

## AGES AND INTENSITIES OF METAMORPHIC PROCESSES IN THE BATOČINA AREA, SERBO-MACEDONIAN MASSIF.

KAD. BALOGH, É. SVINGOR\*

Institute of Nuclear Research of Hungarian Academy of Science

V. CVETKOVIĆ\*\*

Faculty of Mining and Geology, University of Belgrade

### ABSTRACT

The rocks of the polymetamorphic complex of Batočina were studied by the Rb/Sr and K/Ar isotopic methods in order to determine the age and intensity of metamorphic phases.

Rb/Sr data of eight whole rock samples are arranged along two regression lines defining model ages of  $709 \pm 51$  Ma and  $488 \pm 19$  Ma. The older age is chronologically meaningless since RL-1 is a mixing line. The younger datum of  $488 \pm 19$  Ma gives the age of the oldest recognized metamorphism.

Several K/Ar ages on amphiboles indicate Hercynian age, while on the basis of K/Ar ages on muscovite and K-feldspar  $0.30 \pm 0.13$  mm/year uplift rate was obtained for the time interval from 150.6 Ma to 127.3 Ma.

### INTRODUCTION

The metamorphic series of the Batočina area, representing the northernmost exposed parts of Serbo-Macedonian Massif, consists of various metamorphic rocks originating from different protolites. The petrological and geological significance of these rocks enforced this investigation to explain some problems concerning the age of different phases of metamorphism. The only existing radiometric data for this terrain (BALOGH and CVETKOVIĆ, 1992 in print) closely agree with the earlier investigations in the central parts of the Serbo-Macedonian Massif by DIMITRIJEVIĆ (1971) and MILOVANOVIĆ (1990). According to the above mentioned data as well as to the geological evidences (PETROVIĆ and KARAMATA, 1970) the latest metamorphic phases were Hercynian (275 Ma – hornblende analysis) and Alpine (127–160 Ma – mica and potassium feldspar analysis).

This study was enabled by collaboration of the Institute of Nuclear Research of the Hungarian Academy of Sciences in Debrecen and Serbian Academy of Sciences and Arts as a part of the Project "GEODYNAMICS".

\* H-4001 Debrecen, P. O. Box. 51.

\*\* YU-11000 Belgrade, Djušina 7.

## GEOLOGICAL SETTING

The Batočina series (about 900 m thick) represents the furthestmost northern parts of the "Lower complex" of the Serbo-Macedonian Massif (DIMITRIJEVIĆ, 1959) – a terrain which plays an important role in the geological structure of Yugoslavia and the central part of the Balkan peninsula (Fig. 1). It consists of various types of gneisses, micaschists, amphibolites, marbles, quartzites and other schists. Earlier investigations (BOUE, 1836; HERDER, 1846; MILOJKOVIĆ, 1892; UROŠEVIĆ, 1912; DIMITRIJEVIĆ, 1950; ČMILJANIĆ and DJORDJEVIĆ, 1969; KALENIĆ *et al.*, 1975; VUJISIĆ *et al.*, 1977) suggested a prograde metamorphism corresponding to the epidot-amphibolite to amphibolite facies. According to petrological and especially geochemical evidences the complex in a whole represent a metamorphosed deep-water sedimentary unit of Riphean-Cambrian age (VUJISIĆ *et al.*, 1977) with late shallow-water facies, while amphibolites correspond to the ancient subalkaline within-plate tholeiites (CVETKOVIĆ, 1992). On the basis of chemical characteristics of the minerals in the equilibria CVETKOVIĆ (1992) has concluded that metamorphism occurred at a temperature between 550 and 600°C and a pressure at about 6 kb. The mentioned values are strongly supported by the mineral assemblage (garnet – staurolite – kyanite in gneisses and micaschists and epidote – hornblende – garnet in amphibolites.)

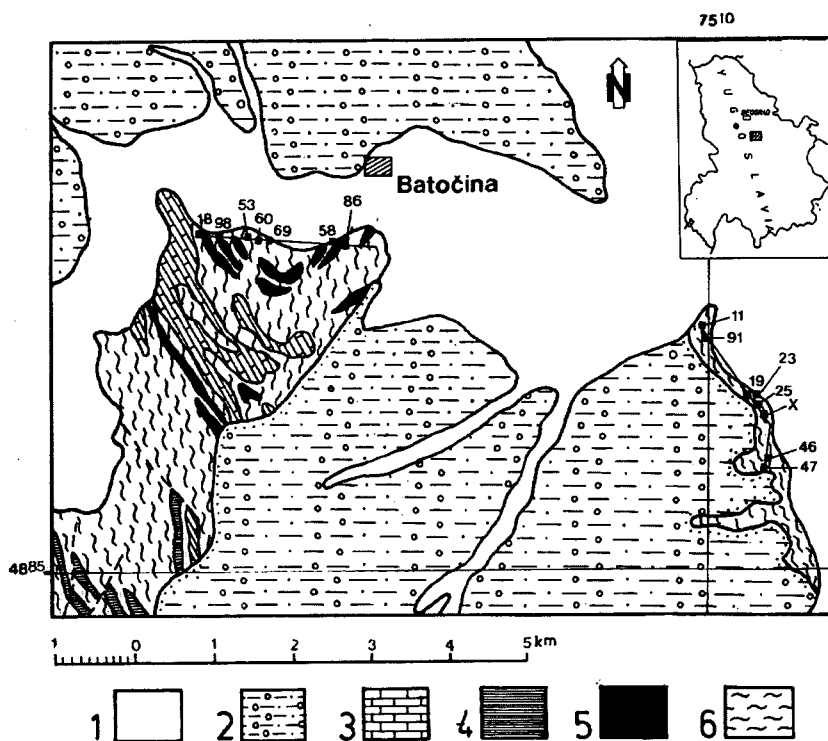


Fig. 1. Geological sketch of the Batočina region

- Legend: 1 – Quaternary;  
 2 – Lower and Upper Miocene sediments;  
 3 – Marbles and dolomite marbles;  
 4 – Quartzites;  
 5 – Amphibolites;  
 6 – Gneisses and micaschists.

