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PRELIMINARY INVESTIGATIONS INTO THE MINERALOGY AND POTENTIAL USES OF THE STILBITE RICH TUFFS FROM KRATOVO–ZLETOVO VOLCANIC AREA, REPUBLIC OF MACEDONIA

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Abstract

This paper presents preliminary results of investigation of the stilbite ($NaCa_2Al_5Si_{13}O_{36}$ – $14H_2O$) rich tuffs from Rajcani and Kriva Krusa. Investigation tuffs are situated in the south part of the Kratovo–Zletovo volcanic district and they are a part of this big volcanic complex. No presence of zeolites in these tuffs is determined in all previous publications.

In our investigation we found out that stilbite, about 57%, is presented in Rajcani deposit while in Kriva Krusa stilbite is presented by 27%.

Cation exchange capacity (CEC) and ammonium exchange capacity (AEC) values for samples from Rajcani deposit are in the range of 69–82 meq/100 g for CECs and 71–87 meq/100 g for AECs. Kriva Krusa deposits are in the range of 94–102 meq/100 g for CECs and 109–114 meq/100 g for AECs.

All the values show that these tuffs could be very effective in a wide range of applications such as waste water ammonium removal, in animal nutritions, fertilizers, fish farming, additives to cement and others.

The preliminary results of this study warrant further characterization, because these zeolitic tuffs have not received an overall and systematic study of their physical and chemical properties, necessary for the exploitation and utilization.

Key words: zeolite, tuff, stilbite

Introduction. The zeolite history began in 1756 with the discovery of stilbite by Cronstedt, a Swedish mineralogist. According to [1], zeolites are formed in various conditions and geological systems. This is also supported by Ljima [2], who reported that zeolites were formed in various sediments or rocks in varying physical and chemical environment. Genetic classification of the occurrence was attempted by some authors in [3–7].

Tuffs, subject of this research, are located in the volcanic sediments area upon the contact between Vardar zone and Serbo Macedonian massif. From geological aspect the investigation deposits are situated in the south part of the Kratovo–Zletovo volcanic area and are a part of these big volcanic complexes (Fig. 1).

Petrological characteristics of the rocks of Kratovo–Zletovska volcanic area and its individual locality is published in some previous materials [8–10]. A classification of the individual types of the volcanic rocks of this volcanic complex was carried out mainly on the basis of the mineral composition. Volcanic rocks of this volcanic area have mainly intermediate character. They are the product of granodiorite tonalite to kvarcmonconite magma resulting in volcanic rocks whose differential trend ranges from intermediate to basic equivalents in the final stages of the volcanic activity. The presence of zeolites in tuffs in all previous publications is not still determined [11, 12].

Materials and methods. Four samples for examination were taken from Rajcani deposit on the principle of vertical furrow through all the following formations: silificated tuffs, kaolinisated tuffs, andesite tuffs and clay layer.

Silicificated tuffs are Pliocene volcanic rocks covered with intense silification. Average thickness of 3.5 m spread at the area of 70 000 m^2.

Kaolinisated tuffs are situated under silicificated tuffs. At the average they are 3 m thick and spread at an area of 40 000 m^2.

Andesite tuffs are gray-white, yellow and of pink colour. They are kaolinisated, alunitisated and limonitisated.

Clay layer vary from gray-white to greenish colour, found at a depth of 7–10 m.

Zeolitization is present in all formation, but it is most intense in the kaolinisated tuffs.

Four samples for testing on the same principle were taken from Kriva Krusa deposite. Unlikely Rajcani andesite, tuffs are not found in Kriva Krusa.

Zeolitization is also present in all formations, but is most intense in the kaolinisated tuffs.

Optical and chemical analyses were carried out at the Faculty of Natural and Technical Science, Stip.

Major and trace elements were determined by an ICP–AES method. Dissolution of the sample was made by procedures described in [13, 14]. Results of the chemical analyses and cation exchange capacity (CEC) and ammonium exchange capacity (AEC) exchangeable cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) available for exchange in zeolite samples are given in Table 1. The units are units milliequivalents per 1 g zeolite meq/g [15].

