Geologia Croatica | 64/2 | 153–162 | 4 Figs. | 2 Tabs. | Zagreb 2011

X-ray study of potassium feldspars from different granitoid types and gneisses of Papuk Mt. (Slavonia, Croatia)

Marija Horvat[1], Darko Tibljaš[2], György Buda[3] and György Lovas[3]

[1]Vukomerečka cesta 55A, 10040 Zagreb, Croatia; (horvatmarija@hotmail.com)
[2]Department of Geology, Faculty of Science, Horvatovac 95, HR-10000 Zagreb, Croatia; (dtibljas@geol.pmf.hr)
[3]Department of Mineralogy, Eötvös Loránd University, Pázmány Péter st. 1/C, H-1171 Budapest, Hungary; (buda@ludens.elte.hu; lovas@ludens.elte.hu)

doi: 104154/gc.2011.13

Geologia Croatica

ABSTRACT

Potassium feldspars from different granitoids and gneisses of Papuk Mt. (Slavonia, Croatia) have been investigated by X-ray powder diffraction. Diffraction patterns classically observed as well as patterns calculated by Rietveld refinement were compared and discussed. Triclinicity was calculated according to GOLDSCHMIDT & LAVES (1954) while the structural state of the feldspars was determined using the methods of KROLL & RIBBE (1983) and GODINHO & JALECO (1973). Results showed that the type of potassium feldspar depend on the investigated host-rock, indicating variation in the structural state from orthoclase, intermediate microcline to highly ordered microcline. Potassium feldspar megacrysts in biotite-granodiorites and monzogranites are intermediate microcline or orthoclase, while two-mica monzogranites contain low microcline. Gneisses contain low microcline and orthoclase in Brzaja Creek and low microcline in Djedovica Quarry. Classically observed and digital diffraction patterns calculated by the Rietveld refinement method produced comparable results and provided a very good correlation of the results obtained by different methods. High triclinicity values of feldspars from investigated granitoid and gneiss samples from Papuk Mt. (Slavonia, Croatia) are in accordance with a high Al content in the T_1o site and their fully ordered state indicates a slow(er) cooling-rate. Low triclinicity values, an Al content in T_1o site around 0.60 and ordering index smaller than 0.80 can be interpreted as a result of relatively fast(er) cooling which allowed lower ordering of the potassium feldspar.

Keywords: X-ray powder diffraction, potassium feldspars, triclinicity, structural state, ordering index, granitoids and gnesses, Papuk Mt., Croatia

1. INTRODUCTION

X-ray powder diffraction is the most common method for determining symmetry and ordering of potassium feldspars. For monoclinic crystals the *hkl* and $h\bar{k}l$ reflections show a single sharp peak on the diffraction pattern. For triclinic crystals the *hkl* and $h\bar{k}l$ peaks have different 2θ values and form a double peak. In the case of alkali feldspars, the splitting of the 131 and $1\bar{3}1$, that occur at ~29.9° 2θ CuKα, is called triclinicity (Δ) (GOLDSCHMIDT & LAVES, 1954). WRIGHT & STEWART (1968), developed a method which was revised by STEWART & WRIGHT (1974) that uses *b* and *c* cell edges and α* and β* cell angles for estimations of obliquity.

KROLL (1971, 1973 and 1980) and KROLL & RIBBE (1983) developed the method for calculating Al occupancy of tetrahedral sites based on lattice translations along [110] and [1$\bar{1}$0] directions: named tr [110] and tr [1$\bar{1}$0], respectively. Assuming that the angular difference of $\bar{2}$04 and 060 peaks, in the 29–31° region changes linearly with degree of order, GODINHO & JALECO (1973) defined an ordering index (Δ_{Sm}) based on this difference.

Various potassium feldspar polymorphs and their structural states, from the different granitoid types and gneisses found at Papuk Mt. in Croatia are presented (Fig. 1). Results obtained from the classically observed and digital X-ray diffraction patterns calculated by Rietveld refinement are compared. For both of these patterns GOLDSCHMIDT & LAVES's (1954) triclinicity and KROLL & RIBBE's (1983) ordering path calculations were undertaken and are discussed. Results for the T_1o site occupancy estimated by KROLL & RIBBE's (1983) method, are compared with the results calculated by NEVES & GODINHO's (1995) formulae. Finally, the structural state of these feldspars derived from triclinicity and Al occupancy of tetrahedral sites is discussed.

2. GEOLOGICAL SETTING

Papuk Mt. is part of the Slavonian Mountains in Croatia which are located in the southernmost part of the Pannonian Basin in the Bihor nappe system (Fig. 1) of Tisza Mega-Unit (SCHMID et al., 2008). The published geological maps 1:100 000, Orahovica sheet (JAMIČIĆ & BRKIĆ, 1987) and Daruvar sheet JAMIČIĆ (1989), report that it is primarily composed of metamorphic and granitoid rocks. The main mineralogical features, geochemistry and detailed structural-tectonic investigations of granitoids and related gneisses and pegmatites in the area are discussed in many papers, including; TAJDER (1957), RAFFAELLI (1965), VRAGOVIĆ (1965), TAJDER (1969), SLOVENEC (1976, 1978, 1982, 1984), JAMIČIĆ (1983, 1995, 2001), PAMIĆ & LANPHERE (1991), PAMIĆ et al. (1988, 1996), HORVAT et al. (2002), HORVAT (2004), HORVAT & BUDA (2004), BALEN et al. (2006), BIŠEVAC et al. (2009), BIŠEVAC et al. (2010), HORVÁTH et al. (2010). Feldspars are the most abundant minerals in these rocks.

