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An X-ray diffraction investigation of trioctahedral micas

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Biotite crystals, taken from porphyroblastic gneiss, paragneiss and pegmatite, found various locations in Papuk mountain, Croatia, have been studied by X-ray diffraction in order to identify their particular polytypes. Widely used powder X-ray diffraction methods (counter diffractometer, Guinier-de Wolff camera) have not in this case yielded a definite answer. According to the powder diffraction patterns the 1M (3T) polytype of the studied biotite crystals might be preferred. However, the single crystal X-ray diffraction patterns, taken by a Weissenberg goniometer, have showed that the biotites from porphyroblastic gneiss and pegmatite belong to the $2M_1$ polytype, whereas the biotites from paragneiss are mixtures of more complex polytypes.

The determination of the polytypes of micas by X-ray diffraction, besides its complexity, is, ofen, even more troublesome. The platelet-like specimens may have small dimensions or may be bent and, therefore, they are not suitable for taking single-crystal diffraction patterns. According to Smith & Yoder (1956) it is possible from powder diffraction patterns to distinguish simple polytypes 1M, $2M_1$ and 3T for dioctahedral micas, and the polytypes 1M (3T) and $2M_1$ for trioctahedral micas. This simple and relatively fast method for the determination of mica polytypes has been applied by many authors, esepecially in cases of a larger number of specimens. However, during our study of biotites, from various rocks of Papuk mountain, powder diffraction has not vielded satisfactory results. The investigated biotites have been taken from porphyroblastic gneiss, pegmatite and paragneiss and the results obtained are briefly presented in this paper. A chemical analysis of the same biotites has already been made and reported on (Slovenec, 1977).

At first, the interplanar spacing d_{001}/N (where N is the number of mica layers contained in the crystal unit cell) have been accurately determined from the counter diffractometer patterns of highly oriented samples. The method of pairs of the 0l reflections at high Bragg angles ($\Theta > 49^0$) has been applied (Popović, 1971, 1973). Keeping the angular separation of the reflections in the interval from 15^0 to 20^0 (Θ), four pairs of reflections have been chosen for the biotite from porphyroblastic gneiss and paragneiss, and nine pairs of reflections for the biotite from pegmatite. After the angular dependence of the systematic

Table 1. X-ray diffraction data for biotites

Tabela 1. Rendgenografski podaci za prah biotita

biotite from porphyroblastic gneiss			biotite from paragneiss			biotite from pegmatite	
biotit iz porfiroblastičnog gnajsa			biotit iz paragnajsa			biotit iz pegmatita	
d (Å)	I (f)	I (c)	d (Å)	I (f)	I (c)	d(Å)	I (f)
10.062 (b)	8	(100)	10.065 (b)	8	(100)	10.075 (b)	8
5.0310 (b)		(<1)			(<1)		
4.594	2	3	4.595	3	2	4.611	2
						4.475	<1
3.669	<1		3.670	<1			
3.3540 (b)	3	(48)	3.3550 (b)	3	(50)	3.3583 (b)	3
			3.150	<1			
2.660	1		2.659	<1		2.657	<1
2.632	10	10	2.625	10	10	2.627	10
						2.565	<1
2.5155 (b)	<1	(6)	2.5163 (b)	<1	(6)	2.5188 (b)	<1
2.445	6	5	2.441	7	5	2.439	7
2.304	1	1	2.305	1	1	2.307	1
2.275	1	1	2.269	1	2	2.668	1
2.186	3	4	2.180	3	4	2.179	3
2.0124 (b)	<1	(5)	2.0130 (b)	<1	(7)	2.0150 (b)	<1
2.003	1	2	2.000	1	2		
1.918	<1	1	1.918	<1	1		
1.749		1	1.749	1	1	1.745	1
1.679	1	4	1.679	1	3	1.679	1
						1.646	<1
						1.618	<1
1.546	7	5	1.534	6	5	1.540	6
1.529	2	2	1.523	1	3	1.522	2
			1.404	<1			
1.638		2	1.367	<1	1		
1.336	2		1.332	1		1.328	1
1.316	1		1.315	<1			
1.306	1		1.303	<1		1.302	<1
1.277	<1		1.276	<1		1.273	<1

(b) — basal reflections 001

I (f) — the relative intensities as observed in the film powder patterns (estimated visually)

I (c) — the relative intensities as observed in the counter diffractometer powder pattern; the values for the basal reflections, given in brackets, are on a scale different from the scale for other reflections — therefore the two groups of intensities are not directly comparable, this being because of the presence of the preferred orientation