Finegrained biotite and coarsegrained two-mica paragneisses, which with micaschists together usually form layer units up to 15 m thickness at the best exposures, and augen-ortho(?) gneisses were distinguished. Paragneisses and micaschists often show transition while augen-gneissen are usually interlayered with host metasediments or form, rather seldom, small discordant bodies always with sharp contacts. The amphibolites are relatively scarce in comparison to the metapsammitic and metapelitic country rocks; they occur as lens shaped bodies originated by boudinage from 0.5 m to 15 m in length, usually 0.5–1m thick, parallel to the foliation.

Both finegrained biotite and coarsegrained two-mica gneisses are of granoblastic to lepidoblastic texture and of distinctive schistosity. Elements of finegrained blastopsammitic texture also occur. They consist of quartz, plagioclase (32–52% An), rare alkali feldspar, fragments of quartzites, gneisses, granodiorite and rarely phylites, biotite, muscovite, garnet, apatite, tourmaline and opaque minerals. Secondary minerals are chlorite, sericite and seldom epidote. In some varieties close to micaschists rare euhedral staurolite and kyanite crystals were also observed.

Otherwise, the augen-gneisses show lepidoblastic and granoblastic texture and augens, sometimes even amygdaloidal structure. They are composed of quartz, alkali feldspar (microcline, ortoclase and albite often with myrmekite), muscovite, biotite, apatite, zircon, opaque minerals and secondary chlorite and sericite.

The Batočina amphibolites can be divided into two groups well distinguishable in the field:

- garnet-amphibolites mainly of massive structure and nematoblastic to granoblastic texture essentially consisting of hornblende, plagioclase, garnet, sphene, zoisite, epidote, ilmenite and quartz,

- garnet -biotite amphibolites prevailing of schistose structure with biotite as an abundant constituent, compared with the above mentioned amphibolites, very rare zoisite and sphene.

Eight samples of paragneisses and micaschists, two of augen-gneisses and four samples of amphibolites have been collected across the two exposed profile (*Fig. 1*). Sample distances range from several tens of meters to a few decimeters depending on rock unit homogeneity. The main petrographic features as well as mineral compositions of the analyzed samples are presented in Table 1.

## EXPERIMENTAL METHODS

### *Rb/Sr Method*

Rb and Sr were measured by stable isotope dilution methods. The spike solution was added to the weighed sample at the beginning of the procedure. Following this the samples were taken into solution in a mixture of hydrofluoric and perchloric acids and subsequently converted to chlorides. Sr was separated and purified on a cation exchange column using Dowex 50W resin. All Rb and Sr analyses were made with a modified MI-1309 mass spectrometer. At least 50 scans of the Sr mass spectrum were used in the final data compilation. During the period of this study the average  $^{87}\text{Sr}/^{86}\text{Sr}$  obtained for EIMER and AMAND Sr-standard ( $^{87}\text{Sr}/^{86}\text{Sr}=0.70802\pm 2$ ) was  $0.7079\pm 2(2\sigma$  of the mean, 10 analyses). To control also the chemical procedure,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of a basalt sample from Diszel (W-Hungary) was measured, the ob-

TABLE 1

## Main petrographic features and mineral composition of the analyzed metamorphic rocks from the Batočina complex

No	Rock Type	Texture	Mineral composition													
			Q	Af	Pl	Mu	Bi	Ho	Gt	St	Ky	Ap	Sph	Ep	OM	To
BČ-X	TMG	lpb, gbl, pbl	+	*	+	+	+	-	+	-	-	*	-	-	*	-
BČ-10	FBG	lpb, gbl	+	-	+	-	+	-	+	*	-	*	-	-	*	-
BČ-11	AOG	gbl, lpb	+	+	-	*	+	-	-	-	-	*	-	-	*	-
BČ-18	GA	nmb, gbl	-	-	*	-	-	+	+	-	-	*	+	*	*	-
BČ-19	FBG	bpsm	+	-	+	-	+	-	+	-	-	*	-	-	*	-
BČ-23	TMG	lpb, gbl, pbl	+	-	+	+	+	-	*	*	-	*	-	-	*	-
BČ-25	TMG	lpb, gbl, pbl	+	*	+	+	+	-	+	-	-	*	-	-	*	-
BČ-46	FBG	lpb, gbl	+	*	+	-	+	-	+	*	-	*	-	-	-	-
BČ-47	TMG	lpb, gbl, pbl	+	-	+	+	+	-	+	*	-	*	-	-	*	-
BČ-53	AOG	gbl, lpb	+	+	-	*	+	-	-	-	-	*	-	-	*	-
BČ-58	GBA	nmb, gbl, lpb	*	-	*	-	+	+	+	-	-	*	-	+	*	-
BČ-60	MSC, TMG	lpb, gbl	+	-	*	+	+	-	+	*	*	*	-	-	-	-
BČ-69	MSC	lpb, gbl, pbl	+	-	-	+	+	-	*	-	-	-	-	-	-	*
BČ-86	GBA	nmb, gbl, lpb	*	-	+	-	*	+	+	-	-	*	-	*	*	-
BČ-91	MSC	lpb, gbl, pbl	+	-	*	+	+	-	+	*	*	*	-	-	*	-
BČ-98	GA	nmb, gbl, pbl	*	-	+	-	-	+	+	-	-	*	+	*	*	-