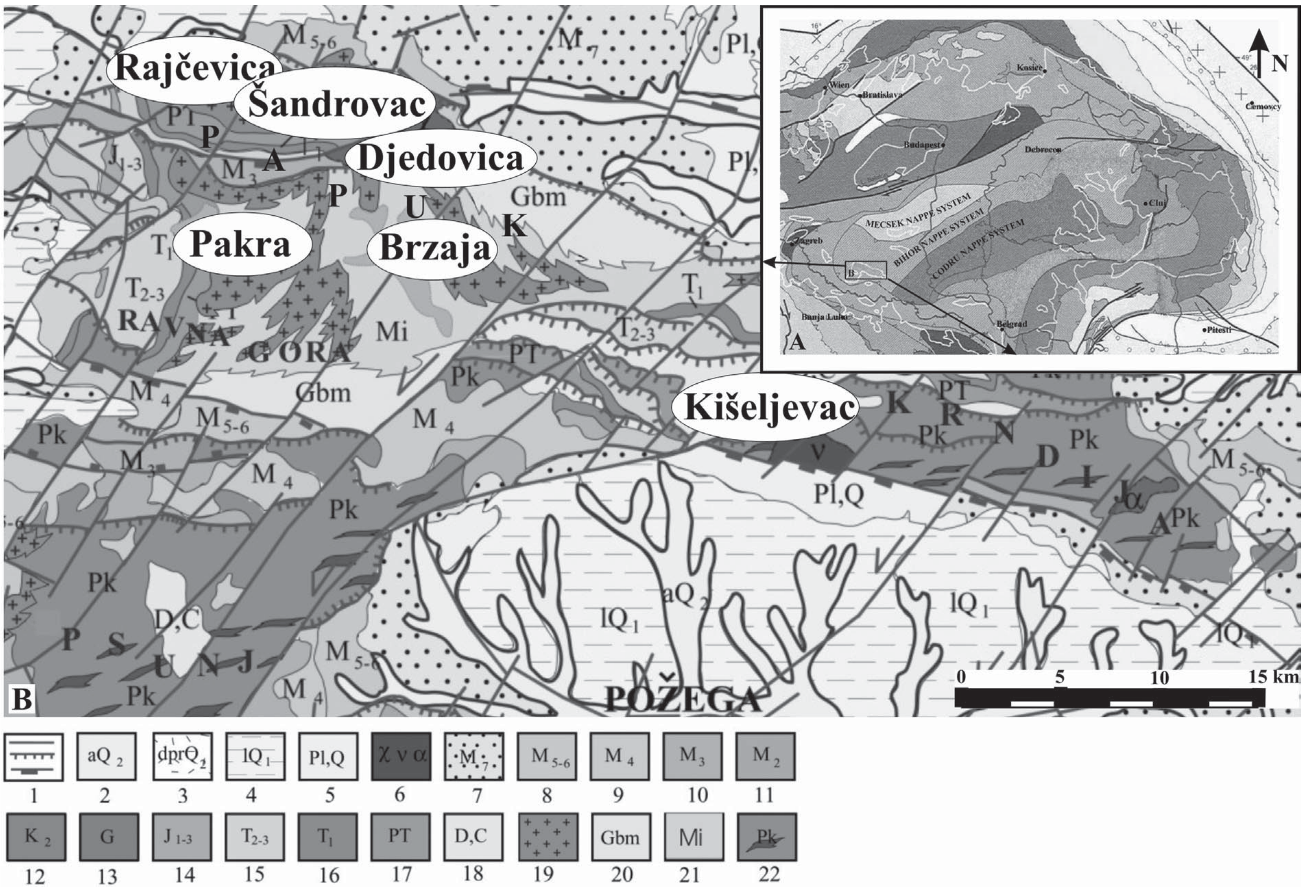

Figure 1: (A) Segment of the map (SCHMID et al., 2008) showing the major tectonic units of the Alps, Carpathians, Dinarides and Hellenides with the position of Papuk Mt. within the Tisza Mega-Unit composed of the Mecsek, Bihor and Codru nappe systems. (B) A section of the Geological Map of the Slavonian Mts. (Papuk, Krndija, Ravna gora and Psunj) (JAMIČIĆ, 2001) with sampling localities (Table 1).

Legend: 1 – Main tectonic lines; 2 – Alluvium of creeks; 3 – Deluvial-proluvial deposits; 4 – Loess; 5 – Pliocene-Quaternary: gravel and sands; 6 – albite rhyolite, andesite, basalt; 7 – Pontian: sand, marl and clay; 8 – Sarmatian-Pannonian: marl and limestone; 9 – Badenian: conglomerate, limestone, marl; 10 – Karpatian: conglomerate, sand, clay and marl; 11 – Ottnangian: conglomerate, sand, gravel; 12 – Upper Cretaceous: sandstone and limestone; 13 – Granite of Požeška gora; 14 – Jurassic: limestone; 15 – Middle and Upper Triassic: dolomite, dolomitic limestone; 16 – Lower Triassic: sandstone, siltstone, shale; 17 – Permotriassic: quartz sandstone, conglomerate; 18 – Devonian-Carboniferous: graphitic schist, conglomerate, sandstone, siltstone; 19 – Granitoids; 20 – Gneiss; 21 – Migmatite; 22 – (Precambrian): chlorite-sericite schist, metagabbro, marble, amphibolite, amphibole-schist, phlaseride granitoid, garnet-staurolite gneiss.

Table 1: List of investigated samples showing locality, rock type and triclinicity values (Δ = 12.5*[d(131)-d(1$\bar{3}$1)]) calculated according to GOLDSCHMIDT & LAVES (1954), for potassium feldspars from: (1) non-magnetic, low density fractions of bulk rock (mixture of quartz, alkali feldspar and plagioclase) and (2) megacrysts from porphyric rock types. (a,b) two megacrysts from one rock sample. Determination of mineral phases was according to the following reference data: quartz (Q) – JCPDS 33-1161; low albite (LA) – JCPDS 20-0554; albite, calcian (A) – JCPDS 20-0548 ; low microcline (LM), intermediate microcline (IM) and orthoclase (O) from BORG & SMITH (1969); muscovite (Ms) from GRIM, BRAY & BRADLEY (1937) in BROWN (1961) and chlorite (Chl) from SHIROZU (1958) in BROWN (1961).

Locality (Fig. 1)	Sample name	Rock type (based on mineralogical and/or geochemical data)	Determined mineral phases in classical X-ray pattern (1)	Δ Calculated from classical diffraction pattern (1)	Δ Calculated from Rietveld refinement diffraction pattern (2)
Brzaja Creek	PPM-3	gneiss	LM, O, LA, Q, Ms	0.92	
Brzaja Creek	PPG-4	granodiorite	LM, LA, Q, Ms	0.87	
Brzaja Creek	PPM-5	gneiss	O, LM, LA, Q	0	
Brzaja Creek	PPG-8	two-mica monzogranite	LM, LA, Q	0.81	0.96
Brzaja Creek	PPM-9	gneiss	O, A, Q, Ms	0	
Brzaja Creek	PPG-12	two-mica monzogranite	LM, LA, Q, Ms	0.87	
Djedovica Quarry	PP-13/1	gneiss	LM, LA, Q, Ms, Chl	0.92	
Djedovica Quarry	PP-13/2	gneiss	LM, LA, Q, Ms, Chl	0.96	
Djedovica Quarry	PP-13/4	gneiss	LM, A, Q, Ms, Chl	0.97	
Djedovica Quarry	PP-13/5	gneiss	LM, LA, Q, Ms	1	
Djedovica Quarry	PP-13/6	gneiss	LM, LA, Q, Ms	0.90	
Pakra Creek	2PPG-3	porphyric granodiorite	O, A, Q	0	
Pakra Creek	2PPG-4	porphyric granodiorite	O, A, IM, Q, Ms	0	
Pakra Creek	2PPG-5	porphyric granodiorite	IM, A, Q, Ms	0.29	0.33
Pakra creek	2PPG-6 (a)	porphyric granodiorite	O/IM, A, Q, Ms	0	
Pakra Creek	2PPG-6 (b)	porphyric granodiorite	O/IM, A, Q, Ms	0	
Pakra Creek	PPG-19	granodiorite	O, LA, Q, Ms	0	0
Pakra Creek	PPG-24	porphyric granodiorite	IM, A, Q	0.32	0.29
Pakra Creek	PPG-18	two-mica monzogranite	LM, O, LA, Q, Ms	0.87	
Pakra Creek	PPG-20	monzogranite	LM, A, Q, Ms, Chl	0.70	0.72
Pakra Creek	PPG-23	two-mica granodiorite	LM, LA, Q, Ms	0.56	
Šandrovac Creek	2PPG-32	two-mica monzogranite	LM, O, LA, Q, Ms	0.83	
Rajčevica Creek	2PPG-33	monzogranite	LM, LA, Q, Ms, Chl	0.68	
Kišeljevac Creek	HEG-31	biotite monzogranite	LM, O, LA, Ms, Chl	0.88	

A short review about the previous study of feldspars in this area can be found in and KOVÁCS KIS et al. (2004) and references within.