(b) — bazni refleksi 001

I (f) — relativni intenziteti kako su opaženi na filmskoj difrakcijskoj slici (određeni vizuelno)

I (c) — relativni intenziteti kako su opaženi na difrakcijskoj slici dobivenoj s brojačem; vrijednosti za bazne reflekse, dane u zagradama, odnose se na skalu koja je različita od skale za ostale reflekse — prema tome dvije grupe intenziteta nisu direktno usporedive, a to je zbog postojanja preferirane orijentacije errors has been taken into account, the random errors have been minimized by the least-squares refinement. The following values have been obtained:

biotite from porphyroblastic gneiss $d_{001}/N = 10.062 \pm 0.005$ (Å),
biotite from paragneiss $d_{001}/N = 10.065 \pm 0.005$ (Å),
biotite from pegmatite $d_{001}/N = 10.075 \pm 0.002$ (Å).

Having determined the values d_{001}/N the reflections 001 have been used as angular standards in the measurement of other interplanar spacings from the powder diffraction patterns. The powder diffraction patterns of all three biotites studied have been taken by means of the Guinier - de Wolff film camera, and the powder diffraction patterns of the biotites from porphyroblastic gneiss and paragneiss have also been obtained by means of the counter diffractometer. The samples for the counter diffractometer have been prepared by mixing powdered biotite with a small amount of amorphous cement such as that used in dental technique. In this way the effect of the preferred orientation has been significantly reduced. The measured interplanar spacings *d* (Å) are listed in Table 1 (for the biotites from porphyroblastic gneiss and paragneiss the *d* values in Table 1 are the averages of film and counter diffractometer patterns). On the basis of the data in Table 1, it is not possible to determine with certainty the polytypes of the biotites, although these data indicate more closely the polytype 1M (3T) than the polytype $2M_1$. In order to obtain reliable information about the structure of biotites, single crystal diffraction patterns have been taken by means of a Weissenberg goniometer.

For each biotite five approximately isometric platelets have been chosen. The Weissenberg diffraction patterns of all the platelets of the biotites from porphyroblastic gneiss and pegmatite (zero-layer line for the *a* axis, and zero-, first — and second — layer lines for the *b* axis) have indicated that the chosen platelets approach very closely single crystal conditions with the space group *C2/c*, i. e. the polytype $2M_1$. Therefore one can assume that biotites from porphyroblastic gneiss and pegmatite belong to the polytype $2M_1$, or, more precisely, that the polytype $2M_1$ is dominant in these rocks. Out of the five platelets of biotite from paragneiss one specimen has been rather far from single crystal conditions, three specimens have shown a complex polytype, and one has had a higly disordered structure.

The present study indicates that the powder diffraction may be invalid in a determination of the mica polytypes, at least for the biotites from the Papuk mountain. However, one has to state that many authors have found, when using the powder diffraction, the polytype 1M (3T) in all (e. g. Babu, 1969; Sapountzis Elias, 1976) or almost all (e. g. Center & al., 1972; Koval & al., 1975) biotites from rocks of different genesis. On the other hand, by means of single crystal diffraction various polytypes of biotite have been determined even from the same sort of rocks (e. g. Levinson & Heinrich, 1954; Ross & al., 1966). In the present study of the biotites from Papuk mountain the single crystal diffraction patterns have been taken for more than fifty platelets from various rocks and various localities. In most cases the polytype $2M_1$ and more complex polytpes have been found.

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Prilog istraživanju trioktaedrijskih tinjaca rendgenskom difrakcijom

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Određivanje politipnih modifikacija tinjaca pomoću rendgenske difrakcije je pored složenosti samog postupka često otežano i zbog malih dimenzija ili zakrivljenosti listića, koji su stoga nepodesni za snimanje difrakcijskih slika monokristala. Prema Smithu & Yoderu (1956) moguće je prema difrakcijskim slikama praha razlikovati jednostavne politipe 1M, $2M_1$ i 3T kod dioktaedrijskih tinjaca, te 1M (3T) i $2M_1$ kod trioktaedrijskih tinjaca. Taj jednostavni i relativno brzi način određivanja politipa tinjaca primjenjuje niz istraživača, naročito u slučaju većeg broja uzoraka. Međutim, prilikom naših istraživanja biotita iz različitih stijena Papuka difrakcija na prahu nije dala zadovoljavajuće rezultate. Istraživani su biotiti iz po jednog uzorka porfiroblastičnog gnajsa, pegmatita i paragnajsa, a dobiveni rezultati su prikazani u ovom radu. Kemijske analize tih biotita provedene su već ranije (Slovenec, 1977).

