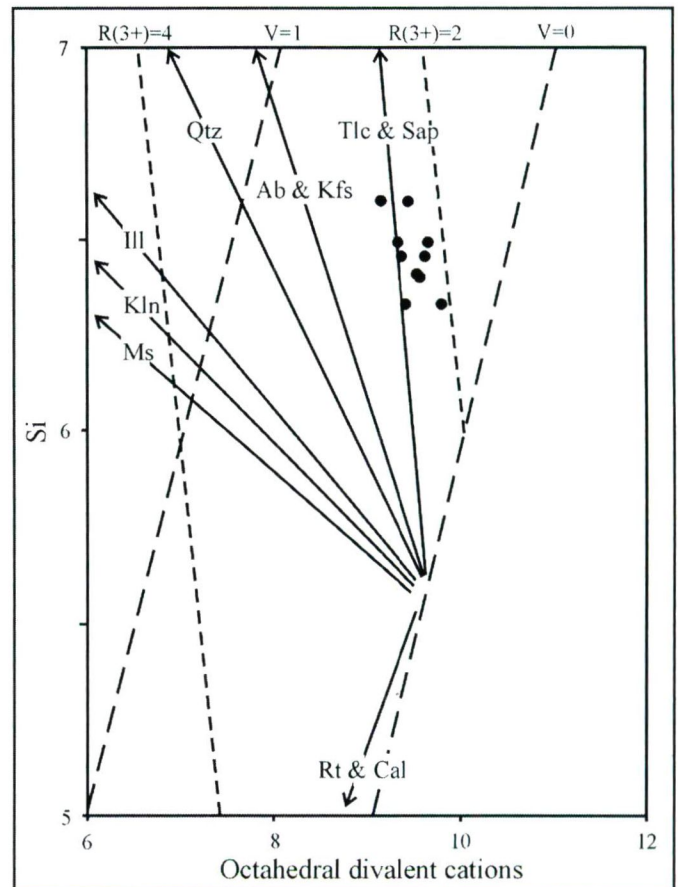

Fig. 6. Si *vs.* octahedral divalent cations plotted after Jiang et al. (1994). Arrows indicate schematic trends of compositional deviations generated from mixtures of an assumed composition of chlorite and other minerals. V: apparent octahedral divalent cations. Cation numbers on the basis of 28 oxygens.

ophiolitic mélange could be affected by minimum alteration and the appearance of corrensite, together with irregulary interstratified chlorite/smectite and discrete smectite suggest "intermediate" temperature conditions.

Certainly, the weathering as a possible mechanism being responsible for the formation of corrensite cannot be
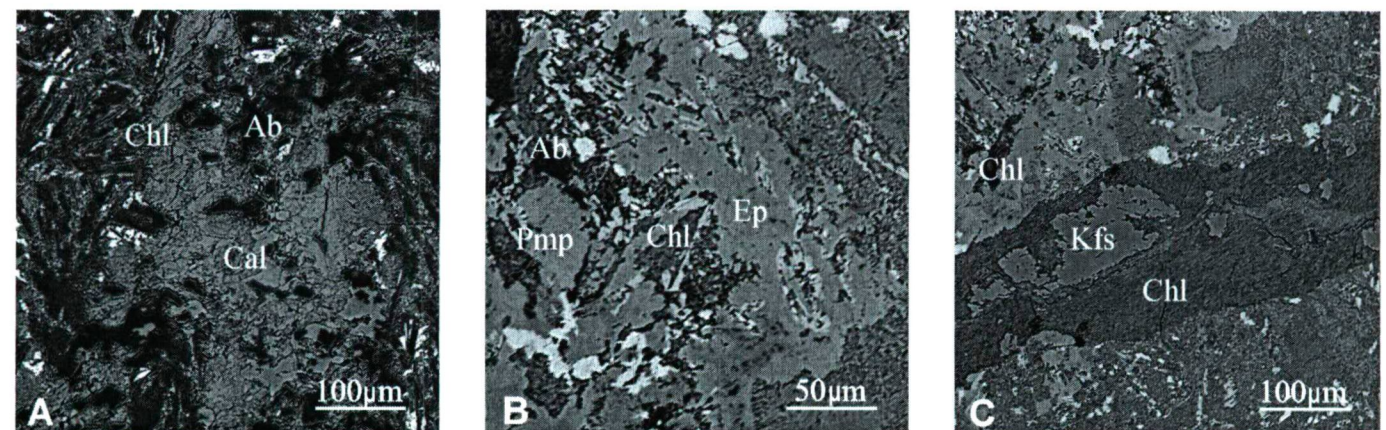

Fig. 7. *(A)* BSE image of the calcite-rich part of metabasalt sample PA 2/C containing mainly "chloritic materials" and albite, *(B)* pseudomorphs presumably after clinopyroxene and plagioclase containing "chloritic materials", pumpellyite, epidote and albite in the pseudomorph-rich part and *(C)* vein containing dominantly "chloritic materials" and K-feldspar, "chloritic materials", albite and prehnite in the matrix of the metabasalt.

