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KRISTALOGRAFSKO – MINERALOŠKE KARAKTERISTIKE ALUNITA I NATROALUNITA SA VELIKOG BUKOVIKA KOD RAŠKE

Ključne reči: Veliki Bukovik, Raška, alunit, natroalunit, jarozit, rendgenska difrakciona analiza, dimenzije jedinične ćelije, kristalohemijske formule.

Izvod: Alunit i natroalunit sa Velikog Bukovika kod Raške su određeni rendgenskom difrakcionom analizom. Dobijene su sledeće dimenzije jediničnih ćelija i kristalohemijske formule:

alunit:
a_0=6,976(1)Å, c_0=17,295(6)Å, V_0=729,0(3)Å^3, c_0/a_0=2,479
$(K_{0,83}(H_3O)^+_{0,17})_{1,00}Al_{3,00}(S_{0,99}O_4)_2(OH)_6$.

natroalunit:
a_0=6,981(1)Å, c_0=16,884(6)Å, V_0=712,6(3)Å^3, c_0/a_0=2,419
$(Na_{0,50}K_{0,38}(H_3O)^+_{0,12})_{1,00}(Al_{2,95}Fe_{0,13})_{3,08}(S_{0,99}O_4)_2(OH)_6$.

jarozit:
a_0=7,291(4)Å, c_0=17,23(2)Å, V_0=793(1)Å^3, c_0/a_0=2,363.

Kod alunita i natroalunita značajan deo alkalija je zamenjen sa hidronijum jonom, što ukazuje na prelaz ka hidroalunitu i hidronatroalunitu.

Prisustvo hidronijum jona u strukturama ovih minerala takođe ukazuje na nisku temperaturu i nizak pritisak stvaranja, a pri kiselim uslovima i sa visokom sulfatnom aktivnošću.

UVOD

Alunit i minerali alunitske grupe, kao i srodne izostrukturne plumbogumitske i bejdantitske grupe, zbog svojih karakteristika i širokih mogućnosti jonskih izmena, izazivaju pažnju mnogih istraživača u svetu, pa delimično i u našoj zemlji. Vršena su razna ispitivanja u smislu njihovih struktura, hemijskog sastava, čvrstih rastvora, izomorfizma, postanka, upotrebljivosti u industriji, sinteze, itd.

Ovde ćemo spomenuti neka od najvažnijih prethodnih ispitivanja, a koja su u vezi sa našim.

Minerali alunitske grupe imaju opštu formulu $AB_3(SO_4)_2(OH)_6$, gde je $A=K^+$, Na^+, H_3O^+ (po nekim autorima (D a n a i D a n a, 1951; B r o p h y i dr., 1962; itd.) i Pb^{2+}, NH_4^+, Ag^+ i Rb^+), a $B=Al^{3+}$ i Fe^{3+}.

Krajnji članovi su:
alunit $KAl_3(SO_4)_2(OH)_6$
natroalunit $NaAl_3(SO_4)_2(OH)_6$
jarozit $KFe_3(SO_4)_2(OH)_6$

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natrojarozit $NaFe_3(SO_4)_2(OH)_6$

Kristalnu strukturu alunita je prvi odredio H e n d r i c k s (1937) na osnovu heksagonalne jedinične ćelije sa Z=3 i bez centra simetrije na osnovu piroelektričnog testa.

Joni K^+ su u koordinaciji 12 između $6O^{2-}$ i $6(OH)^-$ jona, dok je Al^{3+} (ili Fe^{3+}) u koordinaciji 6 između $2O^{2-}$ i $4(OH)^-$ jona.

Za jarozit je pretpostavio da verovatno ima istu strukturu i tom prilikom je dao dimenzije jediničnih ćelija (u Å):

alunit: a_0=6,97; c_0=17,38; i

jarozit: a_0=7,21; c_0=17,03.

B r o p h y, S c o t t i S n e l l g r o v e (1962) su ispitujući čvrsti rastvor između sintetičkih alunita i jarozita utvrdili da Fe^{3+}-Al^{3+} jonska izmena izaziva mali efekat na c_0-osu (17,21Å za jarozit, do 17,29Å za alunit), ali da prouzrokuje kontinualnu promenu a_0-ose od 7,30Å (jarozit) do 6,98Å (alunit).

Pri tome su odredili i dijagram linearne zavisnosti a_0 i c_0-ose u zavisnosti od sadržaja Al^{3+} i Fe^{3+}.

P a r k e r (1962) je ispitivao izomorfne zamene kod prirodnih i sintetičkih alunita i natroalunita.

Utvrđeno je da se sintetički aluniti razlikuju od prirodnih po nešto manjim dimenzijama jediničnih ćelija kalijumskih predstavnika alunitsko - natroalunitskog sistema. Ove razlike su pripisane delimičnom zamenom $(H_3O)^+$ (0,99Å) umesto K^+ (1,33Å) i Na^+ (0,95Å) jona kod sintetičkih alunita.

Predstavljen je i dijagram zavisnosti a_0 i c_0-ose od relativnog atomskog sadržaja K i Na, odnosno alunitsko - natroalunitske izomorfne serije. Utvrđeno je da izmena K^+ sa Na^+ izaziva veliku promenu u c_0-osi, dok a_0-osa ostaje gotovo nepromenjena.

B r o p h y i S h e r i d a n (1965) su ispitivali čvrsti rastvor između prirodnih i sintetičkih jarozita, natrojarozita i hidronijum jarozita, tj. K^+-Na^+-$(H_3O)^+$ izmenu.

Utvrđeno je da sa porastom sadržaja $(H_3O)^+$ postoji razlika u c_0-osi koja opada od 17,192Å za K-jarozit do 16,980Å za hidronijum jarozit, ali raste od 16,620Å za Na-jarozit do 16,980Å za hidronijum jarozit. Promena u a_0-osi je vrlo mala.

Sa porastom temperature i pritiska, sadržaj $(H_3O)^+$ u strukturi sintetičkih minerala opada. Uklapanje hidronijum jona u jarozitsku strukturu je pokazatelj formiranja pod niskom temperaturom i niskim pritiskom.

S h e r i d a n i R o y s e (1970) su ispitivali alunit iz Wickenburg-a (Arizona) iz hidrotermalno alterisanog riolita.

Dobijena je sledeća kristalohemijska formula:

$(K_{2,54}Na_{0,46})(Al_{10,21}Fe_{0,01})(SO_4)_{5,52}(OH)_{17,22}$

i dimenzije jedinične ćelije:

a_0=6,986(2)Å, c_0=17,332(5)Å i V_0=732,5(4)Å^3,

koje odgovaraju alunitu kod koga je deo K zamenjen sa 15 at.% Na.

Oni su došli do pretpostavke da dijagenetski ili nisko-temperaturni aluniti imaju deo alkalija zamenjen sa delom $(H_3O)^+$ jona, dok kod hidrotermalnih alunita to nije slučaj.

Što se tiče strukture minerala alunitske grupe, W a n g, B r a d l e y i S t e i n f i n k (1965) su potvrdili strukturni model koji je predstavio H e n d r i c k s (1937), ali su naglasili da je ovaj njegov model ustvari centrosimetričan, tj. da je prostorna grupa ustvari $R\bar{3}m$, a ne R3m.

Kasnije su opisane strukture gojazita, vudhausita (K a t o, 1971) i krandalita (B l o u n t, 1974) koje su alunitskog tipa strukture i u kojima su Ca^{2+} i Sr^{2+} katjoni u A položaju, a PO_4^{3-}, PO_3OH^{2-} i SO_4^{2-} su tetraedarske grupe.

Po W i s e-u (1975) postoji čvrsti rastvor između alunitskih, vudhausitskih i krandalitskih mineralnih serija.

M e n c h e t t i i S a b e l l i (1976) su ispitivali kristalnu strukturu alunita i sintetičkog jarozita i došli do vrednosti R-faktora od 0,037 i 0,024.

Takođe su dobijene i sledeće dimenzije jediničnih ćelija (u Å):

alunit a_0=7,020(2); c_0=17,223(8);
natroalunit a_0=7,010(1); c_0=16,748(4);
jarozit a_0=7,315(2); c_0=17,224(6);
natrojarozit a_0=7,327(2); c_0=16,634(5);

M e n c h e t t i i S a b e l l i su potvrdili varijacije u dimenzijama jedinične ćelije pri čemu se c_0-osa menja sa Na-K izmenom, dok se a_0-osa menja sa Al-Fe^{3+} izmenom, a što su prethodno konstatovali B r o p h y i dr. (1962), P a r k e r (1962) i B r o p h y i S h e r i d a n (1965).

Takođe su potvrdili da svi čvrsti rastvori u okviru alunitskih, vudhausitskih i krandalitskih mineralnih serija pripadaju prostornoj grupi R $\bar{3}$m.

T u ć a n (1938) prvi otkriva alunit u našoj zemlji i to na lokalnosti Majdan u Boljetinu kod Kosovske Mitrovice.

I l i ć (1961) proučava alunitisane stene sa iste lokalnosti kao i T u ć a n (1938), a rendgenskom i hemijskom metodom ispituje jedan uzorak, pri čemu dobija sledeće rezultate:

a_0=6,986Å, c_0=17,106Å; i

Al_2O_3	Fe_2O_3	FeO	CaO	Na_2O	K_2O	H_2O^-	H_2O^+	SO_3
33,92	5,13	0,14	0,33	4,05	6,05	0,63	13,19	36,56

i zaključuje da ispitivani uzorak predstavlja smešu alunita (u kome je manji deo kalijuma zamenjen natrijumom) i jarozita.

D a n g i ć i D a n g i ć (1982) su ispitivali jarozit rendgenskom metodom, elektronskim mikroskopom i spektrohemijskom analizom u oksidacionoj zoni sulfidnih ruda u Srebrenici.