3. MATERIALS AND METHODS

Various types of granitoid and gneiss rock samples (Table 1) were collected from several valleys on Papuk Mt. Sampling localities are shown on the compiled geological map in Figure 1. The potassium feldspars from the aforementioned rocks were differentiated by X-ray powder diffraction measurements. X-ray investigation included measurement and indexing of the X-ray powder diffraction patterns of two kinds of materials: (1) non-magnetic, low density separates of finer-grained rocks (a mixture of quartz, alkali feldspar and plagioclase, i.e. felsic components that were impossible to separate from each other by hand-picking under the stereomicroscope) and (2) feldspar megacrysts picked out from four samples that are representative for different granitoid types and localities.

(1) The separates were prepared by crushing and wet sieving followed by heavy liquid (bromoform) separation of either the 0.25–0.125 mm or 0.125–0.063 mm fractions. The light fraction was further cleaned by a Frantz isodynamic magnetic separator (model LI). Separates that contained K-feldspar, plagioclase and quartz grains, were pulverised in an agate mortar. X-ray powder diffraction patterns were obtained on an analogue Siemens D500 powder diffractometer in the 5° to 65° 2θ range. Instrumental parameters were: CuKα radiation, 40 kV, 20 mA, Ni filter, registration at 0.5° 2θ/min goniometer, 1 cm/min chart speed, 2×10^3 sensitivity and 0.1 mm detector aperture. NaCl was used as zero shift internal

standard. Powder patterns were recorded on the paper and the peak positions were determined manually. The potassium feldspar polymorph(s) have been identified with the help of the JCPDS database. UnitCell software (HOLLAND & REDFERN, 1997) was used for unit cell parameters calculation.

(2) Data for megacrysts were collected in 5–70° 2θ ranges on a Siemens D5000 theta-theta diffractometer equipped with graphite secondary beam monochromator. Conditions were: CuKα_1 radiation, 0.02° 2θ step size and 5 seconds counting time per step. The Rietveld analyses were performed by the DBWS-9006 PC program package (YOUNG et al., 1994).

Triclinicity and ordering were calculated for both type of patterns (classical and digital) i.e. for both type of samples (separeates and megacrysts). Triclinicity was calculated using the formula $\Delta = 12.5*[d(131)-d(1\bar{3}1)]$ of GOLDSCHMIDT & LAVES (1954). Degree of ordering was determined according to [110] method (KROLL & RIBBE, 1983) and Δ_{Sm} method (NEVES & GODINHO, 1995).

Lattice translations tr $[110] = ½ (a^2 + b^2 + 2ab \cos\gamma)^{1/2}$ and tr $[1\bar{1}0] = ½ (a^2 + b^2 - 2ab \cos\gamma)^{1/2}$ were used for graphical estimation of t_1o values (KROLL & RIBBE, 1983) while the ordering index $\Delta_{Sm} = 15.32 - \Delta 2\theta / 0.608$ (NEVES & GODINHO, 1995) is applied for calculation the percentage of T_1o sites occupied by Al: $\Sigma Al(T_1) = 45 \Delta_{Sm} + 55$.

4. RESULTS

The powder diffraction patterns revealed that different polymorphs of feldspar are present in the rocks that differ both

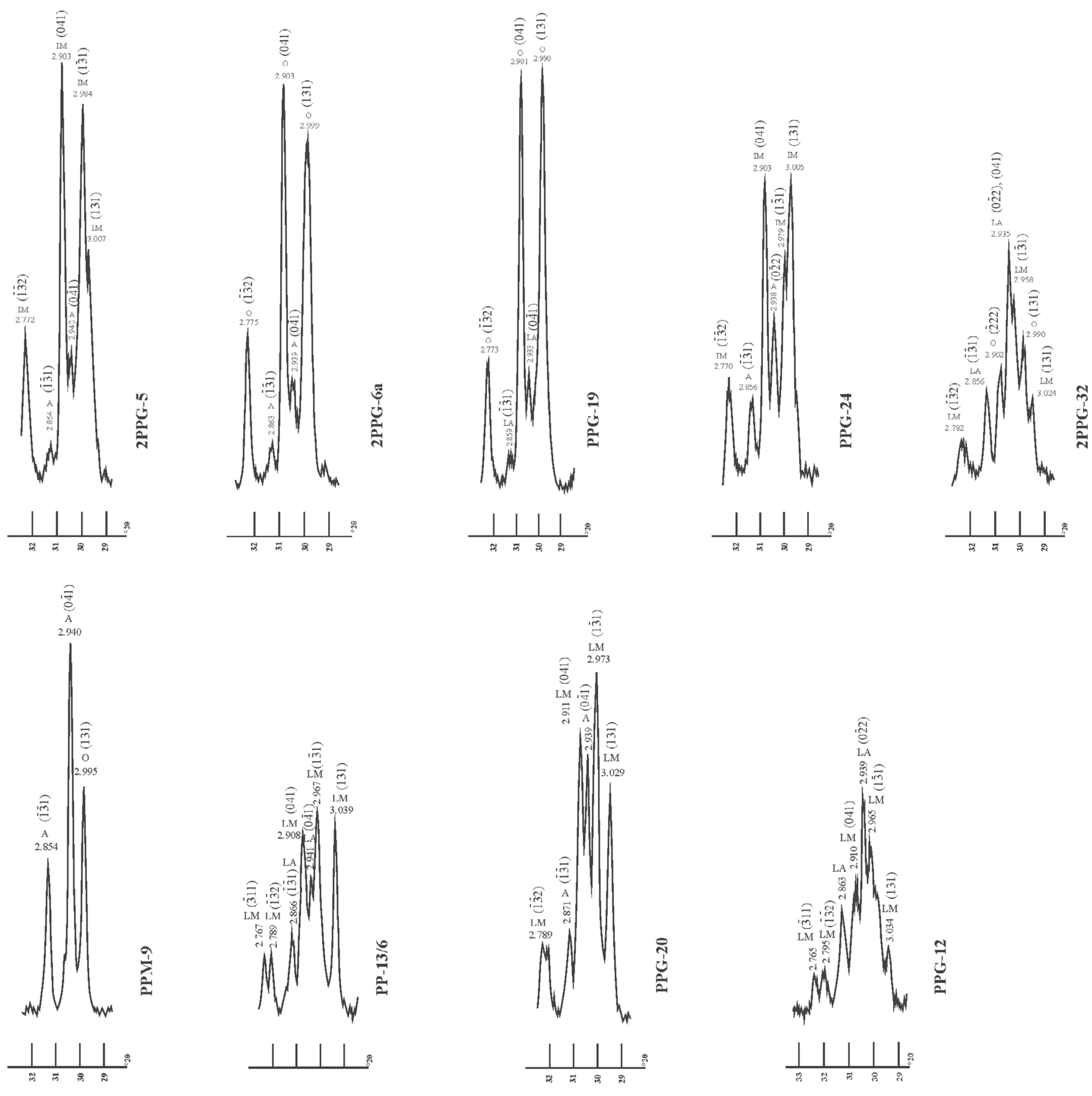

Figure 2: The {131} diffraction region of studied feldspars obtained by the classical method. The sample name is on the right side of the pattern's segment. Peaks are assigned according to the following reference data: quartz (Q) – JCPDS 33-1161; low albite (LA) – JCPDS 20-0554; albite (A) – JCPDS 20-0548; low microcline (LM), intermediate microcline (IM) and orthoclase (O) from BORG & SMITH (1969).