## EXPLANATIONS:

ROCK TYPE: FBG - Finegrained biotite gneisses; TMG - Two-mica gneisses; AOG - Augen orto gneisses; MSC - micaschists; GA - garnet amphibolites; GBA - Barret biotite amphibolites;

TEXTURES: lpb - lepidoblastic; gbl - granoblastic; nmb - nematoblastic; pbl - porphyroblastic; bpsm - blastopsammitic;

MINERAL COMPOSITION: Q - quartz; Af - alkali feldspar; Pl - plagioclase; Mu - muscovite; Bi - biotite; Ho - hornblende; Gt - garnet; St - staurolite; Ky - kyanite; Ap - apatite; Sph - sphene; Ep - epidote (zoisite); OM - opaque minerals; Tou - tourmaline;

SIGNES: + abundant; \* rare; - absent.

tained ratio was  $0.7042 \pm 6$ . This sample was analysed in Royal Holloway and Bedford New College (RHBNC), the measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio was 0.70409 (EMBEY-ISZETIN *et al.*, 1993).

From cumulative data we estimate that two standard deviations of the mean for  $^{87}\text{Sr}/^{86}\text{Sr}$  is 2.0%. This value was used for purposes of regression analysis. The individual  $^{87}\text{Sr}/^{86}\text{Sr}$  run precision was used for each data point because this uncertainty varied considerably for different analyses. The errors given for age and intercept in Table 2 were estimated from these values, the errors given in brackets were calculated from the scatter of data points on the lines.

#### *K/Ar method*

Measurement of K/Ar ages was performed in the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary. The samples were first crushed to a size required by the mineral separation (0,063–0,315 mm, magnetic separation, heavy liquids and shaking off on a sheet were used for mineral separation) then a part of the sample was selected and pulverized for K determination.

An argon extraction line and a mass spectrometer, both designed and built in ATOMKI, were used for the Ar measurement. The rock was degassed by high frequency induction heating, the usual getter materials (titanium sponge, CuO, SAES getter and cold traps) were used for cleaning Ar. The  $^{38}\text{Ar}$  spike was introduced to the system from a gas-pipette before the degassing was started. The cleaned Ar was directly introduced into the mass spectrometer. The mass spectrometer was a magnetic sector type of 150 mm radius and  $90^\circ$  deflection, it was operated in static mode. Recording and evaluation of Ar spectrum was controlled by a microcomputer.

0.1 g of the pulverized samples were digested in HF with the addition of some sulphuric and perchloric acids. The digested sample was dissolved in 100 ml 0.25 mol/l HCl and after a fivefold dilution 100 ppm Na and 100 ppm Li were added as buffer and internal standard. K concentration was measured with a digitized flame photometer of OE-85 type manufactured in Hungary.

The interlaboratory standards Asia 1/65 and GL-O and atmospheric Ar were used for controlling the measurements. Errors were calculated with estimating 1% error ( $1\sigma$ ) for the isotope ratios and 3% for the potassium concentrations. Ages were calculated with the constants suggested by STEIGER and JÄGER (1977). Details of the instruments, the applied methods and results of calibration have been described elsewhere (BALOGH, 1985; ODIN, 1982).

## DISCUSSION

#### *Rb/Sr ages*

Eight whole rock samples were measured by Rb/Sr method. Six of them were paragneisses, one was an amphibolite (BČ-98) and one was a tourmaline bearing micaschist (BČ-69). The isotopic ratios, Rb and Sr concentration data, model ages, as well as initial ratios and ages calculated from regression lines are presented in Table 2. The samples have basic characters, except the sample BČ-69, so we have calculated the model ages with assumed initial ratio of  $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.703$ , characteristic for basaltic magmas.

As it can be seen in Table 2, the model ages form two groups: 455–511 Ma and 699–841 Ma. Accordingly, the eight samples do not define a single regression line, but

TABLE 2

*Rb/Sr ages on whole rocks samples from the Batočina area*

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr ppm	Rb ppm	$^{87}\text{Sr}/^{86}\text{Sr}$ atomic	Model Age (Ma)	Isochron Age (Ma)	$(^{87}\text{Sr}/^{86}\text{Sr})_i$
BČ-19 paragneiss	0.7072± 7	264.63	60.29	0.6361	467± 85		
BČ-23 paragneiss	0.7059±12	292.48	46.63	0.4451	455±206	488±19(10)	0.7030±6
BČ-46 paragneiss	0.7094± 8	265.31	83.99	0.8840	511± 73	RL-II	
BČ-69 micaschist	0.7406± 9	51.94	105.94	5.7139	486± 21		
BČ-10 paragneiss	0.7188±11	172.85	92.94	1.5028	738± 67		
BČ-47 paragneiss	0.7149± 6	226.97	87.98	1.0830	769± 56	709±51(41)	0.7036±6
BČ-60 paragneiss	0.7162±11	200.50	94.60	1.3184	699± 71	RL-I	
BČ-98 amphibolite	0.7068± 4	313.01	35.50	0.3166	841±112		

two definitely different ones (Fig. 2). The data points lie on the individual lines within the analytical uncertainties. The age calculated from regression line fitted on samples BČ-10, BČ-47, BČ-60 and BČ-98 (RL-I) is  $709 \pm 51(41)$  Ma with an initial ratio of  $0.7036 \pm 6$ , the age defined by the other regression line (RL-II, BČ-19, BČ-23, BČ-46, BČ-69) is  $488 \pm 19(10)$  Ma with an intercept of  $0.7030 \pm 6$ .