Diffractometer PHILIPS Tip PW 1051 in the region $2\theta = 5°, 60°$ was used for X-ray investigation to determine the mineral composition. Copper radiation was used CuK $\alpha = 1.54178$ Å, the voltage of the generator "NORELCO" was

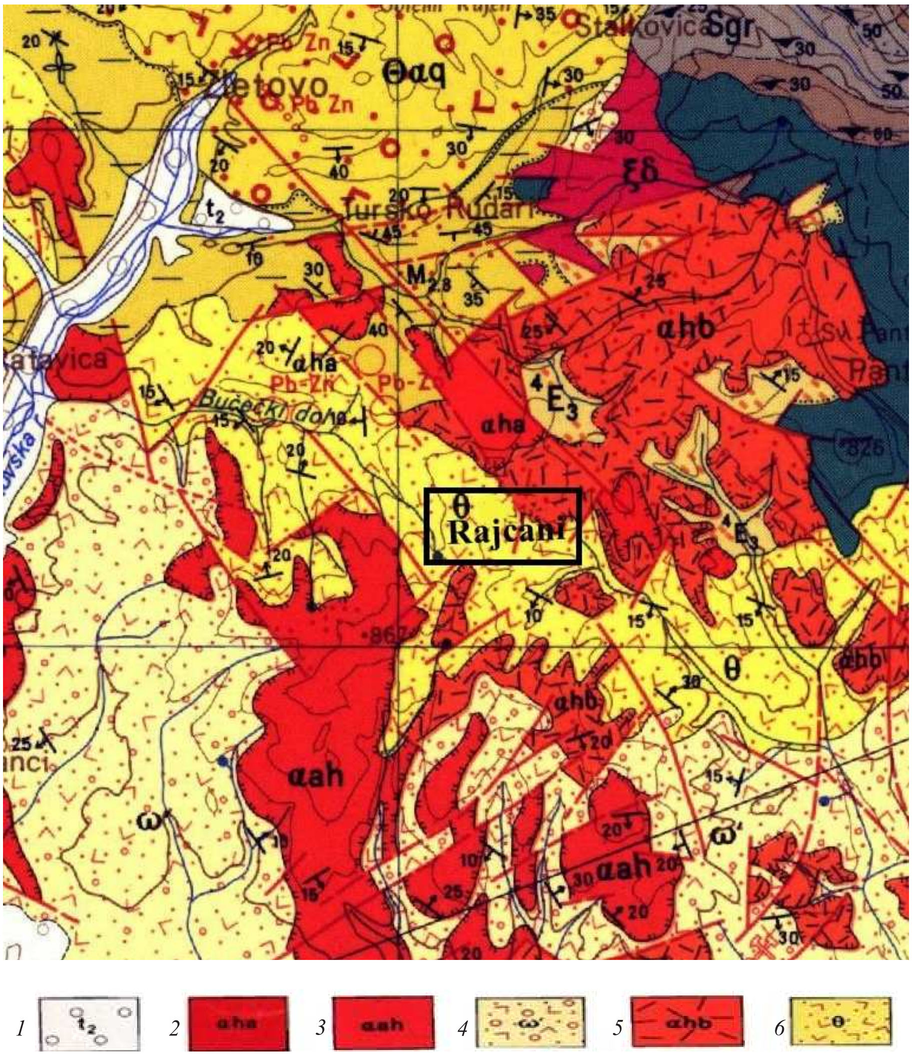

Fig. 1. Geological map of Rajcani 1:100 000: *1.* Higher river terrace; *2.* Hornblende, augite andesite; *3.* Augite, hornblende andesite; *4.* Andesitic breccias; *5.* Hornblende, augite, biotite andesite; *6.* Andesitic tuff

