Geologia Croatica	62/1	63–72	6 Figs.	3 Tabs.		Zagreb 2009

Preliminary results on degree of thermal alteration recorded in the eastern part of Mt. Papuk, Slavonia, Croatia

Vanja Biševac[1], Dražen Balen[1], Darko Tibljaš[1] and Darko Španić[2]

[1] University of Zagreb, Faculty of Science, Horvatovac bb, HR-10000 Zagreb, Croatia; (vabisevac@geol.pmf.hr)

[2] Research and Development Sector, INA – Industrija nafte d. d. – Corporate Processes, Lovinčićeva bb, H-10000 Zagreb, Croatia

Geologia Croatica

ABSTRACT

Samples from the Radlovac metamorphic complex, together with others from the overlying sedimentary rocks, and parts of Psunj metamorphic complex beneath it were studied in order to better constrain metamorphic conditions that have prevailed in the area. Rocks from Mt. Papuk were investigated, in order to determine thermal conditions, by Kübler index (illite "crystallinity") and Árkai index (chlorite "crystallinity") while the b_0-parameter of K-white mica was used to estimate the pressure conditions. Treatment with dimethyl-sulfoxide (DMSO) was used in order to extend application of chlorite "crystallinity" measurements to kaolinite bearing samples. Results suggest temperatures between 250–300°C and pressures of 2–3 kb. Similar temperature data recorded from various lithologies implies the existence of a previously unknown post lower Triassic thermal event, (Alpine very low to low-grade metamorphism) affecting different complexes on Mt. Papuk. New data presented and discussed in this paper provides the basis for further research and interpretation of the tectono-metamorphic history of the studied area and its correlation with other similar European metamorphic complexes.

Keywords: Tisia, Mt. Papuk, very low to low-grade metamorphism, Kübler index, Árkai index, b_0-parameter, DMSO treatment, geothermobarometry

1. INTRODUCTION

The Pannonian Basin, surrounded by the mountain ranges of the Alps, the Carpathians and the Dinarides, is the young depression filled predominately with thick Neogene sediments. The basement of the Pannonian Basin is formed of crystalline rocks separated into two major units: the ALCAPA Composite Mega-unit and Tisia Mega-unit (PAMIĆ & JURKOVIĆ, 2002; HAAS & PÉRÓ, 2004). The Tisia Mega-unit represents a large lithosphere block with complex internal structure. It is made up of Variscan crystalline complexes in the basement and post-Variscan-Alpine overstep sequences. Tisia Mega-unit outcrops occur in the Slavonian Mountains (Psunj, Papuk, Krndija) (Fig. 1), the South Transdanubian ranges (Mecsek, Villány Hills) and the Apuseni Mountains (Bihor, Pădurea Craiuli, Codru-Moma, Higniş) (PAMIĆ & JURKOVIĆ, 2002). The best outcrops of Tisia, which can aid the interpretation of the geological history of this Mega-unit, occur in Mt. Papuk (e.g. CSONTOS, 1995, PAMIĆ & JURKOVIĆ, 2002; PAMIĆ et al., 2002), and comprise a very low to medium grade polimetamorphic complex, together with migmatization and granitoid magmatism (PAMIĆ & LANPHERE, 1991).

Mt. Papuk's Variscan crystalline complexes can be generally divided into two groups: 1. Low and medium-grade metamorphic rocks in combination with migmatites and granitoids and juxtaposed 2. Very low-grade metamorphic rocks with metabasics (metadiabase and metagabro) PAMIĆ & JAMIČIĆ, 1986; PAMIĆ, 1998.

A very low-grade metamorphic complex, called the Radlovac metamorphic complex (JAMIČIĆ, 1983, 1988) or semi metamorphic complex (PAMIĆ & LANPHERE, 1991) occupies the highest structural position of all Variscan complexes, and is covered by Permo-Triassic and Triassic sediments (JAMIČIĆ & BRKIĆ, 1987; JAMIČIĆ, 1983, 1988).

The main aim of this paper is to increase the current knowledge of the metamorphic conditions to which rocks of Mt. Papuk have been subjected, by studying rocks belonging to the Radlovac metamorphic complex as well as the overlying sedimentary rocks and parts of the Psunj metamorphic complex. Although several researchers (JAMIČIĆ, 1983, 1988; SLOVENEC, 1986; PAMIĆ & LANPHERE, 1991) have indicated particular P–T conditions, at least for some parts of the Radlovac metamorphic complex, further research is necessary. For this purpose, a multidisciplinary approach which includes optimal laboratory methods based primarily on X-ray diffraction was used. In order to determine thermal conditions, rocks were investigated by Kübler index (illite "crystallinity") and Árkai index (chlorite "crystallinity"), while the b_0-parameter of K-white mica was used for estimating the pressure conditions.

New P-T data presented in this paper will form the basis for further research, especially age dating on illite fractions, and interpretation of the tectono-metamorphic history of the studied area and its correlation with other similar European metamorphic complexes.

2. GEOLOGICAL SETTINGS

The Slavonian Mts. situated in Slavonia, (the northeastern region of Croatia), represent some of the best outcrops of crystalline basement of the Tisia Mega-unit (PAMIĆ et al., 1996; PAMIĆ & JURKOVIĆ, 2002). This Mega-unit represents the continental fragment broken off from the southern rim of the Eurasian plate (i.e. from the southern margin of the Variscan Europe) during the Alpine evolution of Tethys (GÉCZY, 1973). After complex drifting and multiple rotations during Mesozoic and Cenozoic times, the Tisia Unit occupied its present tectonic position (CSONTOS, 1995; STAMPFLI et al., 2002).