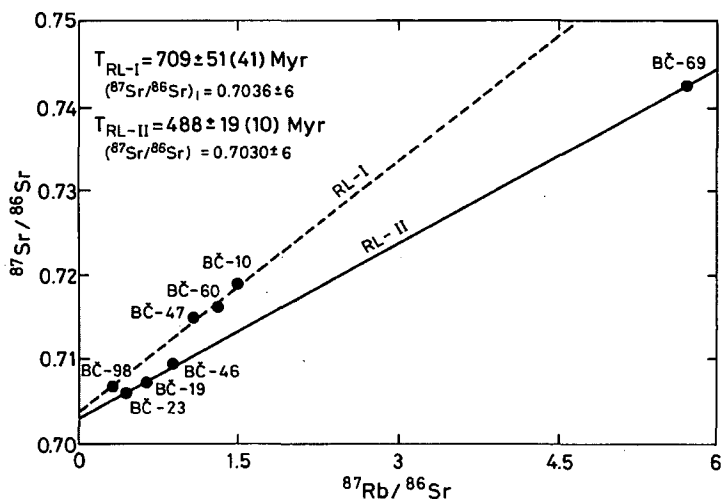


Fig. 2. Rb-Sr regression lines for whole rocks samples from Batočina region.

A regression line may be an isochron dating a geological event or a meaningless mixing line. In this case we have two regression lines, RL-I and RL-II, so the following different possibilities will be considered:

– RL-I and RL-II are isochrons.

RL-I may give the age of sedimentation. This is unlikely, because of the point of BČ-98, which belongs to an amphibolite, and because of the low initial ratio, which is characteristic for basic materials and not for sedimentary rocks. It is more probable, that it gives the time of metamorphism having formed these gneisses. Fluids coming from the upper mantle or the lower crust with high Sr content and low Sr isotope ratio might have resulted in this isotope homogenization.

If RL-I is an isochron, and the rocks forming the two regression lines are not completely independent, RL-II can give neither the age of sedimentation, nor the time of their first metamorphism. It can date a second event, which was intensive enough to form homogeneous isotope composition but did not have any influence on the rocks forming the other isochron. For this we have to suppose again the perfect independence of the two groups. The intercepts of the two lines agree within the analytical uncertainties, and this argues for their relationship. So it is unlikely, that both of the two regression lines are isochrons.

– RL-I is an isochron, RL-II is a mixing line.

In this case the isotope ratios and Rb and/or Sr concentrations of the rocks lying on RL-II regression line were modified by a later event, which was not strong enough to

form a new isotope equilibrium in a large scale, the regression age has no meaning. Sample BC-69 is an argument against it. It has higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, lower Sr and a bit higher Rb content than the others, so its model age is relatively insensitive to the assumed initial ratio giving the most probable time of the metamorphism. Since this sample lies on RL-II, there is an alternative possibility for explaining the results:

– RL-I is a mixing line, RL-II is an isochron.

In this case the regression line RL-II has real meaning giving the time of metamorphism having formed these gneisses. The effect of fluids of low Sr isotope ratio (characteristic for fluids from upper mantle or lower crust) on the old sedimentary rocks might result in complete isotope homogenization in a part of a large area, but not necessarily over the whole area. Where the isotope homogenization wasn't complete, a regression line was produced with a virtual age, so the mixing line will show an older age than the time of metamorphism. If RL-II dates the time of metamorphism, this event might form the RL-I mixing line for a part of the rocks of the area. It can explain the similarity of the two intercepts, and even the fact, that RL-I has a bit higher initial ratio (within the analytical uncertainties). The better fitting of the points on line RL-II also supports this assumption. Sample BC-69 belonging to RL-II is an argument for it, too.

– RL-I and RL-II are both mixing lines.

We have to consider this possibility as well. In this case the regression lines were formed by later events and we can't say anything about the time of metamorphism. But different events can't form two mixing lines with the same intercepts on the same area, they would cause only the scatter of the points.

On the basis of theoretical interpretation of Rb/Sr data we may say: Independently of the meaning of the two regression lines (isochron or mixing line) the values of the intercepts show that the sedimentary rocks had a basic character, but even supposing on extremely basic character for them the fluids effecting on the sediments during the metamorphism would have had  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio not higher than 0.703, therefore they must have originated from the upper mantle or the lower crust. The similarity of their intercepts suggests that the sediments over the studied area had similar Sr content and isotope composition and/or the fluids effecting them were the same. If the fluids were the same, we can exclude the possibilities of having two isochrons or two mixing lines. Among the above mentioned interpretations of the regression lines the third one is the most convincing: RL-II regression line has a real geological meaning, giving  $488 \pm 19(10)$  Ma for the time of metamorphism and RL-I is a meaningless mixing line formed by the same event. At the same time this means, that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of sediments was a little higher than the initial ratios defined by RL-I and RL-II. This moment we have no data contradicting this interpretation.

