Минно-геоложки университет “Св. Иван Рилски”
Годишник, том 47, свитък I, Геология и геофизика, София, 2004, стр. 165-169

OCCURENCE OF ALUNITE AND NATROALUNITE AT VELIKI BUKOVIK (Raska, Serbia)

P. Tancic, V. Janezic
Geoinstitute, Rovinjska 12, 11000 Belgrade, Serbia and Montenegro

ABSTRACT. Alunite and natroalunite from Veliki Bukovik near Raska (Serbia) were determined. 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; $(K_{0.82}(H_3O)^+_{0.19})_{1.01}Al_{3.03}(S_{0.99}O_4)_2(OH)_6$
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; $(Na_{0.51}K_{0.38}(H_3O)^+_{0.12})_{1.01}Al_{3.03}(S_{0.99}O_4)_2(OH)_6$
Presence of the hydronium ion in the structures of these minerals indicate to the low temperature and low pressure of the formation, at acid conditions and with high sulphate activity.

НАХОДИЩЕ НА АЛУНИТ И НАТРОАЛУНИТ ПРИ ВЕЛИКИ БУКОВИК (Раска, Сърбия)

П. Танич, В. Янежич
Геоложки институт, ул. “Ровинарска” 12, 11 000 Белград, Сърбия и Черна гора

РЕЗЮМЕ. Извършени са определения алунита и натроалунита от находище Велики Буковик близо до Раска (Сърбия). Получени са следните стойности за единичните кристали и кристалографски формули:
алунит: 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; $(K_{0.82}(H_3O)^+_{0.19})_{1.01}Al_{3.03}(S_{0.99}O_4)_2(OH)_6$
натроалунит: 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; $(Na_{0.51}K_{0.38}(H_3O)^+_{0.12})_{1.01}Al_{3.03}(S_{0.99}O_4)_2(OH)_6$
Присъствието на водороден йон в структурата на тези минерали е белег, че скалнообразуващите процеси са протекли при ниска температура и ниско налягане, в киселинни условия при висока сулфатна активност.

Introduction

Alunite mineral group because of their characteristics and wide possibilities of ionic substitutions, inspired many researchers to apply various investigations.

There were investigated their structure, chemical compositions, solid solutions, isomorphism, formation, industry applications, synthesis, etc.

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

Crystall structure of alunite was first determined by Hendricks (1937) at basis of the hexagonal unit cell with Z=3 and without the center of the symmetry.

Brophy *et al*. (1962) investigated solid solution between the synthetic alunites and jarosites and established that Al^{3+}-Fe^{3+} ionic exchange induce small effect at the c_0-axis, but it produces continual variation of the a_0-axis.

They constructed the diagram of the linear variation of the a_0 and c_0-axis by the Al^{3+} and Fe^{3+} content.

Parker (1962) investigated isomorphous substitutions at the natural and synthetic alunites and natroalunites. It was established that substitution of K^+ with Na^+ produces large variation at the c_0-axis, while a_0-axis remains almost invariable.

Also, it was represented the diagram of the a_0 and c_0-axis variation by the relative atomic content of the potassium and sodium, respectively to the alunite-natroalunite isomorphous series.

Wang *et al*. (1965) confirmed the structure model which was represented by Hendricks (1937), but they emphasized that it's model is actually centro-symmetric, i.e. that space group is actually $R\bar{3}m$, and not R3m.

Sheridan and Royse (1970) 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.

Menchetti and Sabelli (1976) confirmed the variations of the unit cell dimensions, nevertheless c_0-axis vary with the Na^+-K^+ substitution, while a_0-axis vary with the Al^{3+}-Fe^{3+} substitution, which was previously established by Brophy *et al.* (1962), Parker (1962) and Brophy and Sheridan (1965).

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

Vasic (1986) mostly with the DTA, TGA and chemical analysis explored alunites at Veliki Bukovik (Raska, Serbia).

One of the most representative and pure samples from this locality was chosen and in our paper investigated with the X-ray powder diffraction analysis.

Obtained results from the crystallographical parameters were used for the detemination of the ionic substitutions and for the comparison with the results of the chemical analysis and obtained crystallochemical formulas.

Applied methods

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

It was used long-focus (LFF), Cu-anode (U = 40 kV and I = 30 mA), with monochromated Kα_1 radiation (λ = 1.54060Å) and Xe proportional counter.

Diffraction datas were collected in the 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 the 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 the metallic Si powder.

Results and discussion

X-ray investigations

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 1.