In the Slavonia region, JAMIČIĆ (1983, 1988), distinguished three tectono-metamorphic complexes, characterized by several phases of deformation and metamorphism: (1) *Psunj metamorphic complex* (also named the Kutjevo metamorphic series), was assumed to have been formed by metamorphic events during the Baikalian orogeny. The Psunj metamorphic complex comprises (a) greenshists facies metamorphic sequences composed of metapelites, chlorite schists and micashists, and (b) amphibolite facies sequences composed of paragneisses, garnetiferous micashists, amphibolites, metagabbros and marbles, locally intruded by discordant granodiorites and plagiogranites (i.e. I-type granites according to PAMIĆ, 1986; PAMIĆ & LANPHERE, 1991); (2) *Papuk metamorphic complex* (also named the Jankovac metamorphic series), which was subjected to metamorphism and migmatitization during the Caledonian orogeny. The Papuk metamorphic complex consists mostly of (a) S-type granites which are symmetrically surrounded from the NE and SW sides by zones of (b) migmatites and migmatitic gneisses which grade into (c) amphibolite facies metamorphic sequences composed of garnetiferous amphibolites, paragneisses and micashists (PAMIĆ, 1986; PAMIĆ & LANPHERE, 1991) and (3) *Radlovac metamorphic complex* which underwent very low-grade metamorphism during the Variscan orogeny. The Radlovac metamorphic complex consists of very low-grade, (sub-greenshist facies) metamorphic sequences mostly composed of slates, metagreywackes, metaconglomerates and subordinate phyllites. The lower and middle parts of the complex are intruded by sills of metadiabase and ophitic metagabbro (PAMIĆ & JAMIČIĆ, 1986). According to JAMIČIĆ (1983, 1988) and JAMIČIĆ & BRKIĆ (1987) this very low- to low-grade metamorphic complex occupies the highest structural position in the pre-Alpine complexes from the Slavonian Mts., and originally represented the Carboniferous (BRKIĆ et al., 1974) or Late Silurian to Early Permian (JERINIĆ et al., 1994) sedimentary cover over the Psunj metamorphic complex. It is uncomformably overlain by a clastic-carbonate succession of Late Permian and Triassic age, which is not affected by Alpine metamorphism (JAMIČIĆ & BRKIĆ, 1987).

Based on extensive petrological analysis in combination with radiometric age dating of plutonic and metamorphic rocks, PAMIĆ & LANPHERE (1991) gave an alternative subdivision (see also PAMIĆ & JURKOVIĆ, 2002 and references therein) according to which only two complexes can be distinguished. They proposed that the Psunj (Kutjevo) and Papuk (Jankovac) complexes, distinguished by JAMIČIĆ (1983, 1988), in fact represent one coherent magmatic-metamorphic complex. The second complex is the Radlovac complex.

3. MATERIALS AND METHODS

3.1. Macro- and microscopic characteristics of the studied samples

Ten samples, which were chosen in this pilot study in order to cover rocks with different petrological characteristics and age, which according to JAMIČIĆ & BRKIĆ (1987) range from Late Precambrian (PCm) to the Early Triassic (T_1) (Table 1), were analyzed by several techniques.

Chlorite schist (sample 1), is a grey to green foliated metamorphic rock with abundant phyllosilicate minerals. The well observed schistosity is defined by dominant chlorite and mica (illite-muscovite) together with fine-grained recrystallized quartz (Fig. 2A). Chlorite schist belongs to the Psunj metamorphic complex (PS).

Chloritoid schists (samples 2 and 3) are dark grey, fine-grained metamorphic rocks with well observed schistosity defined by their dominant grano-lepidoblastic matrix (Fig. 2B). The main minerals of the matrix are quartz and subordinate sericite ("white mica"). Prismatic chloritoid porphyroblasts up to 0.5 mm, randomly oriented, occur in the fine-grained matrix. Chloritoids have a distinct postkinematic character as already seen by PAMIĆ & LANPHERE (1991). Chloritoid schists characteristically show microfolds with the

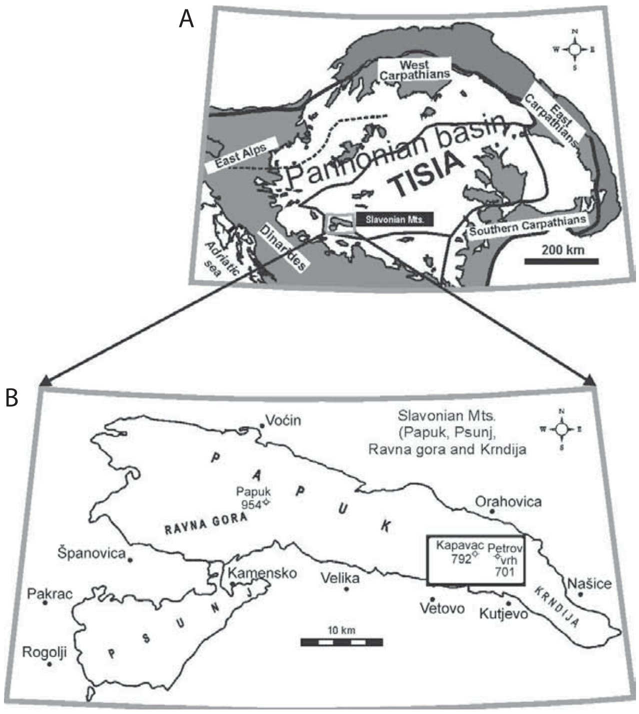


Figure 1: (A) The position of Tisia Mega-unit within the Pannonian Basin and (B) sketch map of Slavonian Mts. (Psunj, Ravna gora, Papuk and Krndija) with an approximate position of the studied area (marked in the black box).

foliation transposed along microfold axial plains. Chloritoid schists belong to the D_3 zone (JAMIČIĆ & BRKIĆ, 1987).