### *K/Ar ages*

K/Ar ages are summerized in Table 3. Ages range from 965 Ma to 127.3 Ma, clearly, they were overprinted by secondary thermal events. In metamorphic rocks K/Ar ages are usually connected with the time, when the rock cooled below the closure temperature of the dated minerals. The closure age of minerals shows either the time when the area was lifted up, or the time of a reheating event; both can be much younger than the age of metamorphism. On the other hand, in metamorphic rocks at elevated temperatures radiogenic Ar may diffuse out of the minerals and a radiogenic Ar atmosphere may evolve at the mineral boundaries. The radiogenic Ar may diffuse in the minerals, and the K/Ar age of low K minerals may increase considerably this way.



TABLE 3

*K/Ar ages on minerals from the Batočina area*

Sample (K/Ar N°)	Dated mineral	K %	<sup>40</sup> Ar(rad) 10 <sup>-5</sup> ccSTP/g	<sup>40</sup> Ar(rad) <sup>40</sup> Ar(tot)	<sup>36</sup> Ar(atm) 10 <sup>-9</sup> ccSTP/g	Age Ma
<b>Paragneisses</b>						
BČ-X (2451)	muscovite	6.28	3.705	0.82		145.9 ± 5.7
	plagioclase	0.21	0.375	0.22		417 ± 46
			0.360	0.65		402 ± 44
BČ-10 (2768)	muscovite	3.56	2.121	0.89		147.2 ± 5.9
BČ-19 (3039)	white mica	1.63	1.135	0.43		171 ± 7.7
BČ-25 (2450)	mica	4.88	4.802	0.83		237 ± 9.0
BČ-47 (2770)	biotite	5.74	4.034	0.91		172.4 ± 6.9
	muscovite	6.80	4.030	0.93		146.4 ± 5.8
	plagioclase	0.16	0.170	0.61		259 ± 27
BČ-69 (3043)	muscovite	8.25	5.177	0.90		154.7 ± 5.8
BČ-91 (2402)	biotite	6.22	3.649	0.84		145.1 ± 5.5
	muscovite	6.23	4.021	0.89		159.0 ± 6.0
<b>Amphibolites</b>						
BČ-18 (2452)	amphibole	0.19	0.913	0.82	6.8	938 ± 103
			0.946	0.85	5.7	965 ± 106
BČ-58 (2771)	amphibole	0.39	1.306	0.63	26.0	711 ± 43
BČ-86 (2401)	amphibole	0.52	0.595	0.78	5.7	276 ± 11
BČ-98 (2769)	amphibole	0.62	0.795	0.72	10.5	303 ± 17
	amphibole	0.58	0.834	0.61	18.0	342 ± 19
	biotite	4.63	3.061	0.52		162.7 ± 6.6
	plagioclase	0.17	0.500	0.65		639 ± 66
<b>Orthogneisses</b>						
BČ-11 (2403)	K-feldspar	8.43	4.283	0.95		127.3 ± 4.8
BČ-53 (2767)	K-feldspar	5.89	3.282	0.86		138.0 ± 5.5
	feldspar	3.01	2.411	0.85		195.6 ± 7.8

In the Batočina region oldest ages were measured on amphiboles (the mineral with highest closure temperature), and the youngest ages on K-feldspar, the mineral that loses Ar at the lowest temperature. The closure temperature of plagioclase is variable, it depends on the crystalline structure of the dated mineral, but it is always lower than that of muscovite. Several old ages in Table 3 (BČ-X, BČ-47 and BČ-98) prove, that radiogenic Ar was incorporated by plagioclase during metamorphism, therefore plagioclase K/Ar ages are older than the time when cooled below their closure temperature.

The concentration of muscovite, biotite and K-feldspar ages in the 172.4–127.3 Ma interval indicates a thermal event (uplift or reheating of the area) during this period. PURDY and JÄGER (1976) determined  $350 \pm 50^\circ\text{C}$  for the closure temperature of muscovite. HARRISON and McDUGALL (1982) and HARRISON *et al.* (1979) calculated  $130^\circ\text{C}$  for microcline and  $160^\circ\text{C}$  for K-feldspar. The closure temperature of biotite is less certain,  $300^\circ\text{C}$ ,  $300 \pm 50^\circ\text{C}$ ,  $300\text{--}345^\circ\text{C}$  and  $280 \pm 40^\circ\text{C}$  were given for it by BERGER and YORK (1979), PURDY and JÄGER (1976), DALLMEYER (1978) and HARRISON and McDUGALL (1980a). However, the analysis by CLIFF (1985) suggests, that the closure temperature of biotite may be a function of the geological environment and can be higher than that of the muscovite. RODDICK *et al.* (1980) have shown that biotite incorporates excess Ar during metamorphic cooling and this may result anomalously old ages. Due to this uncertainties we shall rely on the muscovites and K-feldspar ages.

Five muscovite sample from the paragneiss (BČ-X, BČ-10, BČ-47, BČ-69 and BČ-91) resulted in an average age of  $150.6 \pm 5.8$  Ma. The error of average age is similar to that of the individual ages, therefore at the present state of our study we disregard the scatter of muscovite ages and accept the average for the time of cooling below  $350 \pm 50^\circ\text{C}$ .

Two K-feldspar sample were dated. Excess Ar is likely present in BČ-53, since the feldspar with lower K content from this rock resulted in a remarkably older age. Therefore the age of BČ-11 ( $127.3 \pm 4.8$  Ma) is accepted as the time when the rock cooled below  $145 \pm 5^\circ\text{C}$ , i. e. the average closure temperature for K-feldspar. The muscovite and K-feldspar ages and closure temperatures result in  $8.8 \pm 3.6^\circ\text{C}/\text{Ma}$  cooling rate and assuming  $30 \pm 5^\circ\text{C}$  geothermal gradient  $0.30 \pm 0.13$  mm/year uplift rate is obtained for time interval from 150.6 Ma to 127.3 Ma.