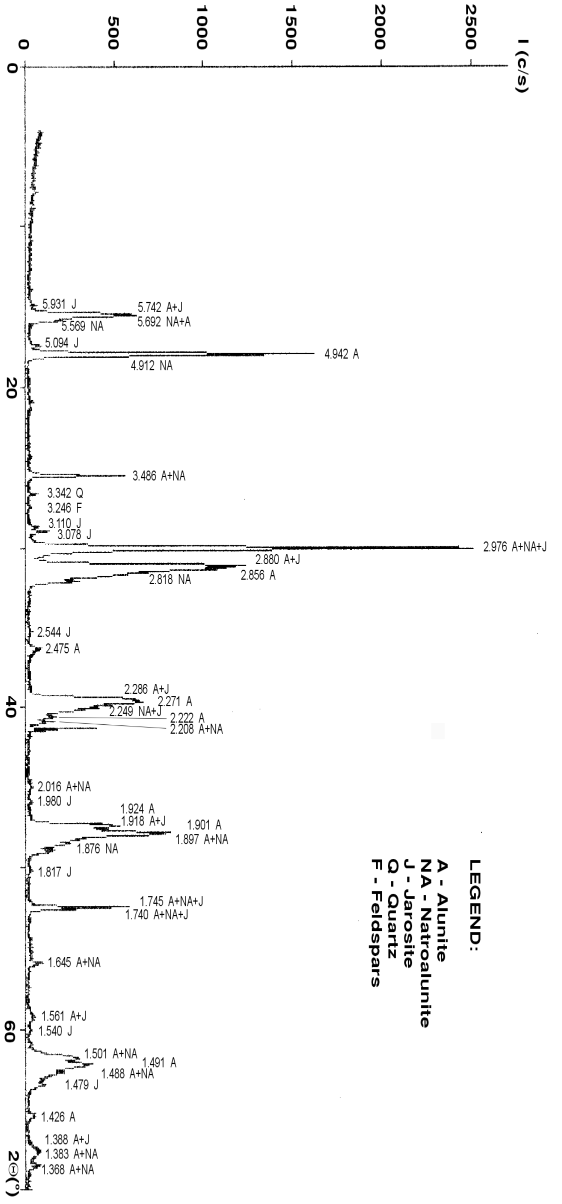

Fig. 1. Indiced X-ray powder diffraction pattern

With the X-ray qualitative, semiquantitative powder diffraction analysis it was established that there are following minerals by their quantity: alunite (≈ 47.5%), natroalunite (≈ 47.5%), and inconsiderable jarosite (≈ 3.5%), quartz (≈ 1%) and feldspars (≈ 0.5%).

Values of the observed (d_{obs}) and calculated (d_{calc}) interplanar spacings, and observed intensities (I_{obs}) of the alunite and natroalunite are represented at Tables 1 and 2.

Table 1.
Values for the interplanar spacings and intensities of alunite

h k l	d_{calc}	d_{obs}	I_{obs}
0 0 3	5.765	5.742	22
1 0 1	5.704	5.692	22
0 1 2	4.953	4.942	63
1 1 0	3.488	3.486	20
0 2 1	2.976	2.976	100
0 0 6	2.882	2.880	47
2 0 2	2.852	2.856	43
0 2 4	2.476	2.475	3
1 0 7	2.287	2.286	21
2 0 5	2.275	2.271	26
1 1 6	2.222	2.222	6
1 2 2	2.208	2.208	6
3 0 0	2.014	2.016	1
0 0 9α_1	1.922	1.924	16
0 0 9α_2	1.922	1.922	20
3 0 3α_1	1.901	1.901	32
3 0 3α_2	1.901	1.902	29
2 2 0α_1	1.744	1.745	21
2 2 0α_2	1.744	1.744	10
3 1 2	1.645	1.645	4
1 3 4	1.562	1.561	1
0 2 10	1.501	1.501	11
2 2 6	1.492	1.491	14
0 4 2	1.488	1.488	13
4 0 4	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 for the interplanar spacings and intensities of natroalunite

h k l	d_{calc}	d_{obs}	I_{obs}
1 0 1	5.692	5.692	22
0 0 3	5.628	5.569	6
0 1 2	4.915	4.912	34
1 1 0	3.491	3.486	20
0 2 1	2.976	2.976	100
0 0 6	2.814	2.818	19
2 0 5	2.252	2.249	13
1 2 2	2.206	2.208	6
3 0 0	2.015	2.016	1
3 0 3	1.897	1.897	29
0 0 9	1.876	1.876	9
2 2 0α_1	1.745	1.745	21
2 2 0α_2	1.745	1.744	10
3 1 2	1.645	1.645	4
3 1 5	1.502	1.501	11
0 4 2	1.488	1.488	13
3 2 1	1.382	1.383	3
2 0 11	1.369	1.368	3

Regardless that jarosite is of the very small ammount, it is also represented it's values of the observed (d_{obs}) and calculated (d_{calc}) interplanar spacings, and observed intensities (I_{obs}) at Table 3.