Prvi korak bilo je točno određivanje međumrežnih razmaka d_{001}/N (gdje je N broj paketa slojeva sadržanih u jediničnoj ćeliji) pomoću difrakcijskih slika visoko-orijentiranih uzoraka snimljenih pomoću difraktometra s brojačem. Primijenjena je metoda parova refleksa 00l kod visokih difrakcijskih kutova ($\Theta > 49^{\circ}$) (Popović, 1971, 1973). Uz kutni razmak refleksa u intervalu od 15° do 20° (Θ) izdvojena su četiri para refleksa za biotit iz porfiroblastičnog gnajsa i paragnajsa, te devet parova za biotit iz pegmatita. Nakon uzimanja u obzir kutne ovisnosti sistematskih pogrešaka, slučajne pogreške minimizirane su metodom najmanjih kvadrata. Dobivene su slijedeće vrijednosti:

biotit iz porfiroblastičnog gnajsa	$d_{001}/N = 10{,}062 \pm 0{,}005$ (Å),
biotit iz paragnajsa	$d_{001}/N = 10{,}065 \pm 0{,}005$ (Å),
biotit iz pegmatita	$d_{001}/N = 10{,}075 \pm 0{,}002$ (Å).

Odredivši točno vrijednosti d_{001}/N bazni refleksi 001 poslužili su kao unutrašnji standard za mjerenje ostalih međumrežnih razmaka iz difrakcijskih slika praha. Difrakcijske slike praha svih triju biotita snimljene su pomoću kamere po Guinieru i de Wolffu, dok su za biotite iz porfiroblastičnog gnajsa i paragnajsa snimljene i pomoću difraktometra s brojačem. Kod pripreme uzoraka za difraktometar s brojačem prahu biotita primiješana je amorfna supstanca koja se koristi u zubarskoj tehnici (Palaferm), čime je utjecaj preferirane orijentacije u znatnoj mjeri smanjen. Vrijednosti izmjerenih međumrežnih razmaka *d* (Å) navedene su u tabeli 1 (za biotite iz porfiroblastičnog gnajsa i paragnajsa navedene vrijednosti *d* su prosjeci sa filmske i brojačke difrakcijske slike). Na osnovi podataka u tabeli 1 nije moguće sa sigurnošću odrediti vrstu politipa, iako ti podaci više upućuju na politip 1M (3T) nego na $2M_1$. S ciljem da se dobiju pouzdane informacije o strukturi biotita snimljene su difrakcijske slike monokristala pomoću goniometra po Weissenbergu.

Iz svakog uzorka biotita odabrano je po pet približno izometričnih listića ravnih ploha. Difrakcijske slike po Weissenbergu svih listića biotita iz porfiroblastičnog gnajsa i pegmatita (nulta slojna linija oko osi *a*, te nulta, prva i druga slojna linija oko osi *b*) ukazuju da odabrani listići praktično dostižu uvjete monokristala s prostornom grupom *C2/c*, odnosno politipom $2M_1$. Na osnovi toga može se pretpostaviti da biotiti iz porfiroblastičnog gnajsa i pegmatita pripadaju politipu $2M_1$, ili, točnije, da politip $2M_1$ prevladava u oba uzorka stijene. Od pet listića biotita iz paragnajsa jedan je bio polikristalan, tri složeni politipi, a jedan je imao nesređenu strukturu.

Provedena istraživanja su ukazala, barem u slučaju biotita s Papuka, na male mogućnosti difrakcije na kristalnom prahu pri odredbi politipa biotita. Treba međutim primijetiti da je niz autora koristeći difrakciju na prahu kod istraživanja biotita iz genetski različitih stijena utvrdilo kod svih (npr. Babu, 1969; Sapountzis Elias, 1976) ili gotovo kod svih (npr. Center & al., 1972; Koval & al., 1975) modifikaciju 1M (3T). Kod primjene difrakcije na monokristalu utvrđene su međutim različite politipne modifikacije biotita čak i u istoj vrsti stijena (npr. Levinson & Heinrich, 1954; Ross & al., 1966). U okviru istraživanja biotita s Papuka do sada je snimljeno preko pedeset listića biotita iz različitih stijena i s različitih lokaliteta. Većinom su to složeni i $2M_1$ politipi.

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