Tada su pretpostavili da, zbog prisustva Pb^{2+}, taj ispitivani jarozit predstavlja prelaz ka plumbojarozitu.

D a n g i ć (1984) sintetiše jarozit na 65°C, pri pH=2,45.

V a s i ć (1986) vrši istraživanje alunita u sektoru Biočina kod Raške i tom prilikom je pomoću DTA, TGA i hemijske analize ispitan jedan uzorak (lab. br. E-61007) i određen kao čist alunit (P e š i ć).

Obzirom da DTA i TGA ne mogu da razlikuju alunit od natroalunita (usmena kom. sa D. P e š i ć-em i S. P e t r o v i ć), ovaj isti uzorak je u našem radu detaljnije kristalografsko-mineraloški ispitan, jer je rendgenska difrakciona analiza praha mnogo preciznija u tom pogledu.

PRIMENJENE METODE ISPITIVANJA

Rendgenska ispitivanja su obavljena na "PHILIPS"-ovom automatskom difraktometru za prah, model PW-1710.

Upotrebljena je LFF, Cu anoda (U = 40 kV and I = 30 mA), pri čemu je korišćeno monohromatizovano $K\alpha_1$ zračenje (λ=1,54060Å) i Xe proporcionalni brojač.

Snimljen je opseg ugla 2θ od 4° do 70°, sa korakom 0,02° i zadržavanjem brojača u vremenu od 2,5 sekundi.

Za merenje ugaonih položaja difraktovanih maksimuma i njima pripadajućih intenziteta, primenjen je bazni program PW-1877.

Preciznost difraktometra kontrolisana je pre i posle eksperimenta pomoću Si standarda.

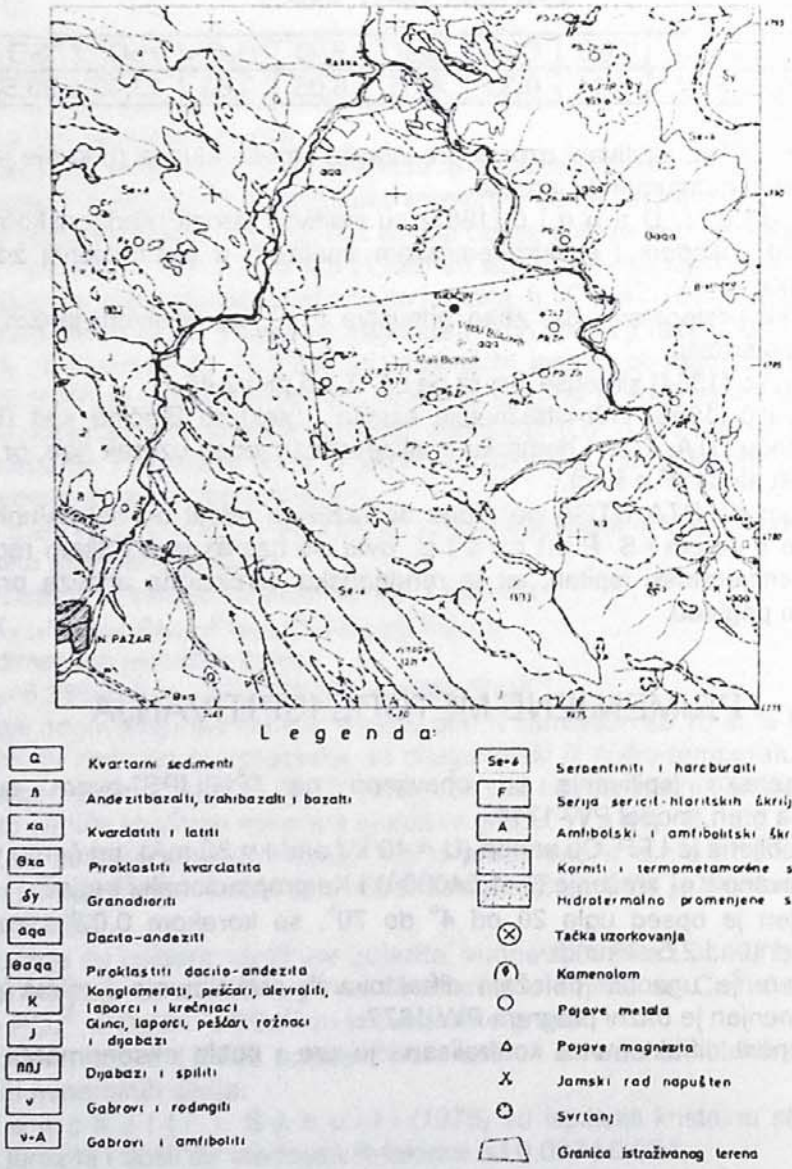
REZULTATI I DISKUSIJA

Koordinate tačke uzorkovanja ispitivanog uzorka su: x=7471,8 i y=4785,5; i ta tačka može se videti na Slici 1.

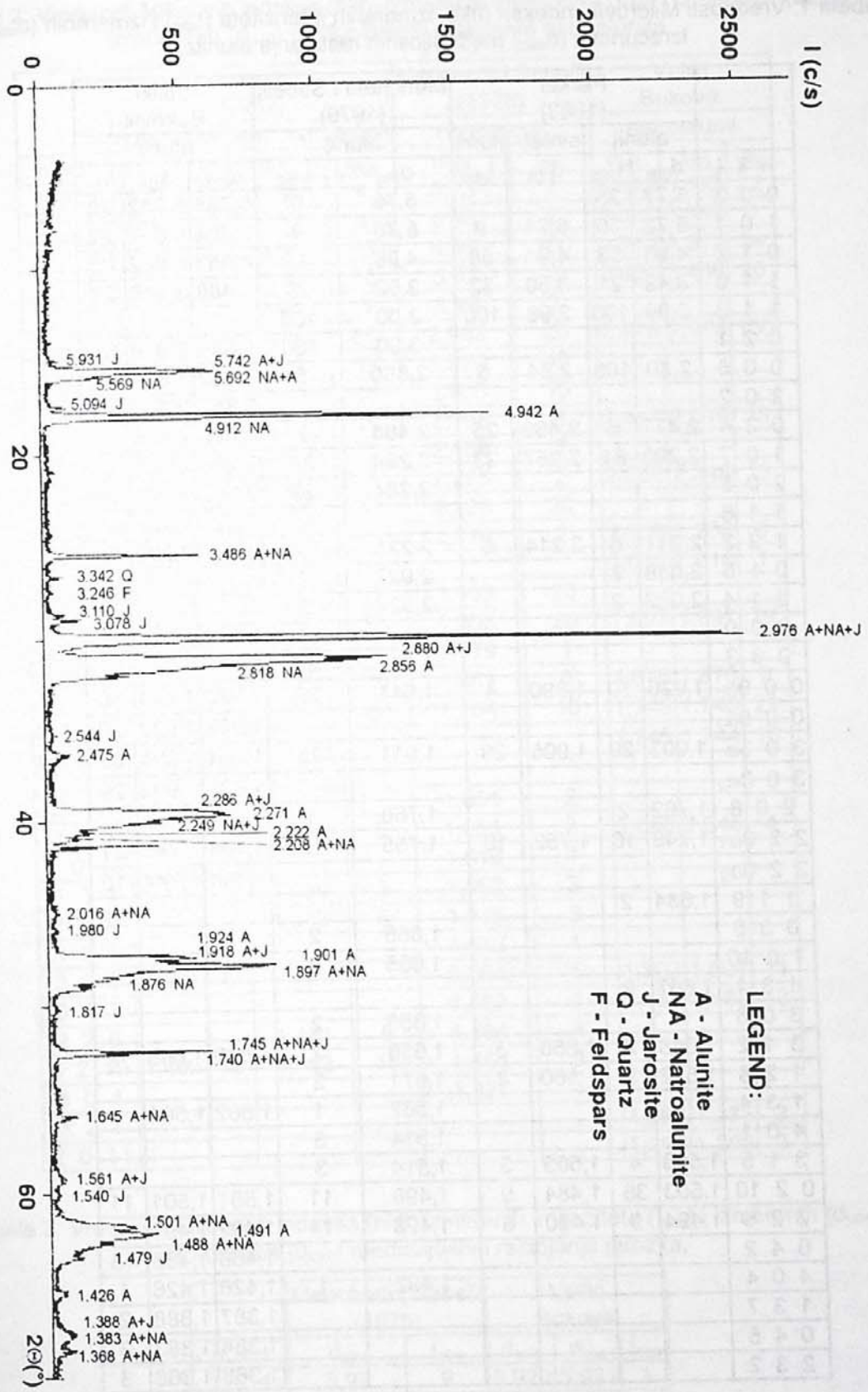
Rendgenski difraktogram praha ispitivanog uzorka sa izmerenim vrednostima međupljosnih rastojanja (d_{obs}) i identifikovanim mineralima prikazan je na Slici 2, gde su: A-alunit, NA-natroalunit, J-jarozit, Q-kvarc i F-feldspati.

Rendgenskom kvalitativnom, semikvantitativnom difrakcionom analizom praha utvrđeno je da se u ispitivanom uzorku sa Velikog Bukovika nalaze sledeće mineralne vrste prema stepenu zastupljenosti: alunit (oko 47%), natroalunit (oko 47%), i neznatno jarozit (oko 4%), kvarc (oko 1,5%) i feldspati (oko 0,5%).

Vrednosti izmerenih (d_{obs}) i izračunatih (d_{calc}) međupljosnih rastojanja, i izmerenih intenziteta (I_{obs}) ispitivanog uzorka sa odgovarajućim iz literature (P a r k e r, 1962; i M e n c h e t t i i S a b e l l i, 1976), kao i odgovarajućim Milerovim indeksima (hkl) alunita, natroalunita i jarozita su prikazane u Tabelama 1, 2 i 3.