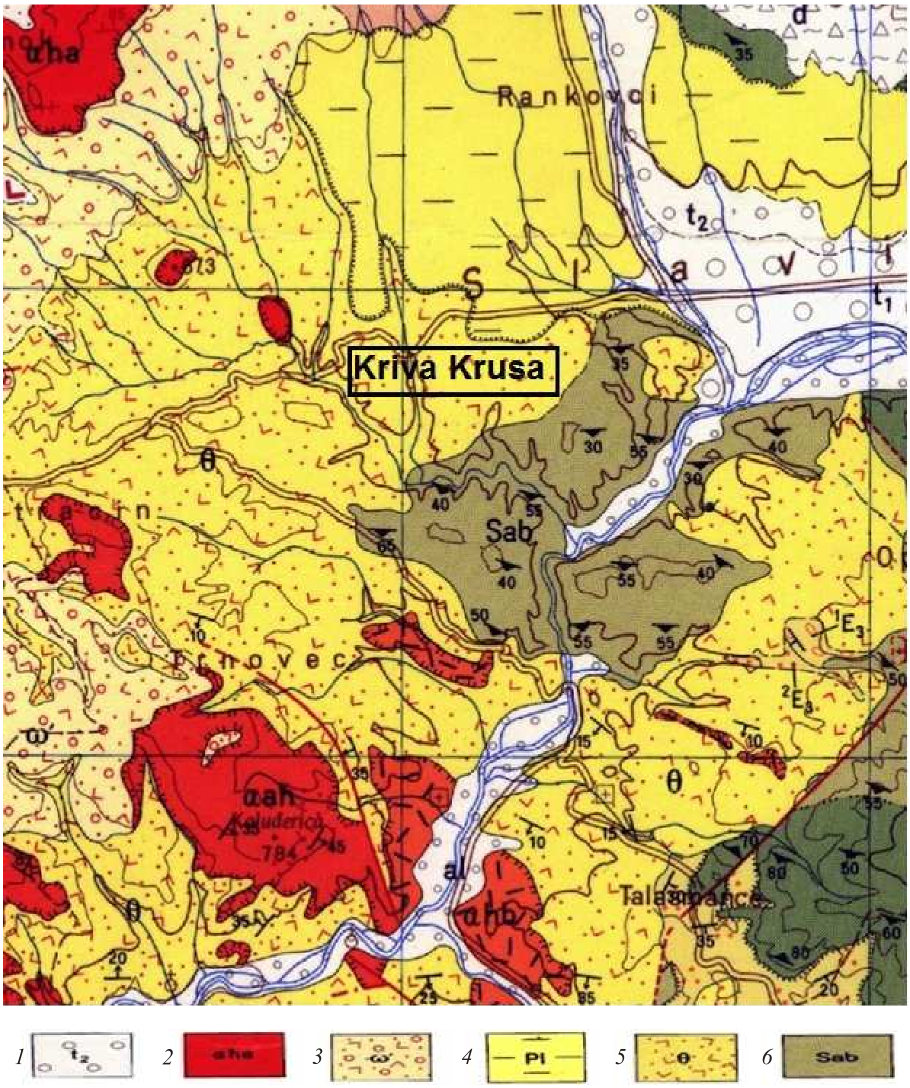

Fig. 2. Geological map of Kriva Krusa 1:100 000: *1.* Higher river terrace; *2.* Hornblende, augite andesite; *3.* Andesitic breccia; *4.* Sand, clay and gravel; *5.* Andesitic tuff; *6.* Albite, quartz, sericite, chlorite schist

Table 1

Chemical composition, CEC and AEC values on tuffs from Rajcani (R) and Kriva Krusa (K)