Table 3.
Values for the interplanar spacings and intensities of jarosite

h k l	d_{calc}	d_{obs}	I_{obs}
1 0 1	5.929	5.931	1
0 0 3	5.742	5.742	22
0 1 2	5.092	5.094	3
0 2 1	3.105	3.110	3
1 1 3	3.078	3.078	4
2 0 2	2.964	2.976	100
0 0 6	2.871	2.880	47
0 2 4	2.546	2.544	1
1 0 7	2.293	2.286	21
1 1 6	2.256	2.249	13
3 0 3	1.976	1.980	1
0 0 9	1.914	1.918	20
2 2 0	1.823	1.818	1
1 3 $1\alpha_1$	1.742	1.745	21
1 3 $1\alpha_2$	1.742	1.744	10
3 1 5	1.561	1.561	1
2 2 6	1.539	1.540	1
4 0 4	1.482	1.479	8
1 3 7	1.427	1.426	1

With the LSUCRI programme (Garvey, 1987) there were calculated in the space group $R\bar{3}m$ unit cell dimensions of alunite, natroalunite and jarosite, and represented at Table 4.

Table 4.
Calculated unit cell dimensions

	alunite	natroalunite	jarosite
a_0(Å)	6.976(1)	6.981(1)	7.291(4)
c_0(Å)	17.295(6)	16.884(6)	17.23(2)
V_0(Å^3)	729.0(3)	712.6(3)	793(1)
c_0/a_0	2.479	2.419	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 (Brophy *et al.,* 1962; Parker, 1962; Menchetti and Sabelli, 1976).

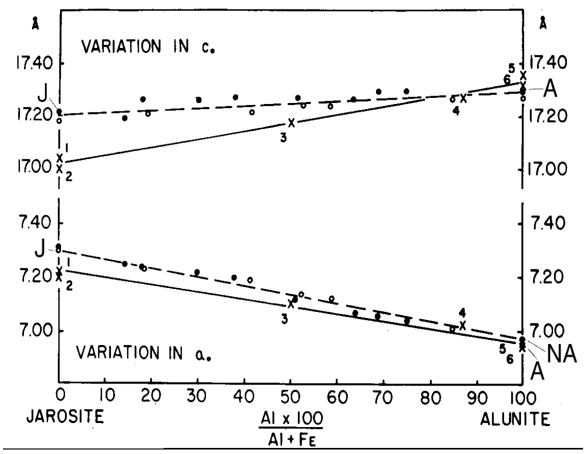

Fig. 2. Variation diagram by Brophy *et al.* (1962)

From the diagram of the linear variation of the a_0 and c_0-axis by the Al and Fe^{3+} content which was established by Brophy *et al.* (1962), and which is here represented at Figure 2, it can be seen that:

1. investigated alunite (A) belongs by the a_0 and c_0-axis to alunite;
2. investigated natroalunite (NA) by the a_0-axis belongs to alunite, while by the c_0-axis not, which indicate to the increased content of the Na-component; and
3. investigated jarosite (J) by the a_0 and c_0-axis belongs to the jarosite part of the diagram.

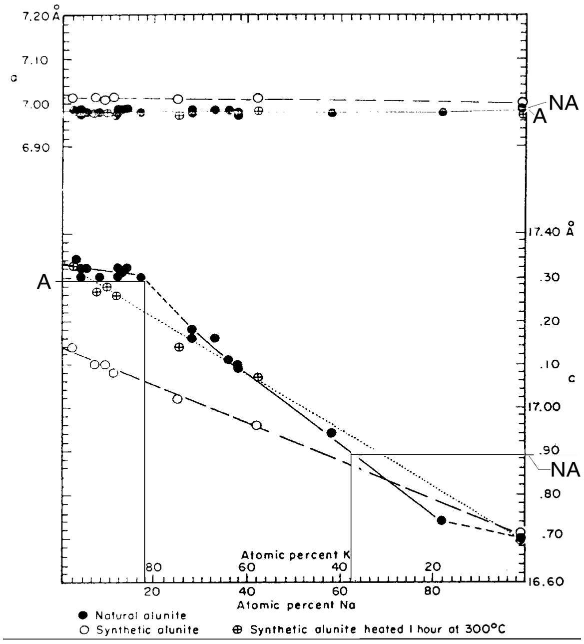

Fig. 3. Variation diagram by Parker (1962)

From the variation diagram of the a_0 and c_0-axis by the relative atomic content of K and Na (respectively alunite-natroalunite component and the curve for the natural alunites) which was established by Parker (1962), and which is here represented at Figure 3, it can be seen that:

1. investigated alunite (A) by the c_0 axis (17.295 Å) belongs to alunite with 82% K : 18% Na;
2. investigated natroalunite (NA) by the c_0 axis (16.884 Å) belongs to natroalunite with 62% Na : 38% K.