Slika 1: Geološka karta šireg područja Raške (List Vrnjci i Novi Pazar, 1:100000).



Slika 2: Indicirani rendgenski difraktogram praha.

Tabela 1: Vrednosti Milerovih indeksa (hkl), izmerenih intenziteta (I_{obs}) i izmerenih (d_{obs}) i izračunatih (d_{calc}) međupljosnih rastojanja alunita.

	Parker (1962)				Menchetti i Sabelli (1976)		Veliki Bukovik		
	alunit		sintet. alunit		alunit		alunit		
h k l	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
0 0 3	5,77	28			5,76	9	5,765	5,742	22
1 0 1	5,72	15	5,71	9	5,76	9	5,704	5,692	22
0 1 2	4,96	53	4,94	56	4,98	45	4,953	4,942	63
1 1 0	3,49	21	3,50	32	3,52	28	3,488	3,486	20
1 1 3	2,99	100	2,98	100	3,00	100			
0 2 1					3,00	100	2,976	2,976	100
0 0 6	2,89	106	2,84	5	2,880	5	2,882	2,880	47
2 0 2							2,852	2,856	43
0 2 4	2,477	6	2,469	25	2,488	2	2,476	2,475	3
1 0 7	2,293	81	2,257	23	2,284	25	2,287	2,286	21
2 0 5					2,284	25	2,275	2,271	26
1 1 6							2,222	2,222	6
1 2 2	2,211	6	2,214	6	2,221	5	2,208	2,208	6
0 1 8	2,038	2			2,027	2			
2 1 4	2,022	2			2,027	2			
3 0 0							2,014	2,016	1
0 3 3					1,911	25			
0 0 9α_1	1,926	70	1,890	4	1,911	25	1,922	1,924	16
0 0 9α_2							1,922	1,922	20
3 0 3α_1	1,903	29	1,905	29	1,911	25	1,901	1,901	32
3 0 3α_2							1,901	1,902	29
2 0 8	1,762	2			1,760	1			
2 2 0α_1	1,746	16	1,752	19	1,755	12	1,744	1,745	21
2 2 0α_2							1,744	1,744	10
1 1 9	1,684	2							
0 3 6					1,655	2			
1 0 10					1,655	2			
1 3 1	1,667	2							
3 0 6					1,655	2			
3 1 2	1,648	2	1,650	3	1,655	2	1,645	1,645	4
1 2 8	1,572	2	1,560	3	1,571	2			
1 3 4					1,567	1	1,562	1,561	1
4 0 1					1,514	3			
3 1 5	1,509	4	1,509	3	1,514	3			
0 2 10	1,503	36	1,484	9	1,498	11	1,501	1,501	11
2 2 6	1,494	9	1,490	6	1,498	11	1,492	1,491	14
0 4 2							1,488	1,488	13
4 0 4					1,432	1	1,426	1,426	1
1 3 7							1,387	1,388	2
0 4 5							1,384	1,383	3
2 3 2							1,368	1,368	3

Tabela 2: Vrednosti Milerovih indeksa (hkl), izmerenih intenziteta (I_{obs}) i izmerenih (d_{obs}) i izračunatih (d_{calc}) međupljosnih rastojanja natroalunita.

	Parker (1962)				Menchetti i Sabelli (1976)		Veliki Bukovik		
	natroalunit		sint. natroalunit		natroalunit		natroalunit		
h k l	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
1 0 1	5,69	12	5,69	4	5,73	2	5,692	5,692	22
0 0 3	5,58	12	5,57	4	5,60	2	5,628	5,569	6
0 1 2	4,90	76	4,91	93	4,93	100	4,915	4,912	34
1 1 0	3,49	24	3,50	30	3,52	15	3,491	3,486	20
1 0 4			3,44	3	3,46	2			
0 2 1	2,97	70	2,98	60	2,992	20	2,976	2,976	100
1 1 3	2,96	100	2,97	100	2,970	40			
0 1 5	2,93	17	2,93	15	2,935	10			
0 0 6	2,79	17	2,79	10	2,796	8	2,814	2,818	19
0 2 4			2,451	3	2,459	3			
2 0 5			2,241	3	2,255	2	2,252	2,249	13
1 0 7	2,221	48	2,220	38	2,228	20			
1 2 2	2,202	12			2,214	2	2,206	2,208	6
3 0 0							2,015	2,016	1
0 3 3					1,903	20			
3 0 3	1,894	29	1,899	35	1,903	20	1,897	1,897	29
0 2 7	1,874	2	1,875	4	1,879	1			
0 0 9	1,857	10	1,856	70	1,861	5	1,876	1,876	9
2 2 $0\alpha_1$	1,744	21	1,749	22	1,754	10	1,745	1,745	21
2 2 $0\alpha_2$							1,745	1,744	10
1 1 9	1,643	5							
2 1 7					1,651	2			
3 1 2			1,648	6	1,651	2	1,645	1,645	4
1 0 10					1,616	1			
1 3 4			1,559	3	1,562	2			
1 2 8			1,543	6	1,546	3			
4 0 1					1,512	1			
3 1 5	1,501	5			1,504	1	1,502	1,501	11
0 4 2					1,493	1	1,488	1,488	13
2 2 6			1,481	6	1,484	4			
0 2 10	1,463	12	1,462	15	1,466	9			
4 0 4					1,427	1			
3 2 1							1,382	1,383	3
2 0 11							1,369	1,368	3

Tabela 3: Vrednosti Milerovih indeksa (hkl), izmerenih intenziteta (I_{obs}) i izmerenih (d_{obs}) i izračunatih (d_{calc}) međupljosnih rastojanja jarozita.

	Menchetti i Sabelli (1976)		Veliki Bukovik		
h k l	d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
1 0 1	5,97	9	5,929	5,931	1
0 0 3	5,75	15	5,742	5,742	22
0 1 2	5,11	77	5,092	5,094	3

1 1 0	3,66	15			
1 0 4	3,56	3			
0 2 1	3,12	47	3,105	3,110	3
1 1 3	3,09	100	3,078	3,078	4
0 1 5	3,03	3			
2 0 2	2,971	4	2,964	2,976	100
0 0 6	2,870	30	2,871	2,880	47
0 2 4	2,553	40	2,546	2,544	1
1 2 2	2,297	33			
1 0 7	2,292	28	2,293	2,286	21
1 1 6			2,256	2,249	13
0 3 3	1,982	30			
3 0 3	1,982	30	1,976	1,980	1
0 2 7	1,943	10			
0 0 9	1,913	10	1,914	1,918	20
2 2 0	1,829	23	1,823	1,818	1
2 0 8	1,781	4			
2 2 3	1,745	4			
2 1 7	1,720	5			
3 1 2	1,720	5			
1 3 $1\alpha_1$			1,742	1,745	21
1 3 $1\alpha_2$			1,742	1,744	10
1 3 4	1,627	4			
1 2 8	1,601	5			
4 0 1	1,575	3			
3 1 5	1,565	4	1,561	1,561	1
0 4 2	1,558	3			
2 2 6	1,542	11	1,539	1,540	1
0 2 10	1,513	19			
4 0 4	1,486	6	1,482	1,479	8
1 3 7			1,427	1,426	1

Preko programa LSUCRI (G a r v e y , 1987) izračunate su u prostornoj grupi R $\bar{3}$m dimenzije jediničnih ćelija alunita, natroalunita i jarozita sa Velikog Bukovika i prikazane skupno u Tabeli 4.

Tabela 4: Izračunate dimenzije jediničnih ćelija alunita, natroalunita i jarozita sa Velikog Bukovika.

	a_0(Å)	c_0(Å)	V_0(Å3)	c_0/a_0
alunit	6,976(1)	17,295(6)	729,0(3)	2,479
natroalunit	6,981(1)	16,884(6)	712,6(3)	2,419
jarozit	7,291(4)	17,23(2)	793(1)	2,363

U uvodu smo istakli da se a_0-osa menja sa sadržajem Al-Fe, dok se c_0-osa menja sa sadržajem Na-K (B r o p h y i dr., 1962; P a r k e r, 1962; B r o p h y i S h e r i d a n, 1965; i M e n c h e t t i i S a b e l l i, 1976).

Iz dijagrama linearne zavisnosti a_0 i c_0-ose od sadržaja Al i Fe^{3+} (odnosno alunitsko-jarozitske komponente) koji su odredili B r o p h y i dr. (1962), a koji je prikazan na Slici 3, može se videti da:

- ispitivani alunit (A) pripada i po a_0 i po c_0 osi alunitu;

- ispitivani natroalunit (NA) po a_0 osi pripada alunitu, dok po c_0 osi ne (što ukazuje na povećan sadržaj Na-komponente); i

- ispitivani jarozit (J) po a_0 i po c_0 osi pripada jarozitskom delu dijagrama.