K/Ar ages on amphiboles from the amphibolites ranges from 965 to 276 Ma. They show that the Upper Jurassic – Lower Cretaceous thermal event didn't reset the K-Ar system of amphiboles. The closure temperature of amphibole is about  $500^\circ\text{C}$  ( $480^\circ\text{C}$  by DALLMEYER (1978);  $400\text{--}540^\circ\text{C}$ , depending on the grain size and cooling rate, by HARRISON and McDUGALL (1980b), this sets an upper limit for the temperature of the Mesozoic thermal event.

The old ages obtained on amphiboles from BČ-18 and BČ-58 may be due to the incorporation of excess Ar or they may reflect the time of older metamorphic events. Since K/Ar age of amphibole cannot be older than the Rb/Sr whole rock age, we tried to demonstrate the presence of excess Ar in BČ-18 according to the method suggested by FECHTIG and KALBITZER (1966). If excess Ar diffused in the amphibole during a metamorphic event, and didn't reach equilibrium, then this Ar will be more easily released during a stepwise degassing experiment. This will result in an Arrhenius diagram as a bias from the straight line, the slope and the activation energy will be less for the lower temperature steps. Fig. 3 shows that this is not so, the points are arranged along a straight line and Ar release is characterized by a single activations energy. This may indicate either that excess Ar is missing from the sample, or that incorporated excess Ar equilibrated in the mineral and it cannot be distinguished from radiogenic

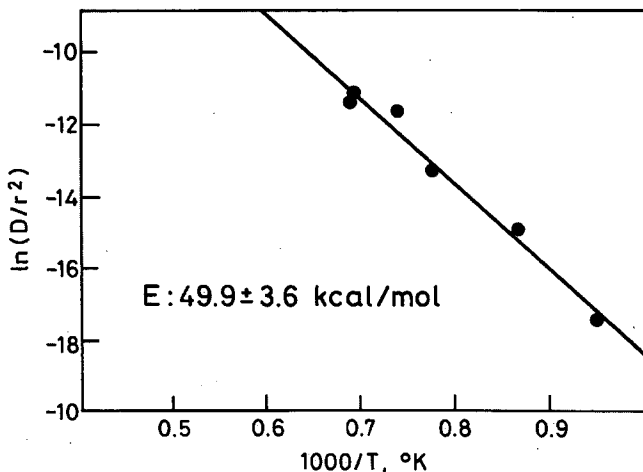


Fig. 3. Arrhenius diagram of Ar release from Amphibole of BČ-18.

Ar. The first possibility is discarded in the light of Rb/Sr ages, the second needs further discussion.

LEE (1993) demonstrated, that Ar release from hornblende in vacuo is not a volume diffusion process, but it is controlled by the internal stress of the mineral, caused by the oxidation of  $Fe^{2+}$  parallel with dehydrogenation. This mechanism of Ar release is termed short circuit diffusion; LEE obtained 45 kcal/mol activation energy for it, it is similar to the value measured by us. Stimulation of Ar release by  $Fe^{2+}$  oxidation explains why Mg-rich amphibole loses Ar in vacuo at higher temperatures than Fe-rich samples do. Ar release from BČ-18 by short circuit diffusion is supported by the lower diffusion parameter at 1461 °C than at 1452 °C (Table 4). However, since radiogenic Ar was observed first at 738 °C, the presence of weakly bound Ar in this sample is very unlikely, i. e. radiogenic and excess Ar cannot be distinguished. This involves, that definite chronologic meaning cannot be assigned to the old ages of samples BČ-18 and BČ-58.

TABLE 4

Stepwise release of  $^{40}Ar(rad)$  from amphibole from BČ-18

Temperature of heating		Released $^{40}Ar(rad)$ ccSTP/g	Diffusion parameter $D/r^2$	Released fraction of $^{40}Ar(rad)$
°C	°K			
680	953			
784	1057	$2.395 \cdot 10^{-7}$	$2.455 \cdot 10^{-8}$	0.0258
885	1158	$6.188 \cdot 10^{-6}$	$3.020 \cdot 10^{-7}$	0.0666
996	1269	$1.175 \cdot 10^{-6}$	$1.648 \cdot 10^{-6}$	0.1264
1087	1360	$2.261 \cdot 10^{-6}$	$8.538 \cdot 10^{-6}$	0.2432
1179	1452	$1.778 \cdot 10^{-6}$	$1.493 \cdot 10^{-5}$	0.1913
1188	1461	$7.792 \cdot 10^{-7}$	$1.075 \cdot 10^{-5}$	0.0838

Amphiboles from BČ-86 and BČ-98 resulted in Hercynian ages. Since the presence of excess Ar, in view of the old plagioclase age, is evident in BČ-98, the obtained amphibole ages may be older than their closure ages. As FOLAND (1979) demonstrated, the concentration and isotopic composition of Ar atmosphere can be rather heterogeneous in a metamorphic terrain within small distances. The potassium content of the dated amphiboles is similar, therefore the application of isochron methods doesn't help to solve the question. If excess Ar was incorporated with uniform isotropic composition (in our case it is not so) than the amount of excess Ar will be proportional to the atmospheric Ar content. In the amphibole samples the Ar(atm) content. vary much more than the ages, and this indicates that in the samples the amount of radiogenic Ar is much more than that of the excess Ar. This is the only argument for a Hercynian event in the studied area.