Metapsammite (sample 4) is a grey to silvery coarse-grained rock with blastopsammitic texture. Weakly recrystallized detrital quartz predominates, while subordinate plagioclase is abundant in a fine-grained matrix of sericite and recrystallized quartz (Fig. 2C). Micaceous minerals and elongated quartz grains have a subparallel orientation.

Metapelites (samples 5 and 6) are reddish or green with blastopelitic texture. Continuous cleavage and foliation defined by fine-grained micaceous material and elongated quartz grains are clearly observed (Fig. 2D).

These metapelites and metapsammite belong to the Radlovac metamorphic complex (RA).

Phyllitic conglomerates (samples 7 and 8) are dark reddish to brown. They contain primarily well-rounded pebbles of quartz and subordinate granites and weathered schists. The matrix contains fine-grained recrystallized quartz, sericite, chlorite and haematite (Fig. 2E). The matrix shows a distinct cleavage developed parallel to the surface layering.

Quartz sandstone (sample 9) is a white, fine-grained rock in which continuous schistosity defined by parallel grains of mica and quartz is well observed (Fig. 2F). The matrix is composed of sericite with subordinate quartz cement. As pointed out by JAMIČIĆ et al. (1983, 1987), the observed schistosity is probably a consequence of multiple tectonic movements in the area.

Sandstone (sample 10) is white in colour. The rock is very compact, hard, and mainly composed of round grains of quartz embedded in a fine-grained matrix of quartz and sericite (Fig. 2G).

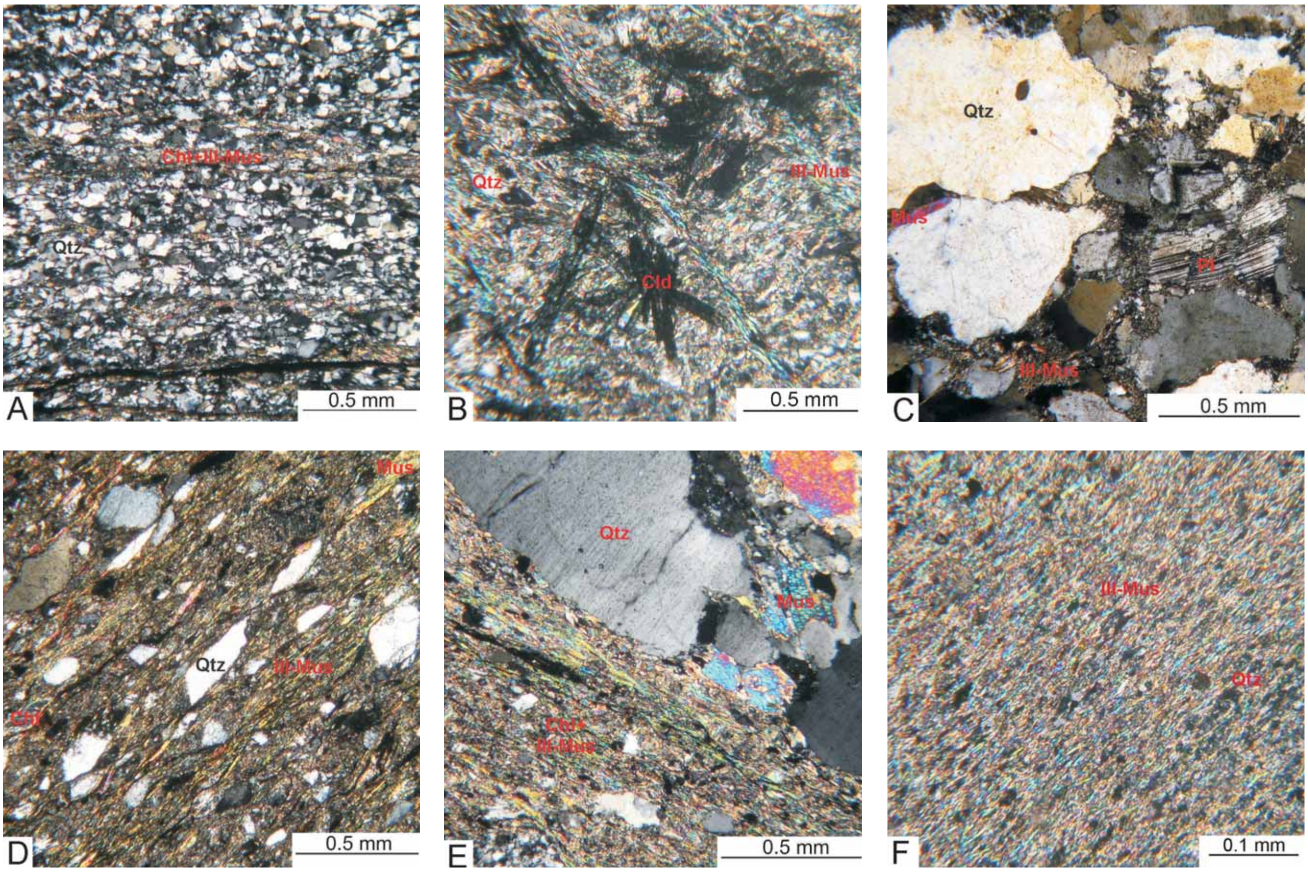
Phyllitic conglomerates and quartz sandstones belong to the Permo-Triassic and the sandstone to the Triassic sedimentary cover (S) – (JAMIČIĆ & BRKIĆ, 1987).

3.2. Modal composition

Whole rock powder XRD analysis of the samples was performed at the Institute of Mineralogy and Petrology, University of Zagreb on a Philips X'Pert Pro diffractometer equipped with an X'celerator detector using CuK_α radiation from tube operated at 40 kV and 45 mA. The step width was 0.017°2θ with 43 s counting time per step; the samples were run between 4 and 65 °2θ.