Iz dijagrama zavisnosti a_0 i c_0-ose od relativnog atomskog sadržaja K i Na (odnosno alunitsko-natroalunitske komponente) koji je odredio P a r k e r (1962) i koji je prikazan na Slici 4, može se videti da:

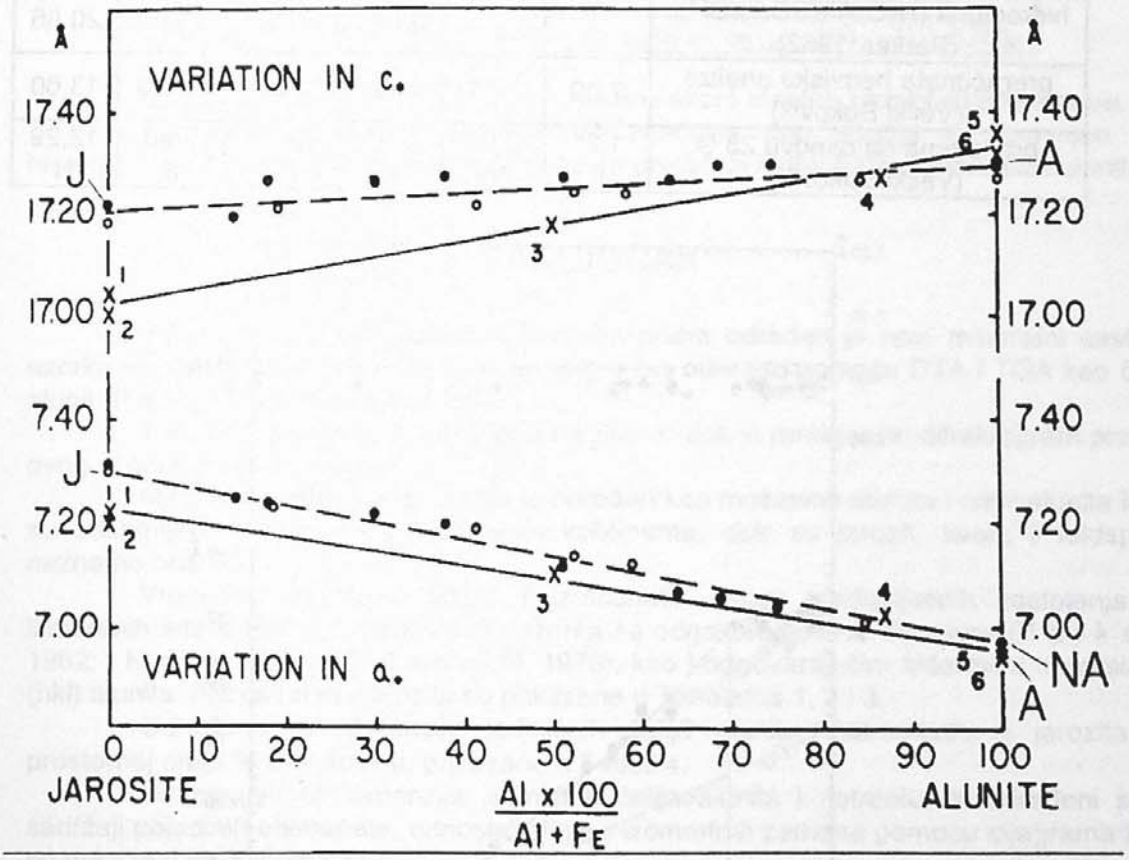
- ispitivani alunit (A) po c_0-osi pripada alunitu sa 82% K : 18% Na;

- ispitivani natroalunit (NA) po c_0-osi pripada natroalunitu sa 62% Na : 38% K.

Hemijska analiza ispitivanog uzorka (B. P o t k o nj a k kod V a s i ć-a, 1986) prikazana je u Tabeli 5.

Tabela 5: Hemijska analiza ispitivanog uzorka.

SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	SO_3	H_2O^-	H_2O^+
1,40	36,51	0,00	1,24	0,21	0,02	0,002	6,86	1,87	38,17	0,23	13,32



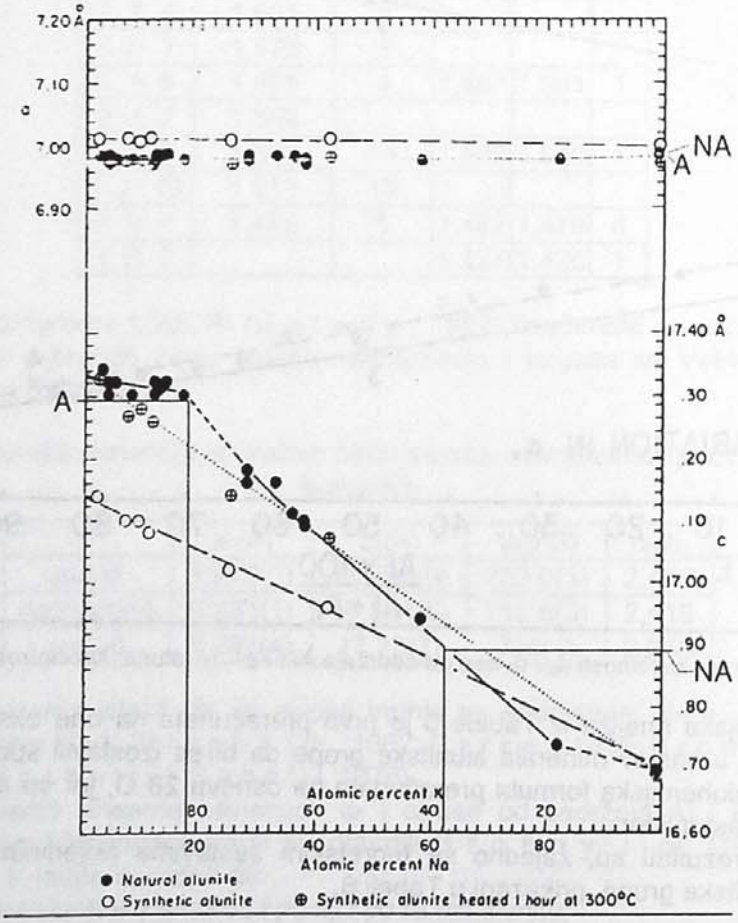
Slika 3: Dijagram zavisnosti a_0 i c_0-ose od sadržaja Al i Fe^{3+} (A-alunit; NA-natroalunit; i J-jarozit).

Hemijska analiza iz Tabele 5 je prvo preračunata na one okside koji teoretski mogu da uđu u sastav minerala alunitske grupe da bi se izostavili sporedni minerali, a zatim je kristalohemijska formula preračunata na osnovu 28 O, jer su alunit i natroalunit podjednako zastupljeni.

Ovi rezultati su, zajedno sa teoretskim sastavima pojedinih krajnjih članova minerala alunitske grupe, prikazani u Tabeli 6.

Tabela 6: Teoretski sastavi krajnjih članova minerala alunitske grupe, preračunata hemijska analiza ispitivanog uzorka i izračunati broj atoma na osnovu 28 O.

	K_2O	Na_2O	Al_2O_3	Fe_2O_3	SO_3	H_2O
alunit $KAl_3(SO_4)_2(OH)_6$ (Brophy i dr., 1962)	11,37		36,92		38,66	13,05
alunit $KAl_3(SO_4)_2(OH)_6$ (Parker, 1962)	11,35		36,96		38,65	13,04
jarozit $KFe_3(SO_4)_2(OH)_6$ (Dana i Dana, 1951)	9,41			47,83	31,97	10,79
jarozit $KFe_3(SO_4)_2(OH)_6$ (Brophy i dr., 1962)	9,40			47,90	31,90	10,80
natrojarozit $NaFe_3(SO_4)_2(OH)_6$ (Dana i Dana, 1951)		6,40		49,42	33,04	11,14
natroalunit $NaAl_3(SO_4)_2(OH)_6$ (Parker, 1962)		7,79	38,44		40,20	13,56
hidroalunit $(H_3O)Al_3(SO_4)_2(OH)_6$ (Parker, 1962)			38,83		40,61	20,56
preračunata hemijska analiza (Veliki Bukovik)	7,00	1,91	37,27	1,27	38,96	13,60
broj atoma na osnovu 28 O (Veliki Bukovik)	1,21 K	0,50 Na	5,95 Al	0,13 Fe	3,96 S	12,29 H



Slika 4: Dijagram zavisnosti a_0 i c_0-ose od relativnog atomskog sadržaja K i Na (A-alunit i NA-natroalunit).

Iz dijagrama zavisnosti a_0 i c_0-ose od relativnog atomskog sadržaja K i Na (Slika 4) videli smo da je kod ispitivanog natroalunita na osnovu c_0-ose (koja iznosi 16,884(6)Å), određen odnos od 62% Na : 38% K.

Ta činjenica je iskorišćena da kod natroalunita (na osnovu tog odnosa) možemo izračunati:

0,38 K i 0,50 Na + 0,12 $(H_3O)^+$,

jer Na^+ i $(H_3O)^+$ imaju bliske vrednosti (0,95 i 0,99Å).

Ostali deo K koji iznosi 0,83 pripada alunitu, a razlika do 1,00 koja iznosi 0,17 pripada hidronijum jonu $(H_3O)^+$.

Sa Slike 4 može se takođe videti da je kod alunita na osnovu c_0-ose (koja iznosi 17,295(6)Å), oko 18% K zamenjeno, a što je u vrlo dobroj saglasnosti sa izračunatom kristalohemijskom formulom, u kojoj je 17% K zamenjeno.

Izračunate kristalohemijske formule alunita i natroalunita su prikazane u Tabeli 7.

Tabela 7: Izračunate kristalohemijske formule alunita i natroalunita sa Velikog Bukovika.

	kristalohemijska formula
alunit	$(K_{0.83}(H_3O)^+_{0.17})_{1.00}Al_{3.00}(S_{0.99}O_4)_2(OH)_6$
natroalunit	$(Na_{0.50}K_{0.38}(H_3O)^+_{0.12})_{1.00}(Al_{2.95}Fe_{0.13})_{3.08}(S_{0.99}O_4)_2(OH)_6$

Iz Tabele 7 može se videti da su dobijene skoro idealne kristalohemijske formule.

Takođe, kod alunita i natroalunita značajan deo alkalija je zamenjen sa hidronijum jonom, što najverovatnije ukazuje na prelaz ka hidroalunitu i hidronatroalunitu.

ZAKLJUČAK

Rendgenskom difrakcionom analizom praha određen je novi mineralni sastav uzorka sa Velikog Bukovika, a koji je prvobitno bio određen pomoću DTA i TGA kao čist alunit (P e š i ć kod V a s i ć-a, 1986).

Tačka uzorkovanja je prikazana na Slici 1, dok je rendgenski difraktogram praha ovog uzorka prikazan na Slici 2.