Table 1. Chemical composition of "chloritic materials" ("chlorites") in metabasalt sample PA 2/C from the ophiolitic mélange of Mt. Medvednica (* all Fe is calculated as Fe^{2+}, T: total, Oct.: octahedral cations, Int.: interlayer cations, K_2O and MnO are below detection limit). All formulae are normalized to 28 oxygens.

	"chlorites" from the pseudomorphs-rich part								chlorites from matrix of the carbonate rich	
	chlorites from veins		"chlorites from the		"chlorites" from veins		"chlorites" fom the			
SiO_2	31,38	31,11	32,10	31,05	31,56	31,64	30,30	31,18	31,13	32,18
Al_2O_3	15,37	15,30	14,59	15,13	15,33	16,01	16,03	15,19	14,38	15,30
FeO	17,45	17,13	19,05	18,29	17,76	17,38	17,87	18,01	20,39	18,75
MgO	21,53	21,36	22,08	21,36	21,83	21,72	20,72	20,03	18,52	19,41
Na_2O	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,20	0,00
CaO	0,28	0,32	0,45	0,48	0,29	0,39	0,40	0,36	0,65	0,49
Total	86,01	85,22	88,27	86,31	86,77	87,14	85,82	84,78	85,27	86,13
Si	6,41	6,41	6,45	6,37	6,41	6,38	6,33	6,49	6,54	6,60
Al(IV)	1,59	1,59	1,55	1,63	1,59	1,62	1,67	1,51	1,46	1,40
Al(VI)	2,11	2,13	1,91	2,03	2,08	2,18	2,21	2,22	2,10	2,30
Al (T)	3,70	3,72	3,46	3,66	3,67	3,80	3,88	3,73	3,56	3,70
Fe^{2+}*	2,98	2,96	3,20	3,14	3,02	2,93	3,07	3,14	3,58	3,22
Mg	6,56	6,57	6,61	6,53	6,61	6,53	6,35	6,21	5,80	5,93
Oct.	11,65	11,66	11,72	11,70	11,71	11,64	11,63	11,57	11,48	11,45
Na	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,08	0,00
CA	0,06	0,07	0,09	0,10	0,06	0,08	0,09	0,08	0,15	0,11
Int.	0,06	0,07	0,09	0,10	0,06	0,08	0,09	0,08	0,23	0,11
Total	19,71	19,73	19,81	19,80	19,77	19,72	19,72	19,65	19,71	19,56

disregarded, but according to Proust (1982) and Proust et al. (1986) corrensite as an intermediate product of the weathering is characterized as chlorite/vermiculite thus the occurrence of chlorite/smectite in the studied samples may indicate that it is probably not the weathering that may be the main mechanism responsible for its formation. To assure the previous explanation further transmission electron microscopical studies are needed on the "chloritic materials".

Summarizing the above mentioned observations, the formation of the "chloritic materials" in metabasites of the ophiolitic mélange of Mt. Medvednica may be related to one or any combinations of the following mechanisms. One is considered to be the smectite to chlorite transition during diagenetic-incipient metamorphic conditions (a prograde process). Superficial weathering of the metabasites regarding their recent geological position can not be precluded. Progressive burial diagenesis and/or low-grade metamorphism followed by exhumation and superficial weathering being responsible for the formation of irregularly interstratified chlorite/smectite and discrete smectite seem to be an other plausible, although rather complicated alternative.

Conclusions

"Chloritic materials" in metabasalt and metagabbro samples from the ophiolitic mélange unit of Mt. Medvednica were studied by petrographic microscopy, XRPD and electron microprobe techniques. "Chloritic materials" are composed of chlorite, corrensite, first described in this paper from the site, irregularly interstratified chlorite/smectite and discrete smectite (saponite).

Using the empirical chlorite-Al(IV) geothermometer of Cathelineau (1988) the formation temperature of the "chloritic materials" is suggested to be in the range of ca. 160-200 °C.

According to Shau and Peacor (1992) metabasalts from the ophiolitic mélange could be affected by minimum alteration, and the appearance of corrensite, together with irregulary interstratified chlorite/smectite and discrete smectite suggest "intermediate" temperature conditions.

According to Proust (1982) and Proust et al. (1986) corrensite as chlorite/vermiculite can form as an intermediate product of the weathering but the occurrence of chlorite/smectite in the studied samples may indicate that it is not the weathering that may be the main mechanism responsible for its formation.

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