Table 1: Geographical setting, rock type and stratigraphic age of studied samples (PS – Psunj metamorphic complex; RA – Radlovac metamorphic complex; S – Permo-Triassic and Triassic sediments) together with whole rock modal composition of the studied samples determined by XRD. Mineral abbreviation are after KRETZ (1983): Qtz – Quartz; Ill – Mus (Illite–muscovite); Pl – Plagioclase; Kfs – K-feldspar; Chl – Chlorite; Cld – Chloritoid; Prl – Pyrophyllite; Hem – Haematite; Kln – Kaolinite; Mineral quantity: dominant:++++; abundant:+++; significant:++; poor:+

Lithology (macroscopic determination)	Sample numbers	Gauss-Krüger coordinates		Geological complex	Age (JAMIČIĆ & BRKIĆ, 1987)	Modal composition								
						Qtz	Ill-Mus	Pl	Kfs	Chl	Cld	Prl	Hem	Kln
sandstone	10	6489786E	5037679N	S	T_1	++++	+++	+	++					+
quartz sandstone	9	6489952E	5037405N	S	^{2}PT	+++	++++		++	+				+
phyllitic conglomerate	8	6489999E	5037000N	S	^{1}PT	+++	++++	+		++			+	
phyllitic conglomerate	7	6486289E	5038970N	S	^{1}PT	+++	++++	+		++			+	
metapelite	6	6482989E	5038898N	RA	C, P	+++	++++	++		++			+	
metapelite	5	6485299E	5039996N	RA	C, P	++++	++	+++		+				
metapsammite	4	6485258E	5039488N	RA	C, P	+++	++++	++		+++				
chloritoid schist	3	6490363E	5036446N		D_3	+++	++++	+	+	+	+++	++		
chloritoid schist	2	6490197E	5036595N		D_3	++++	++	+	+	+	+++			
chlorite schist	1	6490725E	5036000N	PS	PCm	++++	+++	++		+++			+	



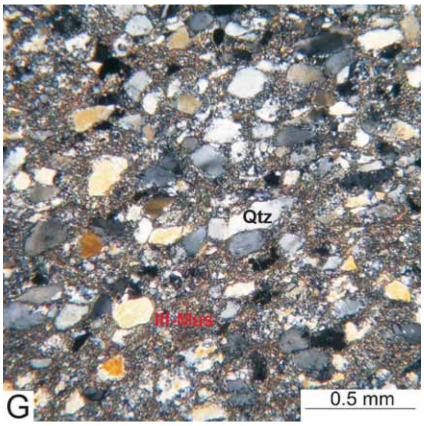


Figure 2: Characteristic textural features of the analyzed samples: A – chlorite schist; B – chloritoid schist; C – metapsammite; D – metapelite; E – phyllitic conglomerate; F – quartz sandstone and G – sandstone. See text for details. Mineral abbreviations are the same as in Table 1.

3.3. Kübler index (illite "crystallinity") and Árkai index (chlorite "crystallinity")

The Kübler index (KI) and Árkai index (ÁI) are widely applied for determining the grade of diagenesis and low temperature regional metamorphism of clastic (pelitic-silty-marly) rocks, which are usually devoid of metamorphic indicator minerals and assemblages (KÜBLER, 1967, 1990; ÁRKAI 1991, ÁRKAI et al., 1995). Methodological approach describing use of KI and ÁI in this paper is the same as in JUDIK et al. (2004; 2006). Illite and chlorite "crystallinity" can be expressed by different indices and the most common ones are the Kübler and Árkai, respectively. They are both defined as the full width at half maximum (FWHM) of the illite (10 Å) and chlorite (7 Å and 14 Å) X-ray diffraction maxima, measured on the <2μm fraction of a highly oriented air dried clay specimen using CuK$_{\alpha}$ radiation (KÜBLER, 1964, 1967, 1968, 1984; KÜBLER & JABOYEDOFF, 2000; ÁRKAI, 1991). Both indices are expressed as $°\Delta 2\theta$ CuK$_{\alpha}$ radiation. Values of KI and ÁI diminish with increasing metamorphic grade. The agreed boundary between the diagenetic zone and anchizone at present is at KI=0.42 $\Delta°2\theta$ while for the anchizone to epizone limit, it is KI=0.25 $\Delta°2\theta$. These boundaries are associated with temperatures of approximately 200 and 300 °C respectively (KÜBLER, 1968; WARR & RICE, 1994). The anchizone is further divided into high and low anchizone. The boundary between these two zones is KI= 0.30 $\Delta°2\theta$ corresponding to a temperature of approximately 260°C (POTEL et al., 2006). The boundaries of the anchizone for the Árkai index were taken from ÁRKAI et al. (1995) and are: ÁI (001) =0.26–0.37 $\Delta°2\theta$ and ÁI (002)=0.24–0.30 $\Delta°2\theta$.

Sample preparation was undertaken according to the recommendation of KISCH (1991) and the FWHM was read manually. "Illite fraction" i.e. fraction <2μm, obtained using a centrifuge (Tehtnica–CENTRIC 322A), was used for KI and ÁI measurements. The XRD measurements were carried out on a Philips X'Pert Pro diffractometer with a graphite monochromator at the Institute of Mineralogy and Petrology, University of Zagreb. Instrumental conditions were 40 kV, 40 mA and constant time 5 s, with step scanning (0.02 °2θ). KI and ÁI were measured on air-dried samples and no shift of the basal white mica reflection after ethylene-glycol (EG) treated was observed, so the results are discussed using only the air-dried scan results.