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

Contribution to that (Table 4) 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.

Crystallochemical formulas

The end members of the alunite mineral group are:

alunite: $KAl_3(SO_4)_2(OH)_6$,
natroalunite: $NaAl_3(SO_4)_2(OH)_6$,
jarosite: $KFe_3(SO_4)_2(OH)_6$ and
natrojarosite: $NaFe_3(SO_4)_2(OH)_6$.

Results of the chemical investigations and various calculations are represented at Table 5.

Table 5.
Chemical analysis (a), calculated chemical analysis (b and c) and calculated number of ions (d)

	a	b	c	d
SiO_2	1.40			
Al_2O_3	36.51	36.30	38.14	6.06 Al
Fe_2O_3	1.24			
FeO	0.00			
CaO	0.21			
MgO	0.02			
MnO	0.00			
K_2O	6.86	6.62	6.96	1.20 K
Na_2O	1.87	1.87	1.96	0.51 Na
SO_3	38.17	37.34	39.24	3.97 S
H_2O^-	0.23			
H_2O^+	13.32	13.04	13.70	12.31 H
Σ	99.83	95.17	100.00	

Chemical analysis (column a) of the investigated sample (Vasic, 1986) was first calculated to that oxides which can theoretically enter into the composition of alunite and natroalunite (column b), and to avoid the minor minerals (jarosite, quartz and feldspars).

From the Fe_2O_3 content which is 1.24% it can be calculated from the jarosite ideal composition (Brophy *et al.,* 1962) that the jarosite content in the investigated sample is 2.59%.

That data is something smaller, but similar to the content which was obtained by the X-ray semiquantitative analysis (≈ 3.5%).

From the content of jarosite which is 2.59%, it can be calculated that it can be also substracted 0.24% of the K_2O, 0.83% of the SO_3 and 0.28% of the H_2O^+, which also belong to this mineral.

Because it was very difficult to determine of what kind are feldspars (K, Na or Ca), and according to the fact that they are of minor ammounts (≈ 0.5%), there were not applied the substraction from the K_2O and Na_2O contents, but it was substracted the part of the Al_2O_3 which is estimated to 0.21%.

That content for the Al_2O_3 was presumed, because it is similar to the average value for the various kinds of feldspars with that ammount.

After that, contents from the column (b) were calculated to 100%, which is represented at the column (c).

Number of ions were calculated at basis of the 28 O (column d) because alunite and natroalunite are of the equally content (≈ 47.5%), and what was determined from the intensities from the X-ray semiquantitative investigations.

Quantity of alunite and natroalunite (≈ 95%) is in very good agreement with the chemical analysis (b) which is 95.17%.

For the calculations of the crystallochemical formulas, as the start, it can be used the obtained ratio for natroalunite from c_0 axis which is 62% Na : 38% K (Figure 3).

At such manner, for natroalunite there were obtained 0.38 of the potassium and 0.51 of the sodium.

Remained part to the 62% of the sodium should be supplemented with the 0.11 of the hydronium ion, because Na^+ and $(H_3O)^+$ have similar values of the ionic radius which are 0.95 and 0.99Å (Parker, 1962).

Remained part of the potassium which is 0.82 (Table 5, column d) belongs to alunite, and the difference to 1.00 which is 0.18 belongs to the hydronium ion $(H_3O)^+$.

As it can be seen from the Table 5, number of the H^+ ions is 12.31. After the all of the calculations there is remained of 0.02 H^+ which can be equally distributed to alunite and natroalunite.

Finally, the obtained crystallochemical formulas from these calculations for these two minerals are represented at Table 6.

Table 6.
Crystallochemical formulas

alunite	$(K_{0.82}(H_3O)^+_{0.19})_{1.01}Al_{3.03}(S_{0.99}O_4)_2(OH)_6$
natroalunite	$(Na_{0.51}K_{0.38}(H_3O)^+_{0.12})_{1.01}Al_{3.03}(S_{0.99}O_4)_2(OH)_6$

These crystallochemical formulas could be something different, but only at the Na^+ and $(H_3O)^+$ distribution, because of their similar ionic radius, while the potassium contents remained constant.