	R1	R2	R3	R4	K1	K2	K3	K4
				%				
SiO_2	75.39	82.52	77.29	73.87	57.27	54.84	52.82	53.73
Al_2O_3	9.42	6.06	8.6	10.5	19.24	19.94	20.89	20.56
FeO	1.53	0.97	1.16	1.33	3.30	3.97	4.66	3.98
CaO	1.42	1.44	1.9	2.5	4.23	4.85	4.94	5.40
MgO	0.56	0.54	0.78	1.27	0.93	1.26	1.01	1.13
Na_2O	0.67	0.52	0.55	0.58	2.67	1.55	1.87	1.78
K_2O	0.87	0.81	0.86	1.18	2.23	2.39	2.55	2.41
TiO_2	0.50	0.48	0.36	0.41	0.60	0.35	0.41	0.42
MnO	0.03	0.01	0.02	0.01	0.06	0.05	0.06	0.06
P_2O_5	0.12	0.17	0.15	0.16	0.20	0.22	0.25	0.27
Loss.ig	9.27	6.28	8.07	8.13	9.15	11.32	10.51	10.01
Sum	99.77	99.80	99.79	99.91	99.88	99.93	99.97	99.75
				ppm				
Sr	1070	737	844	923	1367	1088	1128	1302
Ba	1445	1366	2094	1783	1876	1531	1534	1756
Zn	24.9	16.3	20.8	24.9	87.6	106	119	116
Pb	1434	1180	985	1193	171.2	87	104.3	132.3
Ni	4.9	6.0	6.3	5.9	7.7	6.0	8.1	7.8
Cr	21.2	9.4	9.0	11.3	6.8	5.1	6.4	5.6
Cu	24.7	11.6	10.5	15.4	44.6	33.8	39.9	39.4
Co	8.5	5.1	4.2	4.6	15.4	10.0	12.3	11.5
Cd	0.42	1.0	0.9	0.9	0.7	0.9	1.0	0.9
As	8.3	7.4	10.2	9.8	1.03	2.6	1.08	1.3
Data on CEC and AEC values for Rajcani and Kriva Krusa samples								
	R1	R2	R3	R4	K1	K2	K3	K4
Ca	0.12	0.13	0.11	0.12	0.21	0.21	0.22	0.22
Mg	0.06	0.06	0.06	0.06	0.08	0.09	0.09	0.08
Na	0.07	0.08	0.06	0.06	0.04	0.03	0.04	0.03
K	0.48	0.54	0.47	0.49	0.73	0.61	0.67	0.65
CEC suma meq/100 g	72	82	69	73	107	94	102	104
CEC $NH4^+$ meq/100 g	82	87	71	76	112	109	114	111

40 kV, and the current was 30 mA. $2\theta = 2°/\text{min}$. The determination of the clay minerals was made by two oriented thin sections. One was taped untreated, then saturated with glycerine and taped, the other was annealed at 480 °C. Identifica-

tion of the type of clay minerals was made in the area $2\theta = 3^\circ - 14^\circ$. We used cards JCPDS (ASTM) from Brown and other appropriate literature for identification of the minerals.

Results and discussion. Chemical composition, CEC and AEC values in tuffs from Rajcani and Kriva Krusa are shown on Table 1.

Cation exchange capacity (CEC) and ammonium exchange capacity (AEC) values for samples from Rajcani deposit are in the range of 69–82 meq/g for CECs and 71–87 meq/100 g for AECs. From Kriva Krusa deposit they are in the range of 94–107 meq/g for CECs and 109–114 meq/g for AECs. These values are very similar to the values from Mangatate and Ngakuru zeolitic tuffs. ROBERTS [16], noted that cation exchange capacity (CEC) and ammonium exchange capacity (AEC) values for samples from Mangatete zeolitic tuffs are in the range of 70–97 meq/100 g for CECs and 88–118 meq/100 g for AECs, [17]. MOWATT [18], noted that Ngakuru zeolitic tuffs typically have CECs of 76–113 meq/100 g.

Optical and X-ray investigations confirmed that the following minerals like feldspar, quartz, stilbite and clay minerals are present in these rocks.

The feldspar appears in a half rounded form with sizes from 10–20 µm to 100–250 µm. Thus larger grains look like porphyroide grains.

Quartz is poorly represented than feldspar. It appears in rounded grains with sizes from 10–20 µm to 100–150 µm.

X-ray diagrams (Fig. 3*a* and *b*) from Rajcani show that the reflection dominates the 4 Å derived from the mineral stilbite presented in other reflections. Besides stilbite reflections are also present as well as reflections of feldspar, quartz and clay minerals. Due to the intensity of the most significant reflection one can say that stilbite is represented of about 57%.

There is mostly clay with mixed layers in which montmorilonite layers are very significant, which can be seen on the X-ray diagram, where the reflection of stilbite of 9.1 Å is still present. The reflection indicates that stilbite is in a clay fraction.

The X-ray diagrams (Fig. 3 *c* and *d*) show that in the samples of Kriva Krusa the most common clay minerals and feldspar are present but there is also stilbite (4 Å and 8.8 Å). Based on the height of the peak it can be assumed that stilbite is represented by about 27%.