The standardization of KI and ÁI values of samples measured in the laboratory, to those of Kübler's laboratory, taken as referent values, was made using eight Kisch standards i.e. rock slabs polished parallel to the dominant orientation of phyllosilicate i.e. parallel to the foliation (KISCH, 1990; 1991). The equation representing this case, used here for standardization of the KI and ÁI values of all samples except chlorite schist to the referent Kübler's values, is as follows:

$KI_{(Kübler)} = 0.9684 \text{ X } KI_{(Zagreb)} + 0.0757$ $R^2=0.9844$ (eq. 1)

The same equation was used to obtain Kübler values for WARR & RICE (1994) standards, and the values obtained are listed in Table 2. These CIS standards were used again for monitoring changes in measured FWHM caused by tube ageing. For further explanation see also KISCH et al. (2004).

3.4. Dimethyl-sulfoxide (DMSO) treatment

The presence of kaolinite in the samples can make the ÁI (002) measurement very difficult and uncertain because of the overlapping of the (001) diffraction maximum of kaolinite and the (002) diffraction maximum of chlorite. They both have diffraction maxima at ~12.4 °2θ i.e. ~7.2 Å. In order to get a reliable ÁI value, an attempt was made to separate these two diffraction maxima, using treatment with DMSO. This treatment should separate the maxima one apart from another and shift the (001) diffraction maximum of kaolinite to higher *d* values (from ~7.2 Å to ~11.3 Å) (CALVERT, 1984). Treated samples were measured using standard KI and ÁI measuring conditions.

Table 2: Obtained values for WARR & RICE (1994) standards used for monitoring changes in measured FWHM caused by tube ageing, together with equivalent Kübler's referent values. For further explanation see also KISCH et al. (2004). CIS – Crystallinity Index Standards; KI – Kübler index; AD – air dried

STANDARD (WARR & RICE, 1994)	CIS KI (AD) (WARR & RICE, 1994) °Δ2θ	KI (AD) °Δ2θ our laboratory	KI (AD) KÜBLER referent values using eq. 1 °Δ2θ	KI (AD) our laboratory for this paper °Δ2θ
SW 1	0.63	0.449	0.511	0.423
SW 2	0.47	0.285	0.352	0.274
SW 4	0.38	0.286	0.353	0.263
SW 6	0.25	0.213	0.282	0.190
MF 1	0.11	0.122	0.194	0.056

3.5. Total organic carbon (TOC)

It is usual to correlate KI and ÁI indices with other parameters which alter with thermal conditions changes, including vitrinite reflectance. With this aim TOC was measured in order to find out if the investigated samples are suitable for such kind of analyzes and to find an appropriate correlation. The measurements were made in the INA – Laboratory for Geochemistry, with samples prepared according to BUSH (1970). Standardization of the instrument (LECO IR–212) was undertaken using material of known carbon content (a steel ring containing 0.3–1.0 % carbon).

3.6. b_0-parameter

The b_0-parameter in K-white micas is controlled by pressure (SASSI, 1972, GUIDOTTI & SASSI, 1986). The geobarometric b_0-parameter is measured as 6×d(060,33$\bar{1}$) of muscovite. This parameter monitors the relative pressure environments of very low to incipient low-grade metamorphic terrains and is widely used as a relative geobarometer for interregional comparisons (SASSI & SCOLARI, 1974).

The analytical procedure is based on work by SASSI (1972) and SASSI & SCOLARI (1974) with further development by GUIDOTTI & SASSI (1986). SASSI's (1972) qualitative geobarometer is based on the b_0-parameter value, or more precisely, 6×d(060,33$\bar{1}$) spacing of K–Na white micas, which reflects the increasing celadonite substitution that occurs in muscovite with the pressure increase in the Al-rich portion of the nonlimiting muscovite–albite assemblage (WANG et al., 1996; RIEDER et al., 1998). The good linear correlation between the value of 6×d(060,33$\bar{1}$) and the celadonite content has been well demonstrated by GUIDOTTI et al. (1989).

Using the procedures defined by SASSI & SCOLARI (1974), each sample was cut perpendicular to its schistosity. Quartz present within the samples was used as an internal standard. The diffractometric analyses were carried out directly on these slices using the aforementioned XRD at same conditions used for KI and ÁI determination, ensuring in all cases that the area exposed to x-rays was phyllosilicate rich. The 2θ range scanned was 59.0–63.0°.

4. RESULTS

4.1. Modal composition

The whole rock powder XRD analysis (Table 1) revealed that quartz and illite–muscovite are the main constituent minerals in all samples. Chlorite was found in chlorite schist, chloritoid schists, metapelites, metapsammite, phyllitic conglomerates and quartz sandstone. K-feldspar was detected in chloritoid schists, quartz sandstone and sandstone, while plagioclase is present in all samples except for the quartz

Table 3: Kübler index (KI) and Árkai index (ÁI) measured on <2 μm grain-size air-dried mounts together with the total organic carbon (TOC) content in the studied samples. KI and ÁI values are expressed in $\Delta°2\theta$ (CuK_α). (The (001) diffraction maximum of chlorite of metapelite, phyllitic conglomerate and quartz sandstone was too weak and therefore not suitable for Árkai index measurement. This was also the case for both diffraction maxima of chlorite for the chloritoid schists. The Árkai index of sandstone was not measured (n.m.) because this sample does not contain chlorite.) *ÁI determined after treatment with DMSO.