Mineralni sastav ovog uzorka je određen kao mešavina alunita i natroalunita koji su zastupljeni u otprilike podjednakim količinama, dok su jarozit, kvarc i feldspati neznatno prisutni.

Vrednosti izmerenih (d_{obs}) i izračunatih (d_{calc}) međupljosnih rastojanja, i izmerenih intenziteta (I_{obs}) ispitivanog uzorka sa odgovarajućim iz literature (P a r k e r, 1962; i M e n c h e t t i i S a b e l l i, 1976), kao i odgovarajućim Milerovim indeksima (hkl) alunita, natroalunita i jarozita su prikazane u Tabelama 1, 2 i 3.

Određene su dimenzije jediničnih ćelija alunita, natroalunita i jarozita u prostornoj grupi $R\bar{3}m$, koje su prikazane u Tabeli 4.

Na osnovu tih dimenzija jediničnih ćelija alunita i natroalunita određeni su i sadržaji pojedinih elemenata, odnosno stepen izomorfnih zamena pomoću dijagrama koji su prikazani na Slikama 3 i 4.

To je iskorišćeno za određivanje kristalohemijskih formula alunita i natroalunita, jer ostalih minerala ima toliko malo da pretpostavljamo da nisu mogli mnogo da utiču na preračunatu hemijsku analizu (Tabele 5 i 6).

Da je to tačno, može se videti i iz gotovo idealnih izračunatih kristalohemijskih formula (Tabela 7), dok se mali višak Fe^{3+} jona može pripisati sporednom jarozitu, koji pripada istoj izomorfnoj seriji.

I ovom prilikom je potvrđeno da se a_0-osa menja sa Al^{3+}-Fe^{3+} izmenom, dok se c_0-osa menja sa K^+-Na^+ izmenom.

U prilog tome ide da su:

1. izračunate vrednosti a_0-ose za alunit i natroalunit bliske, dok je za jarozit različita; i

2. izračunate vrednosti c_0-ose za alunit i jarozit su bliske, dok je za natroalunit različita.

Iz kristalohemijskih formula alunita i natroalunita može se videti da je deo alkalija zamenjen sa hidronijum jonom.

Mnogi autori (B r o p h y i dr., 1962; P a r k e r, 1962; B r o p h y i S h e r i d a n, 1965; i S h e r i d a n i R o y s e, 1970) ukazuju da višak vode, tj. ulazak $(H_3O)^+$ jona u strukturu minerala alunitske grupe ukazuje na nisku temperaturu i nizak pritisak stvaranja.

Takođe, po K n i g h t-u (1977) formiranje alunita zahteva kisele uslove i visoku sulfatnu aktivnost.

Obzirom na te podatke, mišljenja smo da su ispitivani alunit i natroalunit (i jarozit) sa Velikog Bukovika najverovatnije postali dijagenetski ili nisko-temperaturno pri kiselim uslovima i sa visokom sulfatnom aktivnošću.

Takođe, pošto je i kod alunita i kod natroalunita značajan deo alkalija zamenjen sa hidronijum jonom, ti podaci najverovatnije ukazuju na prelaz ka hidroalunitu i hidronatroalunitu.

Poređenjem sa literaturnim podacima koji su predstavljeni, mišljenja smo da su dobijeni rezultati u vrlo dobroj saglasnosti sa istim, kao i da predstavljaju doprinos boljem poznavanju mineralogije i geologije u Srbiji, a posebno minerala alunitske grupe.

*

Autori se zahvaljuju Pešić Draganu, dipl. ing. geol. na ustupljenom uzorku, kao i prof. Dr Radovanu Dimitrijeviću i Adamović Branislavu, geol. tehn., na pomoći i dragocenim savetima.

Recenzent: Dr. Danilo Babič, redovan profesor

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CRYSTALLOGRAPHICALLY – MINERALOGICAL CHARACTERISTICS OF ALUNITE AND NATROALUNITE FROM VELIKI BUKOVIK NEAR RAŠKA

by

Pavle Tančić* and Vesna Janežić*

Key words: Veliki Bukovik, Raška, alunite, natroalunite, jarosite, X-ray diffraction analysis, unit cell dimensions, crystallochemical formulas.

Abstract: Alunite and natroalunite from Veliki Bukovik near Raška were determined with the X-ray diffraction analysis. There were obtained following unit cell dimensions and crystallochemical formulas:

alunite:

a_0=6,976(1)Å, c_0=17,295(6)Å, V_0=729,0(3)Å^3, c_0/a_0=2,479

$(K_{0,83}(H_3O)^+_{0,17})_{1,00}Al_{3,00}(S_{0,99}O_4)_2(OH)_6$.

natroalunite:

a_0=6,981(1)Å, c_0=16,884(6)Å, V_0=712,6(3)Å^3, c_0/a_0=2,419

$(Na_{0,50}K_{0,38}(H_3O)^+_{0,12})_{1,00}(Al_{2,95}Fe_{0,13})_{3,08}(S_{0,99}O_4)_2(OH)_6$.

jarosite:

a_0=7,291(4)Å, c_0=17,23(2)Å, V_0=793(1)Å^3, c_0/a_0=2,363.

At alunite and natroalunite considerable part of the alkalies were exchanged with the hydronium ion, which indicates to the transition to hydroalunite and hydronatroalunite.

Presence of the hydronium ion in the structures of these minerals also indicates to the low temperature and low pressure of the formation, at acid conditions and with high sulphate activity.

INTRODUCTION

Alunite and alunite mineral group, and also related isostructural plumbogummite and beudantite groups, because of their characteristics and wide possibilities of ionic exchanges, provoke the attention of many world investigators, and also partially in our Country. There were accomplished variuos investigations by meaning at their structure, chemical compositions, solid solutions, isomorphism, origin, industry applications, synthesis, etc.

Here we will mention some of the most important previous investigations, and which are related to our.

Alunite mineral group has common formula $AB_3(SO_4)_2(OH)_6$, where A=K^+, Na^+, H_3O^+ (by some authors (D a n a & D a n a, 1951; B r o p h y et al., 1962; etc.) and Pb^{2+}, NH_4^+, Ag^+ and Rb^+), and B=Al^{3+} and Fe^{3+}.

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The end members are:

alunite $KAl_3(SO_4)_2(OH)_6$

natroalunite $NaAl_3(SO_4)_2(OH)_6$

jarosite $KFe_3(SO_4)_2(OH)_6$

natrojarosite $NaFe_3(SO_4)_2(OH)_6$

Crystall structure of alunite was first determined by H e n d r i c k s (1937) at basis of the hexagonal unit cell with Z=3 and without the center of the symmetry at basis of the pyroelectric test.

K^+ ions are in coordination 12 between $6O^{2-}$ and $6(OH)^-$ ions, while Al^{3+} (or Fe^{3+}) are in coordination 6 between $2O^{2-}$ and $4(OH)^-$ ions.

For jarosite he presumed that probably has the same structure and at that occasion he gave unit cell dimensions (in Å):

alunite: a_0=6,97; c_0=17,38; and

jarosite: a_0=7,21; c_0=17,03.

B r o p h y, S c o t t and S n e l l g r o v e (1962) during the investigation of the solid solution between synthetic alunites and jarosites established that Fe^{3+}-Al^{3+} ionic exchange induce small effect at c_0-axis (17,21Å for jarosite, to 17,29Å for alunite), but it produces continual variation of the a_0-axis from 7,30Å (jarosite) to 6,98Å (alunite).

Nevertheless, they established diagram of the linear dependence of the a_0 and c_0-axis by Al^{3+} and Fe^{3+} content.

P a r k e r (1962) investigated isomorphous exchangings at natural and synthetic alunites and natroalunites.

It was established that synthetic alunites are different from natural by something smaller unit cell dimensions of the potassium representatives of the alunite - natroalunite system. These differences were assigned to the partly exchangings of $(H_3O)^+$ (0,99Å) instead of K^+ (1,33Å) and Na^+ (0,95Å) ions at synthetic alunites.

It was represented variation diagram of the a_0 and c_0-axis dependence by relative atomic content of the K and Na, respectively to the alunite - natroalunite isomorphous series. It was established that exchanging of K^+ with Na^+ produces large variation at c_0-axis, while a_0-axis remains almost invariable.

B r o p h y and S h e r i d a n (1965) investigated solid solution between natural and synthetic jarosites, natrojarosites and hydronium jarosites, i.e. K^+-Na^+-$(H_3O)^+$ exchanging.

It was established that with increasing of the $(H_3O)^+$ content there is difference at c_0-axis which decrease from 17,192Å for K-jarosite to 16,980Å for hydronium jarosite, but increase from 16,620Å for Na-jarosite to 16,980Å for hydronium jarosite. Variation at a_0-axis is very small.

With increasing of the temperature and pressure, content of the $(H_3O)^+$ in the structure of the synthetic minerals decrease. Fitting of the hydronium ion into the jarosite structure is indicator for the formation under low temperature and low pressure.

S h e r i d a n and R o y s e (1970) investigated alunite from Wickenburg (Arizona) from hydrothermally altered rhyolite.

It was obtained following crystallochemical formula:

$(K_{2,54}Na_{0,46})(Al_{10,21}Fe_{0,01})(SO_4)_{5,52}(OH)_{17,22}$

and unit cell dimensions:

a_0=6,986(2)Å, c_0=17,332(5)Å and V_0=732,5(4)Å^3,

which is adequate to the alunite at which is part of K exchanged with 15 at.% Na.

They presumed that diagenetic or low-temperature alunites has part of the alkalies exchanged with the part of $(H_3O)^+$ ions, while at hydrothermally alunites that isn't occasion.

By considering of the structure of the alunite group minerals, W a n g, B r a d l e y and S t e i n f i n k (1965) confirmed the structure model which was represented by H e n d r i c k s (1937), but they emphasized that his model is actually centro-symmetric, i.e. that space group is actually R $\bar{3}$m, and not R3m.