#### CONCLUSIONS

The metamorphic complex of Batočina (composed of paragneisses, orthogneisses, micaschists and amphibolites) was submitted to metamorphic and thermal events several times.

The Rb/Sr and K/Ar analysis enabled to distinguish the following processes:

1) The sedimentary rocks (unmetamorphosed before?) were metamorphosed above  $500^{\circ}\text{C}$   $488 \pm 19$  Ma ago during the Caledonian orogeny. Fluids from the lower crust or upper mantle equilibrated the Sr isotopic ratios.

2) Hercynian orogeny is indicated by the K/Ar ages of several amphiboles.

3) A thermal event resetting muscovite, biotite and K-feldspar ages ( $> 350 \pm 50^{\circ}\text{C}$ ), but not affecting amphiboles occurred before  $150.6 \pm 5.8$  Ma (Upper Jurassic), and the area cooled below  $145 \pm 15^{\circ}\text{C}$   $127.34.8$  Ma age (Lower Cretaceous). A cooling rate of  $8.8 \pm 3.6^{\circ}\text{C}/\text{my}$  was calculated from the muscovite and K-feldspar ages for the time interval from 150.6 Ma to 127.3 Ma.

Comparing our results with existing U/Pb ages of 270 Ma on zircon by DIMITRIJEVIĆ (1971) from the Bujanovac granite and K/Ar age of 140 Ma on hornblende by MILOVANOVIĆ (1990) from between Tulare and Lebane it can be concluded that in the southern region of the SMM either the intensity of both the Variscan and Upper Jurassic metamorphism was higher than in the Batočina area, or deeper levels of the SMM were exposed in the south.

#### ACKNOWLEDGEMENTS

The authors thank for Prof. S. KARAMATA for his valuable discussions and continuous help. K/Ar dating was supported by the Hungarian National Science Foundation (OTKA) project No. 3002.

#### REFERENCES

- BALOGH, K. (1985): K/Ar dating of Neogene volcanic activity in Hungary: Experimental technique, experiences and methods of chronological studies. *ATOMKI Rep. D/1*, (Debrecen) 277–288.
- BALOGH, K. and CVETKOVIĆ, V. (1992): Prvi podaci o vremenu i intenzitetu metamorfnih faza u području Batočine, Srpsko makedonska masa. *Zapiski SGD, Zbor 24. XII. 1992.*, in print.