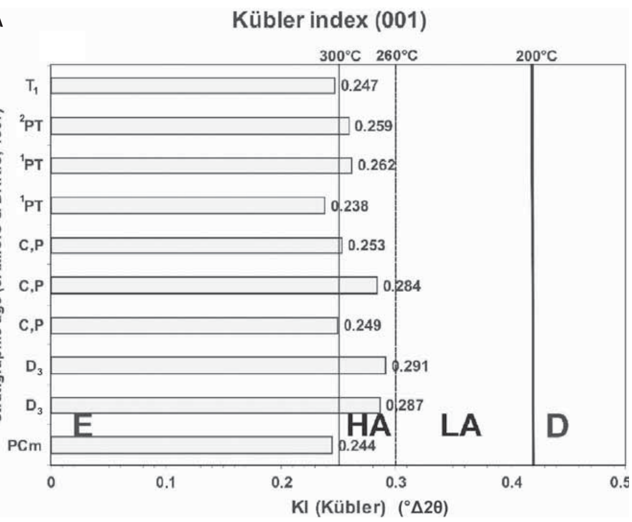
SAMPLE	KI (001)	ÁI (001)	ÁI (002)	TOC (%)
sandstone	0.247	n.m.	n.m.	0.00
quartz sandstone	0.259	weak	0.274*	0.00
phyllitic conglomerate	0.238	weak	0.283	0.00
phyllitic conglomerate	0.262	0.221	0.232	0.00
metapelite	0.253	weak	0.242	0.01
metapelite	0.249	0.234	0.241	0.02
metapsammite	0.284	0.223	0.224	0.00
chloritoid schist	0.291	weak	weak	0.08
chloritoid schist	0.287	weak	weak	0.13
chlorite schist	0.244	0.243	0.265	n.m.

sandstone. Additionally, haematite was detected in chlorite schist, phyllitic conglomerates and metapelite, chloritoid in both chloritoid schists, pyrophyllite in chloritoid schist and kaolinite in quartz sandstone and sandstone.

4.2. Kübler index (illite "crystallinity") and Árkai index (chlorite "crystallinity")

The KI and ÁI results are shown in Table 3. KI was measured for all samples and ÁI only for samples containing chlorite in sufficient quantity. The lowest KI, which indicates the highest thermal alteration, was measured on phyllitic conglomerate (0.238 °$\Delta 2\theta$). The highest KI, which indicates the lowest thermal alteration, was measured on chloritoid schist (0.291 °$\Delta 2\theta$). Árkai indices (001) and (002) range from 0.221 °$\Delta 2\theta$ (phyllitic conglomerate) to 0.243 °$\Delta 2\theta$ (chlorite schist) and from 0.224°$\Delta 2\theta$ (metapsammite) to 0.283°$\Delta 2\theta$ (phyllitic conglomerate), respectively. The ÁI (002) probably has a narrower range due to the fact that the two highest values were obtained from samples with low chlorite content (Fig. 3). Therefore peaks were low and measurements are less precise.

A



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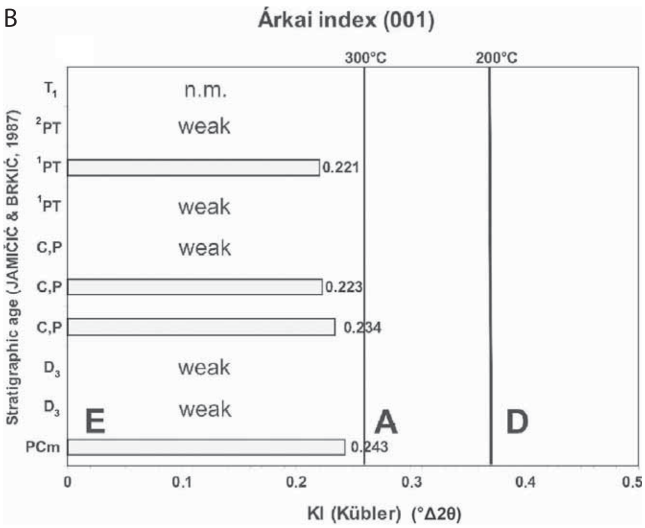

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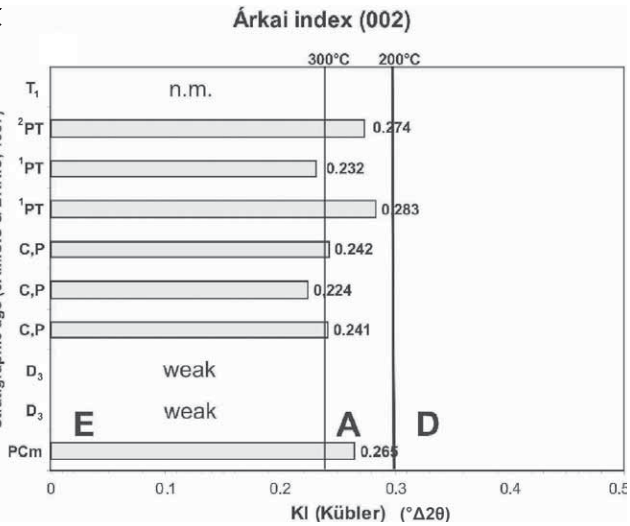

Figure 3: Graphical representation of the degree of thermal alteration according to the data of Kübler and Árkai indices shown in Table 2 for: (A) KI (001), (B) ÁI (001) and (C) ÁI (002). KI and ÁI values are expressed in °$\Delta 2\theta$ (CuK_α). Boundaries of the anchizone were taken from KÜBLER (1968, 1990) for KI and from ÁRKAI et al. (1995) for ÁI. "E" – epizone; "HA" – high anchizone; "LA" – low anchizone; "D" – diagenetic zone; n.m.=not measured; weak=diffraction maximum was not suitable for ÁI measurement.