Later there were described the structures of goyazite, woodhouseite (K a t o, 1971) and crandallite (B l o u n t, 1974) which are of the alunite structure type and at which Ca^{2+} and Sr^{2+} cations are at A position, and PO_4^{3-}, PO_3OH^{2-} and SO_4^{2-} are tetrahedral groups.

By W i s e (1975) there is solid solution between alunite, woodhouseite and crandallite mineral series.

M e n c h e t t i and S a b e l l i (1976) investigated crystall structure of alunite and synthetic jarosite and they obtained values of the R-factor of 0,037 and 0,024.

Also, there were obtained following unit cell dimensions (in Å):

alunite a_0=7,020(2); c_0=17,223(8);

natroalunite a_0=7,010(1); c_0=16,748(4);

jarosite a_0=7,315(2); c_0=17,224(6);

natrojarosite a_0=7,327(2); c_0=16,634(5);

M e n c h e t t i and S a b e l l i confirmed the variations of the unit cell dimensions, nevertheless c_0-axis vary with the Na-K exchanging, while a_0-axis vary with the Al-Fe^{3+} exchanging, which was previously established by B r o p h y et al. (1962), P a r k e r (1962) and B r o p h y and S h e r i d a n (1965).

They also confirmed that all of the solid solutions in the alunite, woodhouseite and crandallite mineral series belong to the space group R $\bar{3}$m.

T u ć a n (1938) for the first time discovered alunite in our Country at the locality Majdan in Boljetin near Kosovska Mitrovica.

I l i ć (1961) researched alunitizated rocks from the same locality as T u ć a n (1938), and with the X-ray and chemical methods he investigated one sample, nevertheless there were obtained following results:

a_0=6,986Å, c_0=17,106Å; and

Al_2O_3	Fe_2O_3	FeO	CaO	Na_2O	K_2O	H_2O^-	H_2O^+	SO_3
33,92	5,13	0,14	0,33	4,05	6,05	0,63	13,19	36,56

and he concluded that investigated sample represents the mixture of alunite (in which small part of potassium was replaced with sodium) and jarosite.

D a n g i ć and D a n g i ć (1982) investigated jarosite with the X-ray method, electron microscopic and spectrochemical analysis in the oxidation zone of the sulphide ores in Srebrenica.

Then they presumed that, because of the presence of the Pb^{2+}, that investigated jarosite represents the transition to the plumbojarosite.

D a n g i ć (1984) synthesized jarosite at 65°C, and at pH=2,45.

V a s i ć (1986) explored alunites in the section Biočin near Raška and at that occasion it was with the DTA, TGA and chemical analysis investigated one sample (lab. N°.E-61007) and determined as pure alunite (P e š i ć).

Considering that DTA and TGA couldn't distinguish alunite from natroalunite (priv. comm. with D. P e š i ć and S. P e t r o v i ć), that same sample was in our paper crystallographicaly-mineralogical investigated in detail, because the X-ray powder diffraction analysis is much more precise at that sense.

APPLIED INVESTIGATION METHODS

The X-ray investigations were performed by automatically diffractometer for powder PHILIPS, model PW-1710.

It was used long-focus (LFF), Cu-anode (U = 40 kV and I = 30 mA), with monochromated $K\alpha_1$ radiation (λ = 1,54060Å) and Xe proportional counter.

Diffraction datas were collected in angle range 2θ from 4° to 70°, with keeping back with 2,5 second on every 0,02°.

For measurement of the angle positions of diffraction maximums and their belonging intensities there was used base program PW-1877.

Precision of the diffractometer was controled before and after the experiment with metallic Si powder.

RESULTS AND DISCUSSION

Coordinates of the sampling point of the investigated sample are: x=7471,8 and y=4785,5; and that point can be seen at Figure 1.

The X-ray powder diffraction pattern of the investigated sample with the observed values of the interplanar spacings (d_{obs}) and identified minerals is represented at Figure 2, where are: A-alunite, NA-natroalunite, J-jarosite, Q-quartz and F-feldspars.

With the X-ray qualitative, semiquantitative powder diffraction analysis it was established that in the investigated sample from Veliki Bukovik there are following mineral species by their quantity: alunite (about 47%), natroalunite (about 47%), and inconsiderable jarosite (about 4%), quartz (about 1,5%) and feldspars (about 0,5%).

Values of the observed (d_{obs}) and calculated (d_{calc}) interplanar spacings, and observed intensities (I_{obs}) of the investigated sample with the responsable from the literature datas (P a r k e r, 1962; and M e n c h e t t i and S a b e l l i, 1976), and also with responsable Miller's indices (hkl) of alunite, natroalunite and jarosite are represented at Tables 1, 2 and 3.

Figure 1: Geological sketch map of the Raška extended area (Sheet Vrnjci and Novi Pazar, 1:100000).

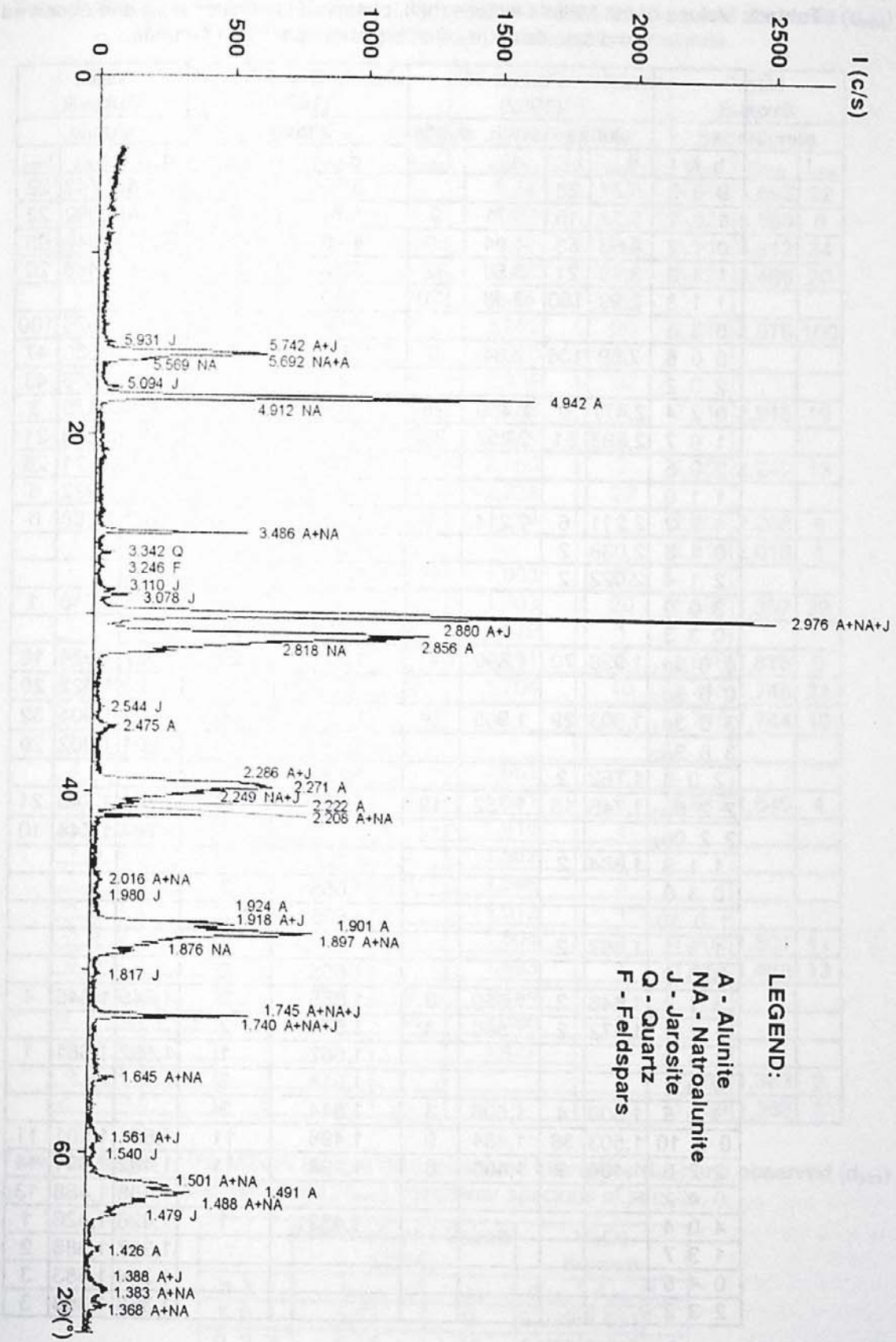

Figure 2: Indiced X-ray powder diffraction pattern.

Table 1: Values of the Miller's indices (hkl), observed intensities (I_{obs}) and observed (d_{obs}) and calculated (d_{calc}) interplanar spacings of alunite.