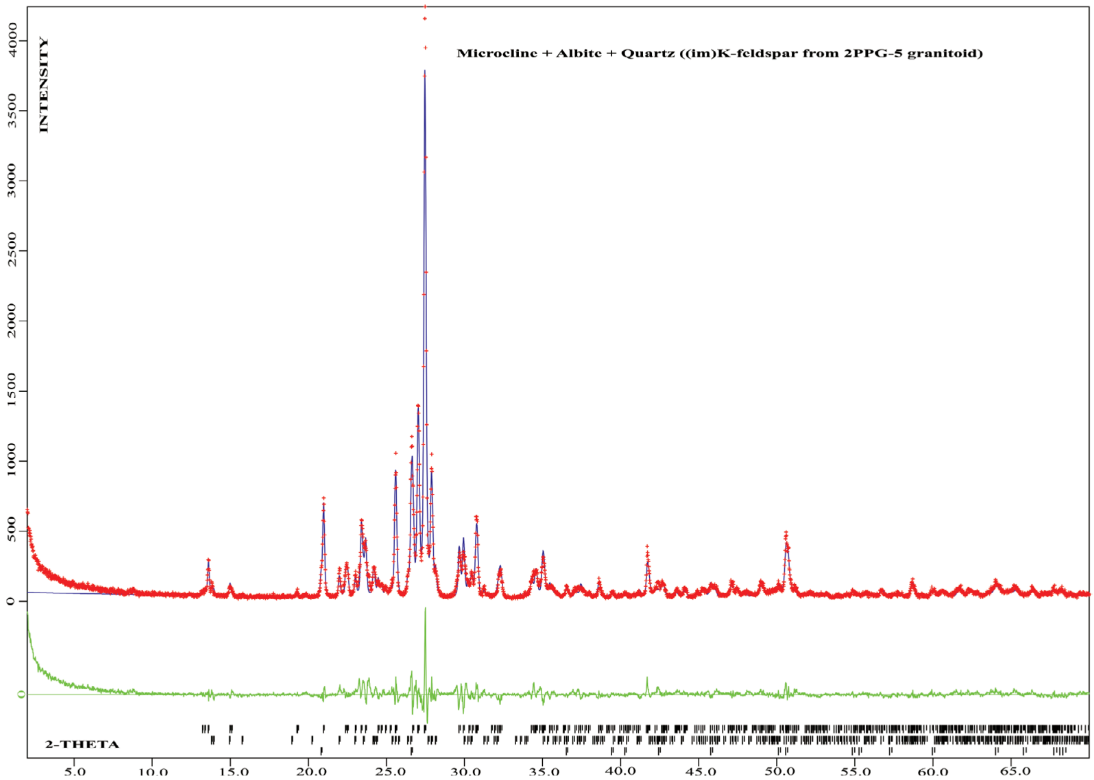

Figure 3: Observed and calculated diffraction pattern (plus signs and line, respectively) of 2PPG-5 sample feldspar megacryst. The lower curve shows the difference between the observed and calculated patterns. Tick marks indicate the positions of the allowed reflections of microcline (upper) and albite (lower). Calculated triclinicity (Δ) is shown in Table 1 (last column).

by rock type and sampling locality. X-ray powder patterns revealed that monzogranites from Rajčevica and Pakra Creeks (Figs. 1 and 2), granitoids from Brzaja Creek and gneisses from Djedovica Quarry contain only low microcline and low albite. Gneisses from Brzaja Creek, monzogranite from Kišeljevac and Šandrovac Creeks and fine to medium-grained granitoid samples from Pakra Creek valley also contain orthoclase. Porphyric and slightly porphyric granodiorites are typical of the Pakra Creek valley. Orthoclase is ubiquitous in these samples. If microcline appears, it is intermediate microcline. The potassium feldspar polymorph in the PPM-9 gneiss sample (Brzaja Creek) is monoclinic orthoclase.

Rietveld refinement for four feldspar megacrysts produced identical results in determination of feldspar polymorphs as the classical method, although small differences in Δ values were present (Table 1). Observed and calculated diffraction patterns of one of the feldspar megacryst samples (2PPG-5) are shown in Figure 3.

Triclinicity (Δ) calculations showed that the majority of the potassium feldspars occurring in the Papuk granitoids have values higher than 0.70 on the scale, where a microcline with maximum triclinicity has value of 1. The exception is the intermediate microcline modification that occurs in granodiorites of the Pakra Creek valley with triclinicity around or < 0.50. The lowest value is characteristic for the porphyric granodiorite of Pakra Creek valley (Δ=0.29). The highest values (Δ >0.90) are obtained on gneisses (Table 1). Pairs of triclinicity values obtained by two methods, classical (1) and Rietveld (2) are as follows: 0.81–0.96 for Brzaja Creek two-mica monzogranite, 0.29–0.33 and 0.32–0.29 for Pakra Creek porphyric granodiorites and 0.70–0.72 for Pakra Creek two-mica monzogranite (Tab. 1 and Fig. 2).

Table 2 presents unit cell parameters, t_1o occupancies and ordering for separates as well as for four potassium feldspar megacrysts. Feldspars from granitoids 2PPG-3, PPG-19 (Pakra Creek) and gneisses PPM-5 and PPM-9 (Brzaja Creek) have lattice parameters that conform to a monoclinic cell. Two grains (patterns a and b) of the 2PPG-6 granitoid sample show initial splitting of peak at 29.79 and 29.75 2°θ (Fig. 2). The splitting is not measurable so they are determined as orthoclase. Feldspars from PPG-4, PPG-8, PPG-20, 2PPG-32, 2PPG-33, HEG-31 and PPG-12 granitoids have a_0 between 8.56 to 8.59Å, b_0 from 12.92 to 13.01Å and c_0 in 7.20–7.22Å range, which correspond to the triclinic symmetry. Feldspar of PPG-18 and previously mentioned 2PPG-32 and HEG-31 samples shows a complicated {131} region with orthoclase and low microcline peaks. These peaks prove a presence of more than one potassium phase i.e. coexistence of phases having monoclinic and triclinic symmetries in various proportions within the same sample (Table 2). Overlapping of peaks on patterns (PPG-18, PPG-23 and PP-13/6 samples) meant that only a limited number of peaks could be used for calculation of unit cell parameters. Consequently the results for these samples are doubtful (Table 2, grey colour-coded samples). In contrast, feldspar from the 2PPG-5 sample shows intermediate microcline peaks, but those peaks are sharp with

Table 2: Unit cell parameters calculated with UnitCell software (HOLLAND & REDFERN, 1997) for classically observed diffraction patterns and calculated by Rietveld refinement (signed by subscript R). Lattice translations tr[1$\bar{1}$0], Al content in the T_1o site (according to KROLL & RIBBE, 1983 method), ordering index Δ_{Sm} and $\Sigma Al(T_1)$ (according to NEVES & GODINHO, 1995) for investigated potassium feldspars from Papuk Mt. Samples PPG-4 to HEG-31 are granitoids, while samples PPM-3 to PP-13/6 are gneisses (see Table 1). The (doubtful) results for samples where overlapping of peaks allowed unequivocal indexing of limited number of peaks are shown in grey.