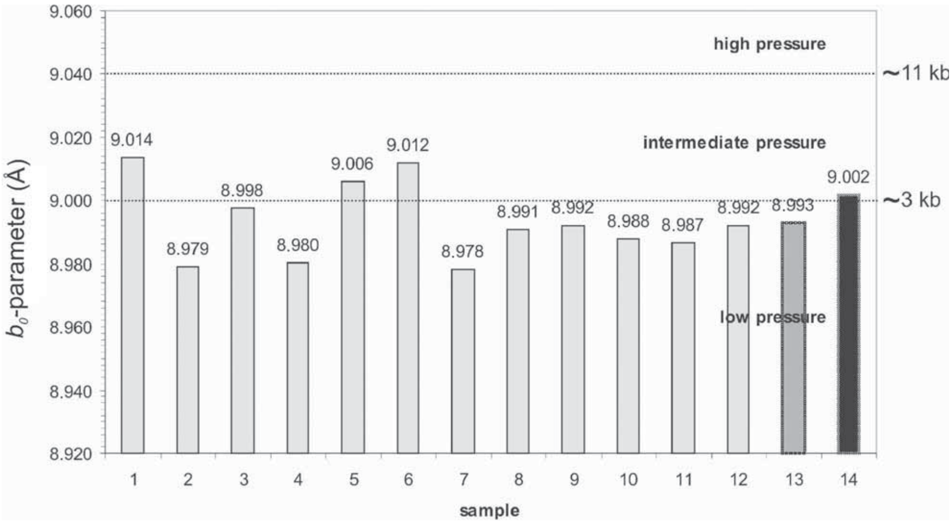

Figure 4: Pressure conditions estimation based on the b_0-parametar for samples from the Radlovac metamorphic complex obtained from K–white micas of K-feldspar-free rock slices (1–12) together with the average b_0-value for this paper (13) and average b_0-values taken from PAMIĆ & LANPHERE (1991) (14). The boundaries between the low, intermediate and high pressure fields are from ÁRKAI et al. (1991).

4.3. Dimethyl-sulfoxide (DMSO) treatment

After treatment of the "illite fraction" in the quartz sandstone (i.e. fraction <2μm), with DMSO shift of (001), a diffraction maximum of kaolinite towards higher *d* values (~7.2 to ~11.1 Å) was observed (Fig. 6). The position of the (002) diffraction maximum of chlorite remained unchanged. In this way (002) diffraction maximum of chlorite becomes more symmetric and therefore suitable for ÁI determination.

4.4. b_0-parameter

The measurements of the b_0-parameter were made on 2 metapelites discussed in this paper and an additional 10 samples from Radlovac metamorphic complex which satisfy the criteria set by SASSI and SCOLARI (1974). The average b_0-parameter value is 8.993 Å (n=12), with a standard deviation of 0.012. The majority of the values fall between 8.980 and 9.006 Å (66% of analyzed samples), two samples have b_0-values higher than 9.006 Å and two samples had a b_0-parameter value lower than 8.980 Å (Fig. 4).

4.5 Total organic carbon (TOC)

Total organic carbon was not found or was very low in all investigated samples (Table 2). Samples containing less than 0.5% TOC for clastites and 0.3% TOC for carbonates are, according to HUNT (1995), not suitable for vitrinite reflectance measurements.

5. DISCUSSION

According to the Kübler and Árkai indices (Table 3, Fig. 3) all analyzed samples show a certain degree of thermal alteration recorded within the "illite fraction". Obtained values of KI and ÁI indicate thermal alteration ranging from the low temperature part of the high anchizone (approximately 250 °C) to the low temperature part of the epizone (approximately 300 °C) i.e. sub-greenschist to greenschist facies (Fig. 3). These data are in good agreement with the previously established presence of paragonite and pyrophyllite reported by SLOVENEC (1986) in some slates from the Radlovac metamorphic complex. According to FREY (1986) these minerals are characteristic of sub-greenschist facies and indicate, as well as Kübler and Árkai indices measured here, that the Radlovac metamorphic complex recorded the younger metamorphic overprint of very low to low-grade metamorphic temperature conditions (BIŠEVAC et al., 2007). Samples from the Psunj metamorphic complex (PS) which

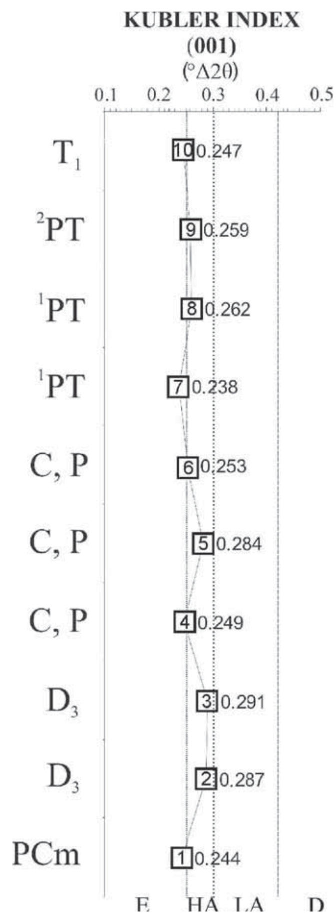

Figure 5: Variation of the Kübler index data with stratigraphic age. Sample numbers are the same as in Table 1. ("E" – epizone, "HA" – high anchizone; "LA" – low anchizone; "D" – diagenetic zone).