- BERGER, G. W. and YORK, D. (1979):  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  dating of multicomponent magnetization in the Arhean Shalley Lake granite, northwestern Ontario. *Can. J. Earth Sci.* **16**, 1933–41.
- BOUE, A. (1836): Resultat de ma première tournée dans le nord et le centre de la Turquie d'Europe faite en partie en compagnie de M. M. de Montalembert et Viquessel. *Bull. de la Soc. geol. de France* **8**, Paris 14–63.
- CLIFF, R. A. (1985): Isotopic dating in metamorphic belt. *J. Geol. Soc. London*, **142**, 97–110.
- CMILJANIĆ, S. and DJORDJEVIĆ, P. (1969): Metaforiti područja Batočine. *Geol. Anali Balk. Poluostrva (Die Metamorphen Gesteine der Umgebung von Batočina)*. *Ann. Geol. Penins. Balk.*, **V. 1**, Beograd, 543–553.
- CVETKOVIĆ, V. (1992): Petrologija metamornih stena severnog dela Srpsko-makedonske mase u području Batočine. Petrology of the metamorphic rocks from the northern parts of the Serbo-macedonian massif in the Batočina area. Magistarski rad. Beograd, 173.
- DALLMEYER, R. D. (1978):  $^{40}\text{Ar}/^{39}\text{Ar}$  incremental-release ages of hornblende and biotite across the Georgia Inner Piedmont: Their bearing on late Paleozoic-early Mesozoic tectonothermal history. *Am. J. Sci.* **278**, 124–149.
- DIMITRIJEVIĆ, B. (1950): Prilog poznavanju petrografskog sastava Juhora i Crnog Vrh. *Zbornik radova SAN*, III, *Geol. inst.* **1**, Beograd 49–69.
- DIMITRIJEVIĆ, M. (1959): Osnovne karakteristike stuba Srpsko-makedonske mase. I Simpozijum SGD, not printed.
- DIMITRIJEVIĆ, M. (1971): Variscijski metamorfizam u aksijalnom delu Balkanskog poluostrva (Hercynian metamorphism in the axial part of the Balkan Peninsula). *Zapiski SGD za 1971. Ext. des Comp. Ren. des Seances de la Soc. Serb. de Geol.* 1971, Beograd, 115–180.
- EMBEY-ISZTIN, A., DOBOSI, G. JAMES, D., DOWNES, H., POULTIDIS, CH. and SCHARBERT, H. G. (1993): A compilation of new major, trace element and isotope geochemical analyses of the young alkali basalts from Pannonian Basin. *Fragmenta Mineralogica et Petrologica (Budapest)* **16**, 5–26.
- FECHTIG, H. and KALBITZER, S. (1966): The diffusion of argon in potassium-bearing solids. In: O. A. SCHAEFFER and J. ZÄRINGER (Eds.), *Potassium Argon Dating*, Springer, New York, N. Y. 68–107.
- FOLAND, K. A. (1979): Limited mobility of argon in a metamorphic terrain. *Geochim. Cosmochim. Acta.* **43**, 793–801.
- HARRISON, T. M., ARMSTRONG, R. L., NAESER, C. W. and HARAKAL, J. E. (1979): Geochronology and thermal history of the Coast Plutonic Complex, near Prince Rupert, British Columbia. *Can. J. Earth Sci.* **16**, 400–410.
- HARRISON, T. M. and MCDUGALL, J. (1980a): Investigation of an intrusive contact northwest Nelson, New Zealand I. Thermal, chronological and isotopic constraints. *Geochim. Cosmochim. Acta.* **44**, 1985–2003.
- HARRISON, T. M. and MCDUGALL, J. (1980b): Investigations of an intrusive contact, northwest Nelson, New Zealand II. Diffusion of radiogenic and excess  $^{40}\text{Ar}$  in hornblende revealed by  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectrum analysis. *Geochim. Cosmochim. Acta.* **44**, 2005–2020.
- HARRISON, T. M. and MCDUGALL, J. (1981): Excess  $^{40}\text{Ar}$  in metamorphic rocks from Broken Hill, New South Wales: implications for  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectra and the thermal history of the region. *Earth Plan. Sci. Lett.* **55**, 123–149.
- HARRISON, T. M. and MCDUGALL (1982): The thermal significance of potassium feldspar K-Ar ages inferred from  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectrum results. *Geochim. Cosmochim. Acta.* **46**, 1811–1820.
- HERDER, F. (1846): Bergmanische reise in Serbie – im auftrag der Fürstlich-Serbischen regierung ausgeführt im jahre 1835. esth, 1946.
- KALENIĆ, M., MARKOVIĆ, B., PANTIĆ, V. and HADŽI-VUKOVIĆ, M. (1975): Gornji proterozoik i stariji paleozoik u profilu Resavski visovi – Batočinska straževica – selo Botunje. *Zapiski SGD za 1974, Ext. des Comp. rend. des Seances de la Soc. Ser. de Geol.*, 1974. Beograd. 35–39.
- LEE, J. K. W. (1993): The argon release mechanism of hornblende in vacuo. *Chem Geol. (Isot. Geosci. Sect.)* **106**, pp. 133–170.
- MILOJKOVIĆ, J. (1892): Izveštaj o rudarskim ispitivanjima po okruzima kragujevačkim. *Godišnjak Rudar. odelj. I. Beograd.* 2–80.
- MILOVANOVIĆ, D. (1990): Petrologija gnajseva Srpsko-makedonske mase u području između Tulara i Lebana (Južna Srbija) (Petrology of gneisses of the lower complex SMM between Tulare and Lebane). XII Kongres geologa Jugoslavije, (12<sup>th</sup> Geol. Congress of Yugoslavia, II, Ohrid. 310–321.
- ODIN, G. S., ADAMS, C. J., ARMSTRONG, R. L., BAGDASARYAN, G. P., BAKSI, A. K., BALOGH, K., BARNES, I. L., BOELRIJK, N. A. I. M., BONDADONNA, F. P., BONHOMME, M. G., CASSIGNOL, C., CHANIN, L., GILLOT, P. Y., GLEDHILL, A., GOVINDARAJU, K., HARAKAL, R., HARRE, W., HEBEDA, E. H., HUNZIKER, J. C., INGAMILLS, C. O., KAWASHITA, K., KISS, E., KREUZER, H., LONG, L. E., MCDUGALL, I., MCDOWELL, F., MEHNERT, H., MONTIGNY, R., PASTEELS, P., RADICATI, F. REX, D. C. RUNDLE, C. C., SAVELLI, C., SONET, J., WELIN, E. and ZIMMERMANN, J. L. (1982): Interlaboratory standards for dating purposes. In ODIN, G. S. (ed): *Numerical Dating in Stratigraphy*. pp. 123–149, Wiley & Sons, Chichester, New York, Brisbane.

- PETROVIĆ, B. and KARAMATA, S. (1970): Metaklistiti – baza gornjeg kompleksa kristalastih škrljaca Srpsko-makedonske mase. (Metaclastites – basis of the upper complex of the Serbo-Macedonian Mass). VII. Kongres geologa SFRJ. (7<sup>th</sup> Geol. Congress of Yugoslavia), II, Zagreb. 303–317.
- PURDY, J. W. and JÄGER, E. (1976): K-Ar ages on rock-forming minerals from the Central Alps. Mem. Inst. Geol. Min. Univ. Padova **30**.
- RODDICK, J. C., CLIFF, R. A. and REX, D. C. (1980): The evolution of excess argon in Alpine biotites – a <sup>40</sup>Ar-<sup>39</sup>Ar analysis. Earth Plan. Sci. Lett. **48**, 185–208.
- STEIGER, R. H. and JÄGER, E. (1977): Subcommission on geochronology : convention on the use of decay constants in geo- and cosmochronology. Earth Planet. Sci. Lett. **36**, 359–362.
- UROŠEVIĆ, S. (1912): Crni Vrh – Studija terena kristalastih škrljaca i granita. Glas Srpske Kraljevske Akademije. LXXXVII, Beograd, 98–135.
- VUJISIĆ, T., KALENIĆ, M. NAVALA, M. and LONČAREVIĆ. Č. (1977): Tumač za OGK Lista “Lapovo” (Geology of the sheet “Lapovo”). Zavod za geol., hidrogeol., geof. i geotehnička istraž., Geol. institut. Beograd. 52.

*Manuscript received 26 May, 1994.*