Sample	a_0 (Å)	b_0 (Å)	c_0 (Å)	α(°)	β(°)	γ(°)	V (Å^3)	tr[1$\bar{1}$0] (Å)	t_1o	Δ_{Sm}	$\Sigma Al(T_1)$ %
PPG-4	8.577(5)	12.971(6)	7.220(3)	90.7(1)	115.87(6)	87.82(8)	722 (1)	7.6379	0.97	0.9	95
PPG-8	8.567(6)	12.95(1)	7.206(3)	90.71(6)	115.93(6)	87.74(6)	718(1)	7.6214	0.96	0.61	82
PPG-12	8.573(4)	13.01(1)	7.211(7)	90.55(8)	116.00(5)	87.83(7)	722(1)	7.6536	0.91	0.85	93
PPG-18	8.460(1)	12.776(5)	7.147(2)	90.56(4)	116.26(3)	87.88(4)	691(1)	7.5299	0.95	0.9	95
2PPG-3	8.574(7)	12.98(1)	7.21(1)		116.00(6)		721(1)				
2PPG-4a	8.592(8)	12.98(1)	7.210(3)	90.02(9)	115.99(7)	89.36(9)	723(1)	7.7429	0.57	0.75	89
2PPG-5	8.568(8)	12.969(6)	7.210(3)	90.10(8)	115.90(6)	89.38(9)	720(1)	7.7309	0.59	0.73	88
2PPG-6a	8.599(5)	12.953(4)	7.219(3)	90.01(4)	116.41(6)	89.64(5)	720(1)	7.7427	0.56	0.53	79
2PPG-6b	8.577(6)	12.972(8)	7.21(1)	90.18(8)	115.93(6)	89.52(8)	721(1)	7.7515	0.53	0.53	79
PPG-19	8.594(6)	12.976(6)	7.209(5)		116.04(6)		722(1)				
PPG-20	8.582(4)	12.924(4)	7.223(3)	90.40(4)	116.07(5)	87.90(4)	719(1)	7.6248	0.96	0.93	97
PPG-23	8.505(4)	12.866(2)	7.145(1)	90.58(2)	115.78(2)	88.42(3)	703(1)	7.6130	0.79	0.83	92
PPG-24	8.575(2)	12.974(2)	7.205(1)	90.285(3)	116.14(2)	89.14(2)	719(1)	7.7220	0.6	0.71	87
2PPG-32	8.575(8)	12.958(7)	7.208(3)	90.751(6)	115.92(5)	87.74(5)	719(1)	7.6269	0.99	0.73	88
2PPG-33	8.572(4)	12.967(6)	7.216(5)	90.69(7)	115.80(6)	87.96(7)	722(1)	7.6438	0.95	0.71	87
HEG-31	8.591(6)	12.966(8)	7.221(5)	90.59(7)	115.91(7)	87.80(6)	721(1)	7.6382	0.98	0.85	93
PPM-3	8.595(7)	12.957(6)	7.217(2)	90.59(4)	115.94(3)	87.78(5)	722(1)	7.6343	0.97	0.98	99
PPM-5	8.59(1)	13.02(1)	7.20(1)		115.95(9)		724(1)				
PPM-9	8.552(8)	12.95(1)	7.179(8)		116.06(8)		714(1)				
PP-13/1	8.571(9)	12.96(2)	7.212(8)	90.716(9)	115.89(9)	87.66(4)	720(1)	7.6216	0.99	0.99	99
PP-13/6	8.571(4)	12.942(7)	7.202(3)	90.842(7)	115.85(5)	87.53(6)	718(1)	7.6059	out of diagram	0.81	91
PPG-8_R	8.577	12.979	7.225	90.653	115.96	87.71	722(1)	7.6341	0.99	0.94	97
2PPG-5_R	8.571	12.965	7.206	90.213	115.98	89.21	720(1)	7.7217	0.61	0.67	85
PPG-20_R	8.577	12.966	7.212	90.520	115.98	88.25	720(1)	7.6629	0.84	0.83	92
PPG-24_R	8.572	12.967	7.205	90.262	115.98	89.14	720(1)	7.7181	0.62	0.70	86

fair intensity and they could be accurately read (Figure 2). Intermediate microcline of the 2PPG-5 sample have a_0 = 8.56, b_0 = 12.96 and c_0 = 7.21Å, with α slightly different from 90°, which also revealed triclinic symmetry (Table 2).

Lattice translation tr[1$\bar{1}$0] and cell volume results (Table 2) obtained from classically observed diffraction patterns gave an Al distribution in the T_1o site as follows; granitoids (PPG-4, PPG-8 and PPG-12) and gneiss from Brzaja Creek (PPM-3), gneiss in Djedovica Quarry (PP-13/1), granitoids from Šandrovac (2PPG-32), Rajčevica (2PPG-33) and Kišeljevac locality (HEG-31) have high Al content in the T_1o site. It is higher than 0.90, in most cases close to 1 (Table 2, Figure 4). However, granitoids in the Pakra Creek valley (2PPG-5, 2PPG-6, PPG-24) have an Al content around 0.60 in the T_1o site. The exception is the PPG-20 Pakra granitoid sample with 0.96 t_1o occupancy value.

Lattice translation tr[1$\bar{1}$0] and cell volume results obtained from diffraction patterns calculated by Rietveld refinement, (Table 2), showed that potassium feldspar from the Brzaja Creek granitoid (PPG-8_R) has a high Al content in the T_1o site (0.98), while megacrysts from Pakra Creek porphyric granodiorites (2PPG-5_R, PPG-24_R, PPG-20_R) have lower values, around 0.60 up to 0.84.

Comparison of the values obtained from the observed and calculated diffraction patterns showed that the results match in case of three samples (PPG-8, 2PPG-5 and PPG-24). For the patterns of the PPG-20 sample there is an obvious discrepancy between the t_1o values obtained by classical and Rietveld refinement methods (0.96 and 0.84, respectively). This cannot be explained as uncertainty in reading the peak positions (see Figure 2), and is most probably the result of the small number of peaks that could be used for unit cell parameter calculations.

Ordering index Δ_{Sm} and ΣAl in the T_1 sites calculated according to NEVES & GODINHO (1995) are also shown in Table 2. Investigated potassium feldspars have Δ_{Sm} from 0.50 to 1 while $\Sigma Al(T_1)$ range from 79% to 99%. According to the fact that the total Al content of the T_1 sites is 55% in