Clay minerals are represented by montmorilonite and layered silicates that can be seen from the X-ray diagram. The reflections of stilbite in the clay fraction is present similarly as in the samples from Rajcani.

Because these zeolitic tuffs have not received an overall and systematical study of their physical and chemical properties, it needs for the exploitation and utilization that the preliminary results of the study warrant further characterization of the tuffs including clay mineralogy and zeolitization using scanning electron microscopy and X-ray diffraction. The attractive physical and chemical properties of natural zeolites could be used worldwide even more in the years to

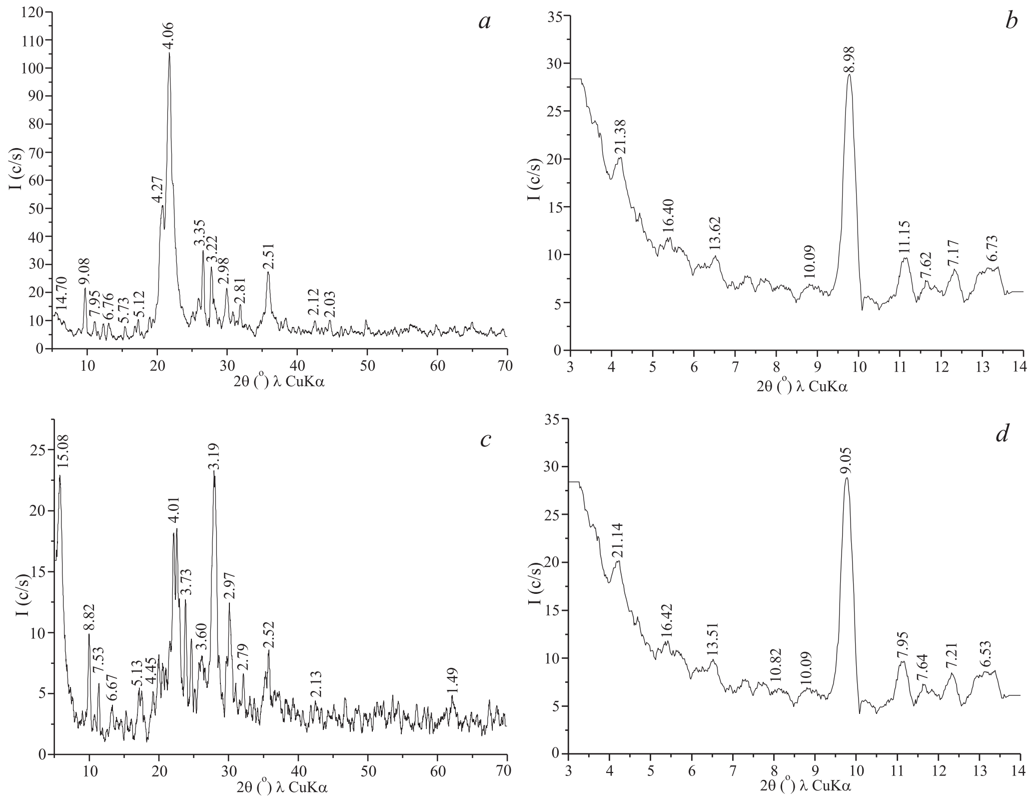

Fig. 3. *a*) X-ray diagram of sample from Rajcani; *b*) X-ray diagram of sample from Rajcani annealed; *c*) X-ray diagram of sample from Kriva Krusa; *d*) X-ray diagram of sample from Kriva Krusa annealed

come in the solutions of different problems in various fields such as agriculture, petrochemical industry, architecture livestock husbandry, environmental protection and energy application [19–21]. Compared to the synthetical zeolite, natural zeolite is not only rich in the deposits but it is also low in price.

Conclusion. Stilbite rich tuffs from Rajcani and Kriva Krusa are potential economic deposits of natural zeolite owing to their average contents of stilbite Rajcani 57% and Kriva Krusa 27% and the cation exchange capacity values 0.69–1.07 meq/g. The values show that these tuffs can be very effective in a wide range of applications such as waste water ammonium removal in animal nutritions, fertilizers, fish farming, additives to cement, ideal host for loading with beneficial organic or inorganic liquids and as pelitization on ferronickle ore.

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