	Parker (1962)				Menchetti and Sabelli (1976)		Veliki Bukovik		
	alunite		synth. alunite		alunite		alunite		
h k l	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
0 0 3	5,77	28			5,76	9	5,765	5,742	22
1 0 1	5,72	15	5,71	9	5,76	9	5,704	5,692	22
0 1 2	4,96	53	4,94	56	4,98	45	4,953	4,942	63
1 1 0	3,49	21	3,50	32	3,52	28	3,488	3,486	20
1 1 3	2,99	100	2,98	100	3,00	100			
0 2 1					3,00	100	2,976	2,976	100
0 0 6	2,89	106	2,84	5	2,880	5	2,882	2,880	47
2 0 2							2,852	2,856	43
0 2 4	2,477	6	2,469	25	2,488	2	2,476	2,475	3
1 0 7	2,293	81	2,257	23	2,284	25	2,287	2,286	21
2 0 5					2,284	25	2,275	2,271	26
1 1 6							2,222	2,222	6
1 2 2	2,211	6	2,214	6	2,221	5	2,208	2,208	6
0 1 8	2,038	2			2,027	2			
2 1 4	2,022	2			2,027	2			
3 0 0							2,014	2,016	1
0 3 3					1,911	25			
0 0 9α_1	1,926	70	1,890	4	1,911	25	1,922	1,924	16
0 0 9α_2							1,922	1,922	20
3 0 3α_1	1,903	29	1,905	29	1,911	25	1,901	1,901	32
3 0 3α_2							1,901	1,902	29
2 0 8	1,762	2			1,760	1			
2 2 0α_1	1,746	16	1,752	19	1,755	12	1,744	1,745	21
2 2 0α_2							1,744	1,744	10
1 1 9	1,684	2							
0 3 6					1,655	2			
1 0 10					1,655	2			
1 3 1	1,667	2							
3 0 6					1,655	2			
3 1 2	1,648	2	1,650	3	1,655	2	1,645	1,645	4
1 2 8	1,572	2	1,560	3	1,571	2			
1 3 4					1,567	1	1,562	1,561	1
4 0 1					1,514	3			
3 1 5	1,509	4	1,509	3	1,514	3			
0 2 10	1,503	36	1,484	9	1,498	11	1,501	1,501	11
2 2 6	1,494	9	1,490	6	1,498	11	1,492	1,491	14
0 4 2							1,488	1,488	13
4 0 4					1,432	1	1,426	1,426	1
1 3 7							1,387	1,388	2
0 4 5							1,384	1,383	3
2 3 2							1,368	1,368	3

Table 2: Values of the Miller's indices (hkl), observed intensities (I_{obs}) and observed (d_{obs}) and calculated (d_{calc}) interplanar spacings of natroalunite.

	Parker (1962)				Menchetti and Sabelli (1976)		Veliki Bukovik		
	natroalunite		synt. natroalunite		natroalunite		natroalunite		
h k l	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
1 0 1	5,69	12	5,69	4	5,73	2	5,692	5,692	22
0 0 3	5,58	12	5,57	4	5,60	2	5,628	5,569	6
0 1 2	4,90	76	4,91	93	4,93	100	4,915	4,912	34
1 1 0	3,49	24	3,50	30	3,52	15	3,491	3,486	20
1 0 4			3,44	3	3,46	2			
0 2 1	2,97	70	2,98	60	2,992	20	2,976	2,976	100
1 1 3	2,96	100	2,97	100	2,970	40			
0 1 5	2,93	17	2,93	15	2,935	10			
0 0 6	2,79	17	2,79	10	2,796	8	2,814	2,818	19
0 2 4			2,451	3	2,459	3			
2 0 5			2,241	3	2,255	2	2,252	2,249	13
1 0 7	2,221	48	2,220	38	2,228	20			
1 2 2	2,202	12			2,214	2	2,206	2,208	6
3 0 0							2,015	2,016	1
0 3 3					1,903	20			
3 0 3	1,894	29	1,899	35	1,903	20	1,897	1,897	29
0 2 7	1,874	2	1,875	4	1,879	1			
0 0 9	1,857	10	1,856	70	1,861	5	1,876	1,876	9
2 2 $0\alpha_1$	1,744	21	1,749	22	1,754	10	1,745	1,745	21
2 2 $0\alpha_2$							1,745	1,744	10
1 1 9	1,643	5							
2 1 7					1,651	2			
3 1 2			1,648	6	1,651	2	1,645	1,645	4
1 0 10					1,616	1			
1 3 4			1,559	3	1,562	2			
1 2 8			1,543	6	1,546	3			
4 0 1					1,512	1			
3 1 5	1,501	5			1,504	1	1,502	1,501	11
0 4 2					1,493	1	1,488	1,488	13
2 2 6			1,481	6	1,484	4			
0 2 10	1,463	12	1,462	15	1,466	9			
4 0 4					1,427	1			
3 2 1							1,382	1,383	3
2 0 11							1,369	1,368	3

Table 3: Values of the Miller's indices (hkl), observed intensities (I_{obs}) and observed (d_{obs}) and calculated (d_{calc}) interplanar spacings of jarosite.

	Menchetti and Sabelli (1976)		Veliki Bukovik		
h k l	d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
1 0 1	5,97	9	5,929	5,931	1
0 0 3	5,75	15	5,742	5,742	22
0 1 2	5,11	77	5,092	5,094	3

1 1 0	3,66	15			
1 0 4	3,56	3			
0 2 1	3,12	47	3,105	3,110	3
1 1 3	3,09	100	3,078	3,078	4
0 1 5	3,03	3			
2 0 2	2,971	4	2,964	2,976	100
0 0 6	2,870	30	2,871	2,880	47
0 2 4	2,553	40	2,546	2,544	1
1 2 2	2,297	33			
1 0 7	2,292	28	2,293	2,286	21
1 1 6			2,256	2,249	13
0 3 3	1,982	30			
3 0 3	1,982	30	1,976	1,980	1
0 2 7	1,943	10			
0 0 9	1,913	10	1,914	1,918	20
2 2 0	1,829	23	1,823	1,818	1
2 0 8	1,781	4			
2 2 3	1,745	4			
2 1 7	1,720	5			
3 1 2	1,720	5			
1 3 $1\alpha_1$			1,742	1,745	21
1 3 $1\alpha_2$			1,742	1,744	10
1 3 4	1,627	4			
1 2 8	1,601	5			
4 0 1	1,575	3			
3 1 5	1,565	4	1,561	1,561	1
0 4 2	1,558	3			
2 2 6	1,542	11	1,539	1,540	1
0 2 10	1,513	19			
4 0 4	1,486	6	1,482	1,479	8
1 3 7			1,427	1,426	1

Through the LSUCRI programme (G a r v e y, 1987) there were calculated in the space group R $\bar{3}$m unit cell dimensions of alunite, natroalunite and jarosite from Veliki Bukovik and represented together at Table 4.

Table 4: Calculated unit cell dimensions of alunite, natroalunite and jarosite from Veliki Bukovik.

	a_0(Å)	c_0(Å)	V_0(Å^3)	c_0/a_0
alunite	6,976(1)	17,295(6)	729,0(3)	2,479
natroalunite	6,981(1)	16,884(6)	712,6(3)	2,419
jarosite	7,291(4)	17,23(2)	793(1)	2,363

In the introduction we emphasized that a_0-axis vary with the Al-Fe content, while c_0-axis vary with the Na-K content (B r o p h y et al., 1962; P a r k e r, 1962; B r o p h y and S h e r i d a n, 1965; and M e n c h e t t i and S a b e l l i, 1976).

From the diagram of the linear dependence of the a_0 and c_0-axis by Al and Fe^{3+} content (respectively alunite-jarosite component) which was established by B r o p h y et al. (1962), and which was represented at Figure 3, it can be seen that:

- investigated alunite (A) belongs by a_0 and by c_0 axis to alunite;

- investigated natroalunite (NA) by a_0 axis belongs to alunite, while by c_0 axis not (which indicate to the increased content of the Na-component); and

- investigated jarosite (J) by a_0 and by c_0 axis belongs to the jarosite part of the diagram.

From the dependence diagram of the a_0 and c_0-axis by relative atomic content of K and Na (respectively alunite-natroalunite component) which was established by P a r k e r (1962) and which is represented at Figure 4, it can be seen that:

- investigated alunite (A) by c_0 axis belongs to alunite with 82% K : 18% Na;

- investigated natroalunite (NA) by c_0 axis belongs to natroalunite with 62% Na : 38% K.

Chemical analysis of the investigated sample (B. P o t k o nj a k at V a s i ć, 1986) is represented at Table 5.

Table 5: Chemical analysis of the investigated sample.

SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	SO_3	H_2O^-	H_2O^+
1,40	36,51	0,00	1,24	0,21	0,02	0,002	6,86	1,87	38,17	0,23	13,32

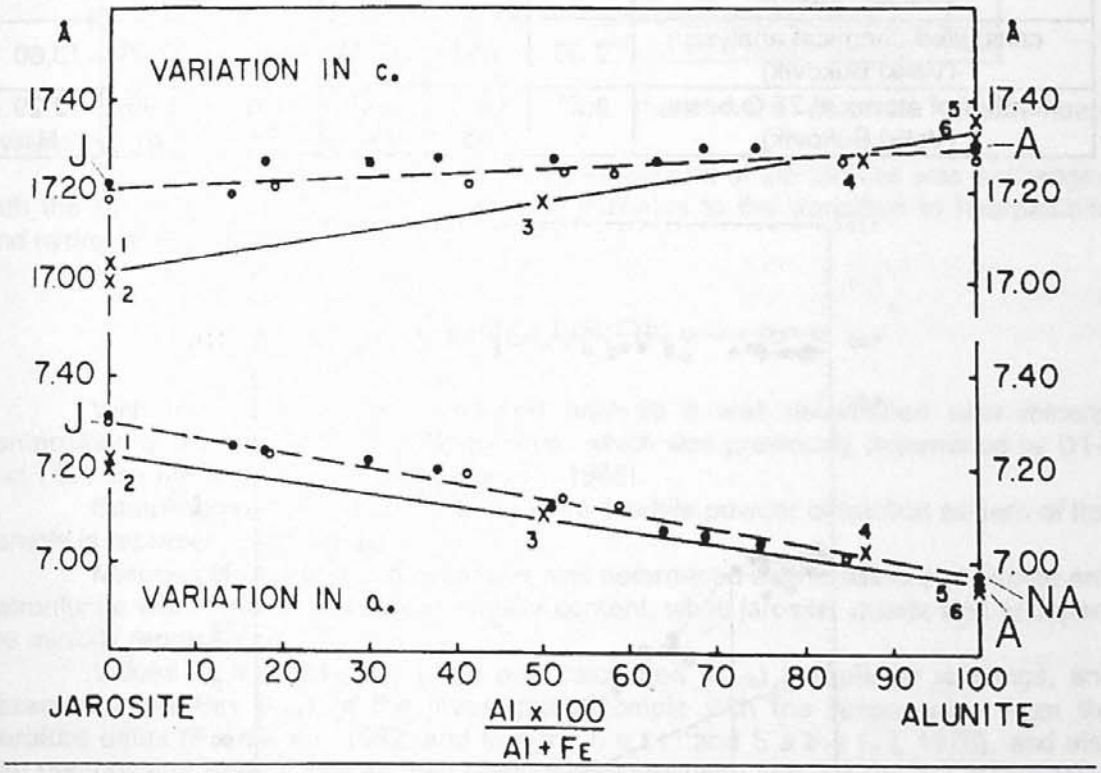

Figure 3: Diagram of the dependence of the a_0 and c_0-axis by Al and Fe^{3+} content (A-alunite; NA-natroalunite; and J-jarosite).