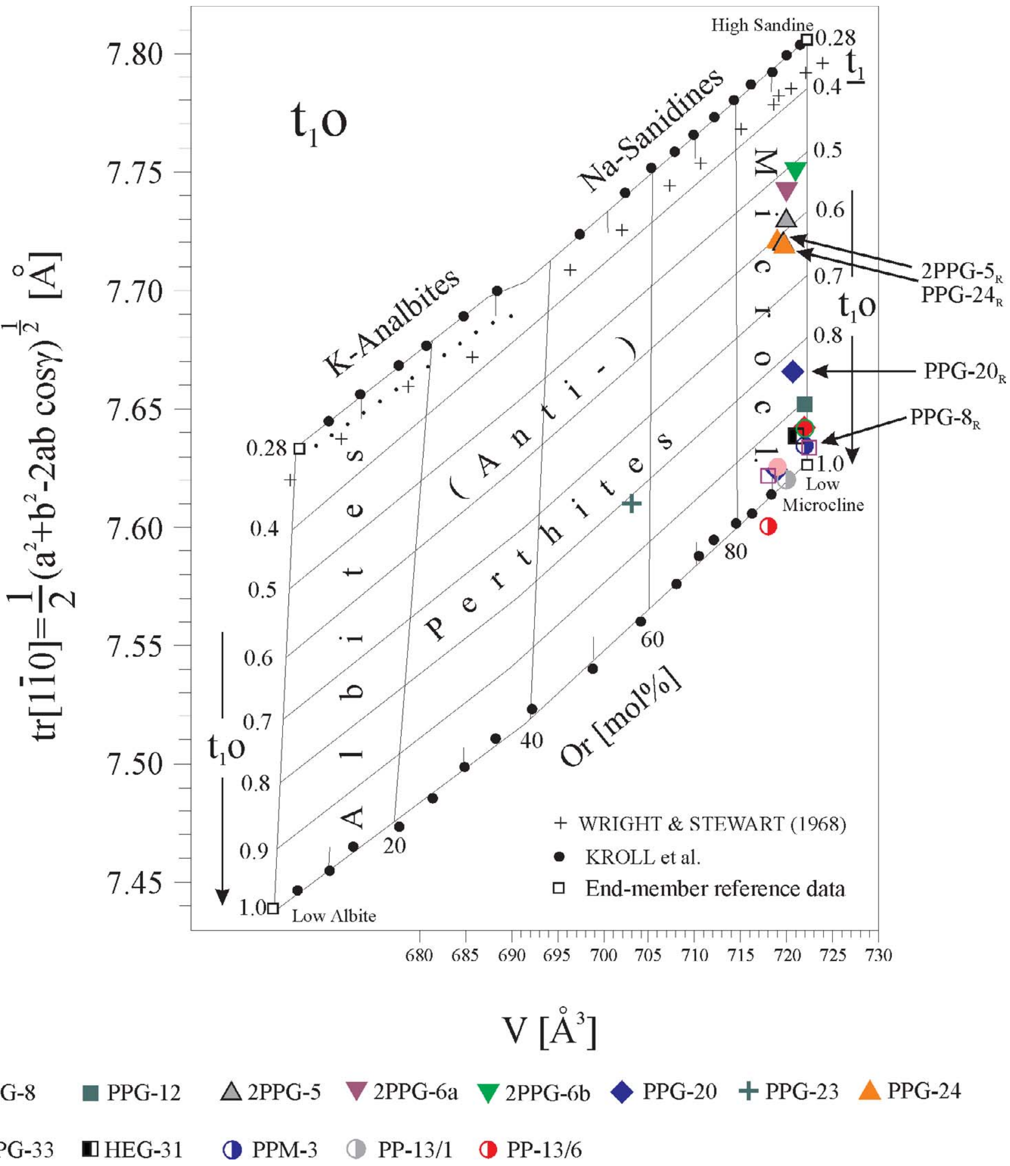

Figure 4: Plots of tr [1$\bar{1}$0] against V [Å^3] showing the estimated t_1o values for investigated feldspars. Values for end members are from KROLL & RIBBE (1987). Dots are from KROLL et al. (1986); crosses from WRIGHT & STEWART (1968). The kink at V = 695Å^3 ($Or_{\sim35}$) is due to the triclinic/monoclinic symmetry change.

high sanidine and 100% in low microcline (KROLL & RIBBE, 1987) these estimated values correlate well with those determined from unit cell parameters.

5. DISCUSSION

Polymorphic modifications of alkali feldspars are the result of the Al-Si distribution in the crystal structure. The way in which the Al content changes in each tetrahedral site (T_1o, T_1m, T_2o and T_2m), from the most disordered (sanidine), to the most ordered state (high triclinic/low microcline), is called the ordering path in alkali feldspars (SMITH, 1974; GRIFFEN, 1992). Ordering is a two-step phenomenon: (1) the migration of Al from the T2 to T1 sites and (2) Al migration from T_1m, T_2o and T_2m to the T_1o site (STEWART & WRIGHT, 1974). If the feldspar is monoclinic, the probability of finding Al at the T_1o and T_1m sites is equal ($t_1o = t_1m$). If the crystal is completely ordered, in the unit cell there will be 1.0 Al + 3.0 Si along *b* (KROLL & RIBBE, 1983). During the ordering process, T-O bond lengths vary and O-T-O and T-O-T bond angles are affected (KROLL, 1973). The T-O bond lengths reflect Al occupancy; therefore the Al occupancy can be estimated by calculating T-O bond lengths. An increase in aluminium occupancy causes an increase in the mean bond length, whereas an increase in silicon occupancy causes their decrease (KROLL, 1973).

During Al-Si ordering, triclinic feldspars expand along [110] and contract along [1$\bar{1}$0]. The translation tr[110] estimates $t_1o+t_2o+t_2m$ and tr [1$\bar{1}$0] estimates $t_1m+t_2o+t_2m$. Because the same amount of Al and Si atoms is present in the unit cell regardless of the structural state (GRIFFEN, 1992), unit cell volume (V) should be a function of composition but not of structural state. If tr[1$\bar{1}$0] is plotted versus cell volume (V), t_1o can be estimated directly from the diagram of KROLL

& RIBBE (1983). Therefore the [110] method can be used for determining the (Al-Si) distributions among the non-equivalent tetrahedral sites. If ordering proceeds as far as possible, all of the aluminium is found in T_1o, therefore t_1o=1.0; t_1m=t_2o=t_2m=0.0 and alkali feldspar is referred to as maximum (or low) microcline. According to the results presented in Table 2 studied granitoids from Brzaja, Kišeljevac, Šandrovac and Rajčevica Creek valleys and gneisses in Djedovica Quarry and one gneiss sample from Brzaja Creek valley contain highly ordered potassium feldspar, because most of the Al atoms are found in the T_1o site (Fig. 4). These potassium feldspars have high triclinicity (0.81–0.99; Table 1) and correspond to the highly ordered microcline (low microcline) (SMITH, 1974; GRIFFEN, 1992). Al occupancy in the T_1o site of Pakra Creek valley granitoid feldspars are between 0.53 and 0.62 (Table 2, Fig. 4); their triclinicity is low (around 0.30 or even 0.0) (Table 1) and they correspond to intermediate microcline or orthoclase. Brzaja Creek valley gneiss feldspars, excluding low microcline in PPM-3 sample, with triclinicity value $\Delta = 0$ revealed to be orthoclase.

Results obtained by GOLDSCHMIDT & LAVES (1954), KROLL & RIBBE (1983) and NEVES & GODINHO (1995) methods indicate variation in the structural state, from orthoclase, intermediate microcline to highly ordered microcline in the investigated rock samples. High triclinicity values of feldspars from granitoid and gneiss samples from Papuk Mt. (Slavonia, Croatia) are in accordance with high Al contents in the T_1o site and their fully ordered state indicate a slow(er) cooling-rate. Low triclinicity values, Al content in T_1o site of around 0.60, and an ordering index smaller than 0.80 can be interpreted as a result of relatively fast(er) cooling which allowed the existence of less ordered potassium feldspar.

Classical and diffraction patterns calculated by the Rietveld refinement method gave comparable results. Obtaining correct cell parameters depends primarily upon accurate measurement of the peak positions and the correct indexing of X-ray powder patterns.