As it was previously mentioned, at alunite at the basis of the c_0 unit cell dimension it was obtained that it is 18% of the potassium substituted, what is in a very good agreement with the calculated crystallochemical formula in which is 18-19% of potassium substituted.

Also, at natroalunite at the basis of the c_0 unit cell dimension it was obtained that it is 62% of the potassium substituted, what is in a very good agreement with the calculated crystallochemical formula in which is 62-63% of potassium substituted.

The excess of the Al^{3+} ions is very small. It could be probably assigned to the accessory feldspars, but it was almost imposible to determine the accurate part of the Al_2O_3 content which could be substracted from the chemical analysis.

Despite of all of that speculations, obtained crystallochemical formulas are almost ideal.

Many authors (Brophy *et al.,* 1962; Parker, 1962; Sheridan and Royse, 1970) signified that excess of water, i.e. entry of the $(H_3O)^+$ ions into the structure of the minerals of the alunite group indicate to the low temperature and low pressure of the origin.

Also, by Knight (1977) formation of alunite requires acid conditions and high sulphate activity.

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

Conclusion

With the X-ray powder diffraction analysis it was determined the mineral composition of one representative sample from Veliki Bukovik, as the mixture of alunite and natroalunite which are of thereabout equally content, while jarosite, quartz and feldspars are minorly represented.

There were determined the unit cell dimensions of alunite, natroalunite and jarosite in the space group $R\bar{3}m$ (Wang *et al.*, 1965; Menchetti and Sabelli, 1976).

At basis of that unit cell dimensions in alunite and natroalunite there were determined the contents of the individual elements, respectively extent of the isomorphous substitutions from the diagrams from the literature datas (Brophy *et al.,* 1962; Parker, 1962).

That datas were used for the determination of the crystallochemical formulas of alunite and natroalunite.

These obtained crystallochemical formulas are in very good agreement with the compositions which were obtained through the crystallographical parameters.

It was confirmed that the a_0-axis vary with the Al^{3+}-Fe^{3+} substitution (for alunite and natroalunite they are similar, while for jarosite it is different), while the c_0-axis vary with the K^+-Na^+ substitution (for alunite and jarosite they are similar, while for natroalunite it is different).

It is very significant that at alunite and natroalunite part of the alkalies was substituted with the hydronium ion.

That excess of water in the structures of these minerals indicates to the low temperature and low pressure of the origin (Brophy *et al.,* 1962; Parker, 1962; Sheridan and Royse, 1970).

Also, alunite formation requires acid conditions and high sulphate activity (Knight, 1977).

According to that datas, alunite and natroalunite from Veliki Bukovik are most probably of diagenetic or low-temperature formation at acid conditions and with the high sulphate activity.

Acknowledgements
Authors are grateful to Dragan Pesic at the concessioned sample, and to prof. Dr Radovan Dimitrijevic and Branislav Adamovic for their assistance.

References

Brophy G. P., Scott E. S. and Snellgrove R. A., 1962. Sulfate studies II, Solid solution between alunite and jarosite, *Am. Min.,* 47, 112-126.

Garvey R. 1987. Least-square unit cell refinement, Version 86,2, Dept. of Chemistry, North Dakota State University.

Hendricks S. B. 1937. The crystal structure of alunite and jarosites, *Am. Min.,* 22, 733.

Knight J. E. 1977: A thermochemical study of alunite, enargite, luzonite and tennantite deposits, *Econ. Geol.,* 72, 1321-1336.

Menchetti S. and Sabelli C. 1976. Crystal chemistry of the alunite series: crystal structure refinement of alunite and synthetic jarosite, *N. Jb. Miner. Mh.,* 9, 406-417.

Parker R. L. 1962. Isomorphous substitution in natural and synthetic alunite, *Am. Min.,* 47, 127-136.

Sheridan M. F. and Royse C. F. Jr. 1970: Alunite: A new occurrence near Wickenburg, Arizona, *Am. Min.,* 55, 2016-2022.

Vasic I. 1986. Izvestaj o istrazivanju alunita u sektoru Biocina kod Raske, FSD: Rep. SIZ za geol. istr., Beograd. (in Serbian)

Wang R., Bradley W. F. and Steinfink H. 1965. The crystal structure of alunite, *Acta Cryst.,* 18, 249-252.

Препоръчана за публикуване от
катедра "Минералогия и петрография", ГПФ