Chemical analysis from Table 5 was first calculated at that oxides which can theoretically enter into the composition of the alunite mineral group to avoid the minor minerals, and then the crystallochemical formula was calculated at basis of the 28 O, because alunite and natroalunite are of equally content.

These results are, together with the theoretically compositions of the individual end members of the alunite group minerals, represented at Table 6.

Table 6: Theoretical compositions of the end members of the alunite group minerals, calculated chemical analysis of the investigated sample and calculated number of atoms at 28 O basis.

	K_2O	Na_2O	Al_2O_3	Fe_2O_3	SO_3	H_2O
alunite $KAl_3(SO_4)_2(OH)_6$ (Brophy et al., 1962)	11,37		36,92		38,66	13,05
alunite $KAl_3(SO_4)_2(OH)_6$ (Parker, 1962)	11,35		36,96		38,65	13,04
jarosite $KFe_3(SO_4)_2(OH)_6$ (Dana & Dana, 1951)	9,41			47,83	31,97	10,79
jarosite $KFe_3(SO_4)_2(OH)_6$ (Brophy et al., 1962)	9,40			47,90	31,90	10,80
natrojarosite $NaFe_3(SO_4)_2(OH)_6$ (Dana & Dana, 1951)		6,40		49,42	33,04	11,14
natroalunite $NaAl_3(SO_4)_2(OH)_6$ (Parker, 1962)		7,79	38,44		40,20	13,56
hydroalunite $(H_3O)Al_3(SO_4)_2(OH)_6$ (Parker, 1962)			38,83		40,61	20,56
calculated chemical analysis (Veliki Bukovik)	7,00	1,91	37,27	1,27	38,96	13,60
number of atoms at 28 O basis (Veliki Bukovik)	1,21 K	0,50 Na	5,95 Al	0,13 Fe	3,96 S	12,29 H

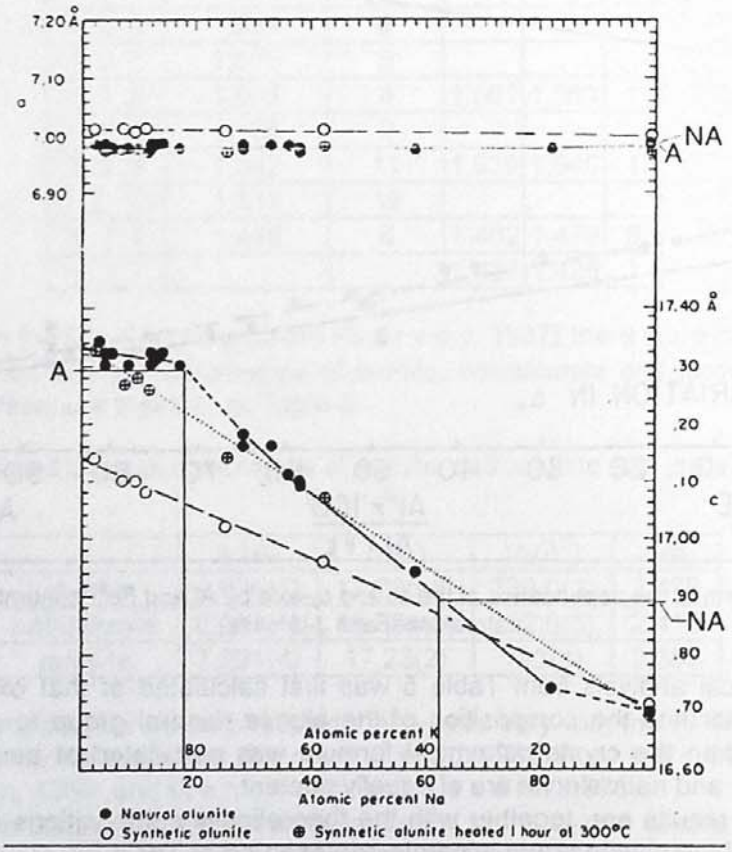

Figure 4: Diagram of the dependence of the a_0 and c_0-axis by relative atomic content of the K and Na (A-alunite and NA-natroalunite).

From the dependence diagram of the a_0 and c_0-axis by relative atomic content of the K and Na (Figure 4) we could seen that in investigated natroalunite at basis of the c_0-axis (which is 16,884(6)Å), it was established ratio of 62% Na : 38% K.

That fact was used that for natroalunite (at basis of that ratio) we could calculate:

0,38 K and 0,50 Na + 0,12 $(H_3O)^+$,

because Na^+ and $(H_3O)^+$ have similar values (0,95 and 0,99Å).

Remained part of the K which is 0,83 belongs to alunite, and the difference to 1,00 which is 0,17 belongs to the hydronium ion $(H_3O)^+$.

From Figure 4 it can be also seen that in alunite at basis of the c_0-axis (which is 17,295(6)Å), there was about 18% K exchanged, and which is in very good agreement with the calculated crystallochemical formula, in which is 17% K exchanged.

Calculated crystallochemical formulas of alunite and natroalunite are represented at Table 7.

Table 7: Calculated crystallochemical formulas of alunite and natroalunite from Veliki Bukovik.

	crystallochemical formula
alunite	$(K_{0.83}(H_3O)^+_{0.17})_{1.00}Al_{3.00}(S_{0.99}O_4)_2(OH)_6$
natroalunite	$(Na_{0.50}K_{0.38}(H_3O)^+_{0.12})_{1.00}(Al_{2.95}Fe_{0.13})_{3.08}(S_{0.99}O_4)_2(OH)_6$

From Table 7 it can be seen that there were obtained almost ideal crystallochemical formulas.

Also, at alunite and natroalunite considerable part of the alkalies was exchanged with the hydronium ion, which most probably indicates to the transition to hydroalunite and hydronatroalunite.

CONCLUSION

With the X-ray powder diffraction analysis it was determined new mineral composition of the sample from Veliki Bukovik, which was previously determined by DTA and TGA as pure alunite (P e š i ć at V a s i ć, 1986).

Sampling point is represented at Figure 1, while powder diffraction pattern of this sample is represented at Figure 2.

Mineral composition of this sample was determined as the mixture of alunite and natroalunite which are of thereabout equally content, while jarosite, quartz and feldspars are minorly represented.

Values of the observed (d_{obs}) and calculated (d_{calc}) interplanar spacings, and observed intensities (I_{obs}) of the investigated sample with the responsable from the literature datas (P a r k e r, 1962; and M e n c h e t t i and S a b e l l i, 1976), and also with responsable Miller's indices (hkl) of alunite, natroalunite and jarosite are represented at Tables 1, 2 and 3.

There were determined unit cell dimensions of alunite, natroalunite and jarosite in space group R $\bar{3}$m, which are represented at Table 4.

At basis of that unit cell dimensions of alunite and natroalunite there were determined the contents of the individual elements, respectively extent of the isomorphous exchangings through diagrams which are represented at Figures 3 and 4.

That was used for the determination of the crystallochemical formulas of alunite and natroalunite, because other minerals are of such minnor content that we suppose that they couldn't much influence to the calculated chemical analysis (Tables 5 and 6).

That is true, it can be seen from the almost ideal calculated crystallochemical formulas (Table 7), while small excess of the Fe^{3+} ions could be assigned to the accessory jarosite, which belongs to the same isomorphous series.

At this occasion it was confirmed that the a_0-axis vary with the Al^{3+}-Fe^{3+} exchanging, while the c_0-axis vary with the K^+-Na^+ exchanging.

Contribution to that is that:

1. calculated values of the a_0-axis for alunite and natroalunite are similar, while for jarosite it is different; and

2. calculated values of the c_0-axis for alunite and jarosite are similar, while for natroalunite it is different.

From the crystallochemical formulas of alunite and natroalunite it can be seen that part of the alkalies was exchanged with the hydronium ion.

Many authors (B r o p h y et al., 1962; P a r k e r, 1962; B r o p h y and S h e r i d a n, 1965; and S h e r i d a n and R o y s e, 1970) signified that excess of water, i.e. entry of the $(H_3O)^+$ ions into the structure of the minerals of the alunite group indicates to the low temperature and low pressure of the origin.

Also, by K n i g h t (1977) alunite formation requires acid conditions and high sulphate activity.

Considering to that datas, our opinion is that investigated alunite and natroalunite (and jarosite) from Veliki Bukovik are most probably of diagenetic or low-temperature formation at acid conditions and with the high sulphate activity.

Also, since in alunite and in natroalunite considerable part of the alkalies exchanged with the hydronium ion, that datas most probably indicates to the transition to hydroalunite and hydronatroalunite.

By comparison with the literature datas which were here represented, our opinion is that obtained results are in very good agreement with that, and also that they represents a contribution to better understanding of the mineralogy and geology in Serbia, and especially of the alunite group minerals.

*

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