6. CONCLUDING REMARKS

According to X-ray powder diffraction results, the porphyric potassium feldspar in biotite-granodiorites and monzogranites is orthoclase or intermediate microcline, while two-mica monzogranite contains maximum microcline (low microcline). Orthoclase and intermediate microcline are typical for Pakra Creek valley granodiorites, while highly ordered microcline (low microcline) characterises monzogranite rock types in the Pakra, Šandrovac, Rajčevica, Kišeljevac and Brzaja Creek valleys. Gneisses associated with granites contain low microcline and orthoclase (Brzaja Creek valley), and low microcline (Djedovica Quarry). Some granitoid and gneiss samples only contain orthoclase.

Intermediate microcline or orthoclase from biotite-granodiorites and monzogranites compared with highly ordered, structured, potassium feldspars from two-mica monzogranites indicate differences in the rate of cooling, as the most important factor controlling the ordering of potassium feldspars. The two-mica granitoids as host rocks, have a eutectic composition and peraluminous character. They are syn-collision granitoids according to HORVAT (2004), HORVAT & BUDA (2004) and their overall triclinic symmetry implies a slow cooling-rate and higher degree of order with the aid of fluid activity or deformation in the case of the gneiss (BROWN & PARSONS, 1989).

Porphyric biotite-granodiorite and monzogranite have a peraluminous-metaluminous character and were probably formed post-collision in an uplifted environment (HORVAT, 2004; HORVAT & BUDA, 2004). They were emplaced at shallower levels in the crust; thus cooling was relatively fast which prevented the symmetry inversion and retarded ordering. Rapid cooling seems to be the most probable explanation for preservation of monoclinic structures and the moderate degree of Al-Si ordering of potassium feldspars in these rocks.

Estimation of three different methods for K-feldspar characterization: triclinicity calculations according to GOLDSCHMIDT & LAVES (1954), structural state determination by the method of KROLL & RIBBE (1983) and the ordering index method introduced by GODINHO & JALECO (1973) once again proved the very good correlation of results obtained by these methods. This fact gives greater weight to conclusions arising from them i.e. makes them more reliable. Simple and relatively fast standard methods for potassium feldspar determination and description produced results that correlate well with those obtained by more accurate but more time-consuming methods.

ACKNOWLEDGMENT

This study was carried out in the Department of Mineralogy, Eötvös Loránd University, Budapest and was supported by the Hungarian Ministry of Education through the Ph.D. scholarship and Hungarian National Research Fund (OTKA project no. K 67787). The authors are very grateful to Judit KIRÁLY-TÓTH (Department of Mineralogy, Eötvös Loránd University Budapest) for the help with recording analogue X-ray powder diffraction patterns and Ivo SUŠA (Croatian Geological Survey, Zagreb) for help with drawings. We are particularly grateful to Julie ROBSON (OCP Consulting, Scotland) for language editing. The authors acknowledge corrections and suggestions referred by Galiba SIJARIĆ (Faculty of Science, University of Sarajevo) and to an Anonymous Reviewer which led to the reorganization of the paper and its improvement.

REFERENCES

BALEN, D., HORVÁTH, P., TOMLJENOVIĆ, B., FINGER, F., HUMER, B., PAMIĆ, J. & ÁRKAI, P. (2006): A record of pre-Variscan Barrovian regional metamorphism in the eastern part of the Slavonian Mountains (NE Croatia).– Mineral. Petrol., 87, 143–162. doi: 10.1007/s00710-006-0120-1

BIŠEVAC, V., BALEN, D., TIBLJAŠ, D. & ŠPANIĆ, D. (2009): Preliminary results on degree of thermal alteration recorded on the eastern part of Mt. Papuk, Slavonia, Croatia.– Geol. Croat., 62/1, 63–72.

BIŠEVAC, V., BALOGH, K., BALEN, D. & TIBLJAŠ, D (2010): Eoalpine (Cretaceous) very low- to low-grade metamorphism recorded on illite-muscovite rich fraction from South Tisia (eastern Mt. Papuk, Croatia).– Geol. Carpath., 61/6, 469–481. doi: 10.2478/v10096-010-0029-9

BORG, I.Y. & SMITH, D.K. (1969): Calculated X-ray Powder Patterns for Silicate Minerals.– Geological Society of America, Inc. Memoir, 122, 896 p.

BROWN, G. (1961): The X-ray identification and crystal structures of clay minerals.– Mineralogical Society, London, 544 p.

BROWN, W.L. & PARSONS, I. (1989): Alkali feldspars: ordering rates, phase transformations and behaviour diagrams for igneous rocks.– Mineral. Mag., 53, 25–42.

GOLDSCHMIDT, J.R. & LAVES, F. (1954): The microcline-sanidine stability relations.– Geochim. Cosmochim. Ac., 5, 1–19.

GODINHO, M.M. & JALECO, J.M.P. (1973): Feldspatos potássicos dos granitóides da região de Castro Daire (Viseu, Portugal). I. Estado estrutural.– Memórias e Notícias, Publ. Mus. Lab. Mineral. Geol. Univ. Coimbra, 76, 44–71.

GRIFFEN, D.T. (1992): Silicate Crystal Chemistry.– Oxford University Press, Oxford, 442 p.

GRIM, R.E., BRAY, R.H. & BRADLEY, R.F. (1937): Mica in argillaceous sediments.– Am. Mineral., 22, 813–829.

HOLLAND, T.J.B. &. REDFERN, S.A.T (1997): Unit cell refinement from powder diffraction data: the use of regression diagnostics.– Mineral. Mag., 61, 65–77.

HORVAT, M. (2004): Geochemistry and petrology of granitoids of Papuk and Psunj Mts. (Slavonia, Croatia).– Unpubl. PhD Thesis, University of Budapest, (133+108) p.

HORVAT, M. & BUDA, GY. (2004): Geochemistry and Petrology of some Granitoids from Papuk and Psunj Slavonian Mountains (Croatia).– Acta Miner. Petrograph., 45/1, 93–100.

HORVAT, M, KOVÁCS KIS, V. & DÓDONY, I. (2002): Crystallization path of K-feldspar megacrysts from Mt. Papuk, Croatia.– In: MICHALIK, J., ŠIMON, L. & VOZAR, J. (eds): Proceedings of the XVIIth Congres of Carpathian-Balkan Geological Association, Bratislava, September 1-4, 2002. Geol. Carpath., 53, 189–190.

HORVÁTH, P., BALEN, D., FINGER, F., TOMLJENOVIĆ, B. & KRENN, E. (2010): Contrasting P-T-t paths from the basement of the Tisia Unit (Slavonian Mts., NE Croatia): Application of quantitative phase diagrams and monazite age dating.– Lithos, 117, 269–282. doi: 10.1016/j.lithos.2010.03.004

JAMIČIĆ, D. (1983): Strukturni sklop metamorfnih stijena Krndije i južnih padina Papuka [*Structural pattern of the metamorphosed rocks of the Mt. Krndija and the southern part of Mt. Papuk* – in Croatian].– Geol. vjesnik, 36, 51–72.

JAMIČIĆ, D. (1988): Strukturni sklop slavonskih planina (sjeverni Psunj, Papuk, Krndija) [*Structural pattern of the Slavonian Mountains (Northern Psunj, Papuk, and Krndija)* – in Croatian].– Unpubl. PhD Thesis, University of Zagreb, 152 p.