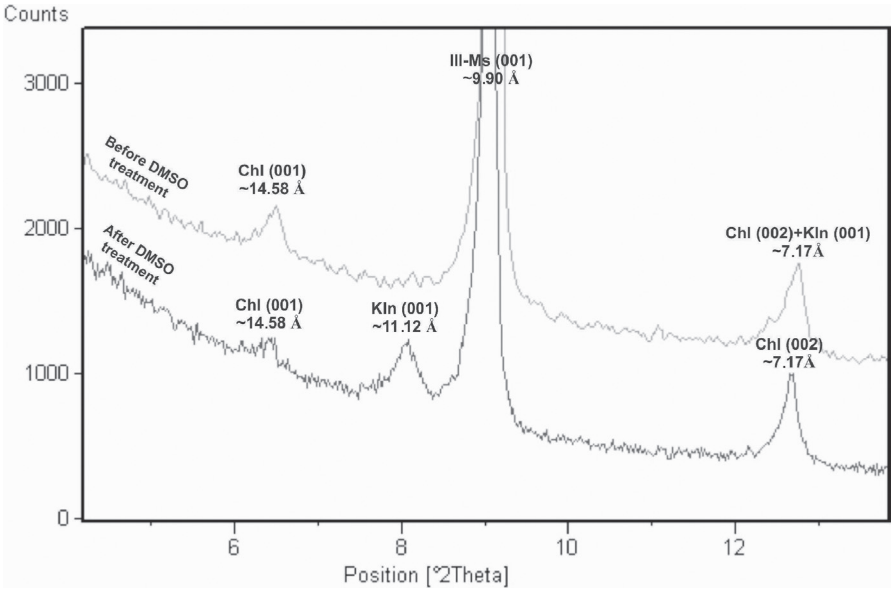

Figure 6:
X-ray diffraction patterns (4–14 °2θ CuK$_{\alpha}$) of quartz sandstone (^{2}PT) (fraction <2µm) before and after treatment with DMSO. Mineral abbreviations are the same as in Table 1.

occurs below the Radlovac metamorphic complex, as well as those from the overlying sediments (S) recorded the same very low to low-grade metamorphic event of the same temperature conditions (approximately 250–300 °C according to KI and ÁI). Since effects of this metamorphism are barely visible without the aid of instrumental techniques, we will not designate these deposits to be metasediments.

Pressure conditions estimated on the basis of the *b*-parameter of K-white mica (average value for analyzed samples is 8.993 Å) (Fig. 4) indicate that samples from the Radlovac metamorphic complex recorded a metamorphic event of low to intermediate pressure conditions of sub-greenshists to greenshists facies. The measured b_0-parameter corresponds to approximately 2–3 kb (SASSI & SCOLARI, 1974; GUIDOTTI & SCOLARI, 1986; ÁRKAI et al., 1991; ÁRKAI et al., 1995). Although PAMIĆ & LANPHERE (1991) pointed out that their measurements of the b_0-parameter of K-white mica were made on a small population of samples (average value for 10 samples was 9.002 Å), their results, which indicate the lowest intermediate pressure (~3 kb) (Fig.4), are in good agreement with the data presented here. It is important to mention that both KI and ÁI can provide more reliable results if samples with similar lithology are compared. Usually fine-grained clastic rocks are suggested in the literature for such purposes. In course grained samples, the effects of inherited (detrital) phyllosilicates may overlap and strongly modify the nature of authigenic (metamorphic, newly-formed) micas and chlorites (ÁRKAI, 1983; 1991; 1995). This is valid even if the <2µm fraction of samples is used (ÁRKAI et al., 1981; ÁRKAI, 1983). In order to confirm that the thermal maturity of the studied samples, especially Permo-Triassic quartz sandstone and Triassic sandstone, is really the result of Alpine tectonism, further investigation of the illite fraction is in progress.

Despite the fact that the analyzed samples clearly differ from one another by their stratigraphic age, protolith, mineral composition and texture, no significant influence of these parameters to KI values was observed. The degree of thermal alteration seems to be constant through the whole analyzed column (Fig. 5). All this data points to the conclusion that the analyzed samples recorded the same event which can be dated as younger than the Early Triassic. The extensive K–Ar dating of suitable illite fractions is in progress and preliminary report points to the Cretaceous (BIŠEVAC et al., 2007).

The appearance of ordered kaolinite in some samples (Table 1) was connected to post-metamorphic hydrothermal alteration which probably occurred during uplift of the basin and it is not connected with the metamorphic overprint reported here.

6. CONCLUSIONS

(1) KI and ÁI measured on samples belonging to the Radlovac metamorphic complex as well as parts of Psunj metamorphic complex and D_3 metamorphic rocks indicate a thermal overprint ranging from the low temperature part of the high anchizone (approximately 250 °C) to the low temperature part of the epizone (approximately 300 °C) i.e. sub-greenschist to greenschist facies.

(2) The clastic-carbonate sedimentary succession (phyllitic conglomerates, quartz sandstone and sandstone) of the Late Permian and Triassic age, which uncomformably overlies the Radlovac metamorphic complex was also affected by the same thermal overprint.

(3) Pressure conditions estimated on the basis of the b_0-parameter of K-white mica (average value is 8.993 Å) indicate that samples from the Radlovac metamorphic complex were metamorphosed under the low to intermediate pressure of the sub-greenshists to greenshists facies (approximately 2–3 kb).

(4) Total organic carbon (TOC) in all samples was either absent or very low.

(5) The degree of thermal alteration i.e. the Kübler index, tend to be constant through the whole analyzed column

implying that the different complexes (PS, D_3, RA and S) all record the same, post Early Triassic metamorphic overprint.

(6) DMSO treatment enabled chlorite "crystallinity" measurements of kaolinite containing samples by separating 001 and 002 diffraction peaks of kaolinite and chlorite respectively.

ACKNOWLEDGEMENT

The authors thank Prof. Dr. Peter ÁRKAI (Geochemical Institute, Budapest, Hungary) and Dr. Domagoj JAMIČIĆ (Croatian Geological Survey, Zagreb, Croatia) for constructive criticism in reviews and comments that helped to improve the manuscript significantly. We thank Prof. Hanan J. KISCH (Department of Geology and Mineralogy, Ben-Gurion University of Negev, Beer-Sheva, Israel) for providing a set of standards necessary for instrument calibration in this study. This study was supported by the Ministry of Science, Education and Sports, project no. 119-1191155-1156 and Croatian–Hungarian scientific bilateral project 'Metamorphic evolution of crystalline basement complexes in the area of the Pannonian Basin and the Internal Dinarides'.

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Manuscript received April 16, 2008
Revised manuscript accepted October, 9, 2008