JAMIČIĆ, D. (1989): Osnovna geološka karta SFRJ 1:100000, list Daruvar, L33-95. [*Basic Geological Map of SFRY, 1:100000, Daruvar sheet* – in Croatian].– Geološki zavod Zagreb, Savezni geološki zavod Beograd.

JAMIČIĆ, D. (2001): Main geological features of the Slavonian Mts. focused to the Našice area.– Matica Hrvatska, Našički zbornik, 6, 29–36.

JAMIČIĆ, D. & BRKIĆ, M. (1987): Osnovna geološka karta SFRJ 1:100000, list Orahovica, L33-96 [*Basic Geological Map of SFRY 1:100000, Orahovica sheet* – in Croatian].– Geološki zavod Zagreb, Savezni geološki zavod Beograd.

KOVÁCS KIS, V., HORVAT, M. & DÓDONY, I. (2004): Microstructures in two alkali feldspar megacrysts from the Papuk Mt., Croatia.– Geol. Croat., 57/2, 149–158.

KROLL, H. (1971): Determination of Al, Si distribution in alkali feldspars from X–ray powder data.– Neues Jb. Miner. Monat., 91–94.

KROLL, H. (1973): Estimation of the Al, Si distribution of feldspars from the lattice translations tr 110 and tr $1\bar{1}0$. I. Alkali feldspars.– Contrib. Min. Pet. 39, 141–156.

KROLL, H. (1980): Estimation of the Al, Si distribution of feldspars from lattice translations tr 110 and tr $1\bar{1}0$. Revised diagrams.– Neues Jb. Miner. Monat., 31–36.

KROLL, H. & RIBBE, P.H. (1983): Lattice parameters, composition and Al, Si order in alkali feldspars.– In: RIBBE, P.H. (ed.): Feldspar Mineralogy, 2nd ed. Rev. Mineral. 2, 57–99.

KROLL, H. & RIBBE, P.H. (1987): Determining (Al-Si) distribution and strain in alkali feldspars using lattice parametres and diffraction-peak positions: a review.– Am. Mineral., 72, 491– 506.

KROLL, H., SCHMIEMANN, I. & VON CÖLLN, G. (1986): Feldspar solid solutions.- Am. Mineral., 71, 1–16.

NEVES, L.J.P.F. & GODINHO, M.M. (1995): Estimação expedita do ordenamento Al-Si do feldspato potássico-uma reapreciação.– Memórias e Notícias, Publ. Dep. Ciências da Terra e do Mus. Lab. Mineral. Geol. Univ. Coimbra, 120, 15–24.

PAMIĆ, J. & LANPHERE, M. (1991): Hercinske granitne i metamorfne stijene Papuka, Psunja, Krndije i okolne podloge Panonskog bazena u Slavoniji (sjeverna Hrvatska) [*Hercynian Granites and Metamorphic Rocks from the Mts. Papuk, Psunj, Krdnija and the Surrounding Basement of the Pannonian Basin in Slavonija (Northern Croatia, Yugoslavia)* – in Croatian].– Geologija, 34, 81–253.

PAMIĆ, J., LANPHERE, M. & McKEE, E. (1988): Radiometric Ages of Metamorphic and Associated Igneous Rocks of the Slavonian Mts. in the Southern Part of the Pannonian Basin, Yugoslavia.– Acta Geologica, 18/2, 13-39.

PAMIĆ, J., LANPHERE, M. & BELAK, M. (1996): Hercynian I-type and S-type granitoids from the Slavonian Mountains (southern Pannonian Basin, northern Croatia).– Neues Jb. Miner. Abh. 171/2, 155–186.

RAFFAELLI, P. (1964): Metamorfizam paleozojskih pelitskih škriljaca u području Ravne Gore [*Metamorphism of Paleozoic politic schists of Ravna gora* – in Croatian].– Geol. vjesnik, Zagreb, 18/1, 61–111.

SCHMID, S.M., BERNOULLI, D., FÜGENSCHUH, B., MATENCO, L., SCHEFER, S., SCHUSTER, R., TISCHLER, M. & USTASZEWSKI, K. (2008): The Alpine-Carpathian-Dinaridic orogenic system: correlation and evolution of tectonic units.– Swiss J. Sci. 101, 139–183. doi: 10.1007/s00015-008-1247-3

SHIROZU, H. (1958): X-ray patterns and cell dimensions of chlorites.– Mineral. Journal, 2, 209–223.

SLOVENEC, D. (1976): Izmjene biotita u pegmatitu iz potoka Brzaje na Papuku u uvjetima površinskog trošenja [*Weathering of biotite in pegmatite from the canyon of the Brzaja stream in the Papuk Mountain (North Croatia)* – in Croatian].– Geol. vjesnik, 29, 243–267.

SLOVENEC, D. (1978): Mogućnost korištenja biotita kao indikatora geneze granitno-metamorfnih stijena Papuka [*On the possible utilization of biotite as a genetic indicator in the Papuk granite-metamorphic rocks (north Croatia)* – in Croatian].– Geol. vjesnik Zagreb, 30/2, 351–357.

SLOVENEC, D. (1982): Kemijski sastav biotita, granata i amfibola kao pokazatelj temperature formiranja granitno-metamorfnih stijena Papuka [*Chemical composition of biotites, garnets and amphiboles as an indicator of the formation temperature of granite-metamorphic rocks of the Papuk Mountain* – in Croatian].– Geol. vjesnik Zagreb, 35, 133–152.

SLOVENEC, D. (1988): Transformacija biotita u klorit u granitno-metamorfnih stijena Papuka [*The alteration of biotite to chlorite in granito-metamorphic rocks from the Mt. Papuk* – in Croatian].– Geol. vjesnik, 41, 87–98.

SMITH, J.V. (1974): Feldspar Minerals, vol. I. Crystal Structure and Physical Properties.– Springer, Berlin, 627 p.

STEWART, D.B. & WRIGHT, T.L. (1974): Al/Si order and symmetry of natural alkali feldspars and the relationship of strained cell parameters to bulk composition.– B. Soc. Fr. Mineral. Cr., 97, 356–377.

TAJDER, M. (1957): Petrografsko istraživanje zapadnog dijela Papuka [*Petrographic investigation of the western part of the Papuk Mt.* – in Croatian].– Ljetopis JAZU, 62, 316–323.

TAJDER, M. (1969): Magmatizam i metamorfizam planinskog područja Papuk-Psunj [*Magmatism and metamorphism of the Papuk-Psunj Mountains* – in Croatian].– Geol. vjesnik, 22, 469–476.

VRAGOVIĆ, M. (1965): Graniti i gnajsi Papuka [*Granites and gneisses of the Papuk Mountain* – in Croatian].– Unpubl. PhD Thesis, University of Zagreb, 222 p.

YOUNG, R.A., SAKTHIVEL, A., MOSS, T.S. & PAIVA-SANTOS, C.O. (1994): DBWS software: Rietveld analysis of X-ray and neutron powder diffraction patterns.– Users Guide.

WRIGHT, T.L. & STEWART, D.B. (1968): X-ray and optical study of alkali feldspar: I. Determination of composition and structural state from refined unit-cell parameters and 2V1.– Am. Mineral., 53, 39–86.

Manuscript received November 04, 2010
Revised manuscript accepted April 20, 2011
Available online June 09, 2011