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# Zeolite bearing tuff in the Vetunica deposit northern marginal part of the famous Kratovo-Zletovo volcanic area, Eastern Macedonia

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## Abstract

Studied zeolite bearing tuff from the Vetunica deposit is localized in northern marginal parts of the well known Kratovo-Zletovo volcanic area (Republic of Macedonia). Zeolite bearing tuff occupies the shallowest parts of the Tertiary volcanic rocks complex in this area. The stilbite ($NaCa_2Al_5Si_{13}O_{36} \cdot 14H_2O$) was determined within the aforementioned zeolite bearing tuff. In our detailed study we found out that in the Vetunica deposit stilbite is present with 27%. Also, cation exchange capacity (CEC) and ammonium exchange capacity (AEC) values for samples from the Vetunica 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. Geochemical data illustrates high concentrations >30 ppm As, 1 g/t Ag, 70 g/t Pb, 17 g/t B etc., as representative elements for this volcanic area.

**Keywords**: volcanic tuff, zeolite bearing tuff, stilbite, clay minerals.

## Introduction

In several known volcanic area at the Balkan Peninsula has been determined presence of natural zeolites within the Tertiary volcanic basins. At the territory of Serbia zeolites occur in the Tertiary basin around the Vranjska Banja (Trgo et al., 2012). At several localities in Greece were determined occurrences of natural zeolites related to volcanic tuff, such are those at the island Santorini (Tsolis-Katagas and Katagas, 1989), as well as in the Northern Greece within the area of Thrace where zeolites occur, also (Tsolis-Katagas and Katagas, 1990, Vouduris et al., 2010). Vein-type zeolites in Kizari area, (western Thrace) are found within fresh to zeolite altered volcanic rocks of andesite to dacite composition.

At the territory of the Republic of Macedonia natural zeolites were not found, but zeolite-bearing tuff were presented for the first time in Hristov et al., 1969 and some preliminary results of the stilbite occurences in the volcanic tuffs in the south part of the Kratovo-Zletovo volcanic area were given in Blazev et al., 2012. Our present study defined some mineralogical, geochemical and morphological features of zeolite-bearing tuffs in the Vetunica deposit, northern part of the Kratovo-Zletovo volcanic area. There were calculated geological ore reserves of zeolite-bearing tuffs of 11 000 000 $m^3$ (Bagasov, 2007). Vetunica Mine started with exploitation in 2011.

## Geology

The geology of the studied area has been represented completely by Tertiary volcanic rocks of the Kratovo-Zletovo volcanic area. As the basic rocks are Precambrian gneiss, Riphean-Cambrian schist, Upper Eocene sediments (flysch) and Tertiary-Quaternary volcanic complex. Tuffs are the most common in the area and represent the basis of the younger effusive complex of the Kratovo-Zletovo area. They lie above the Miocene sediments and below the volcanic breccia Pliocene sediments and other volcanic rocks. Somewhere they lie directly above Eocene sediments and crystalline schist or above ignimbrite of dacite composition. In general they are well stratified (Figure 1). These stratified tuffs occur very close to the surface and their thickness is in the range 15-30 m with certain discontinuities (Figure 1). Discontinuities are represented by thin layers of clay (probably montmorilonite) or illite clays enriched with Fe-oxides.

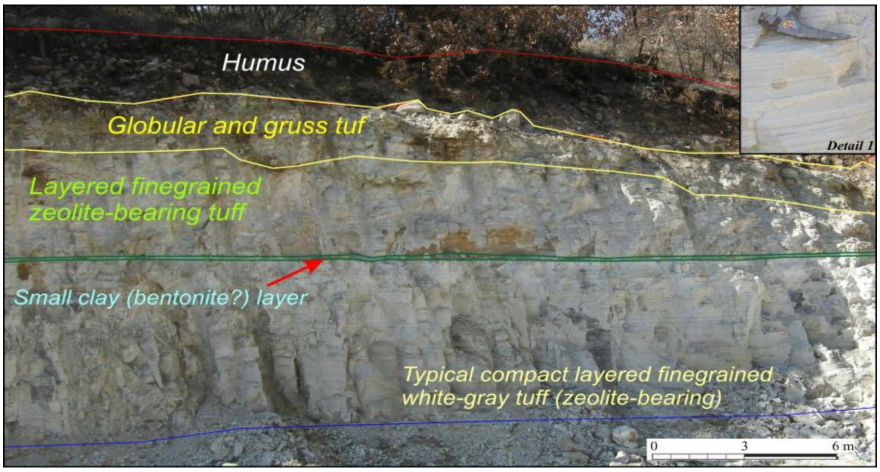



Figure 1. Panoramic view of the open cross section through the Vetunica volcanic tuff deposit

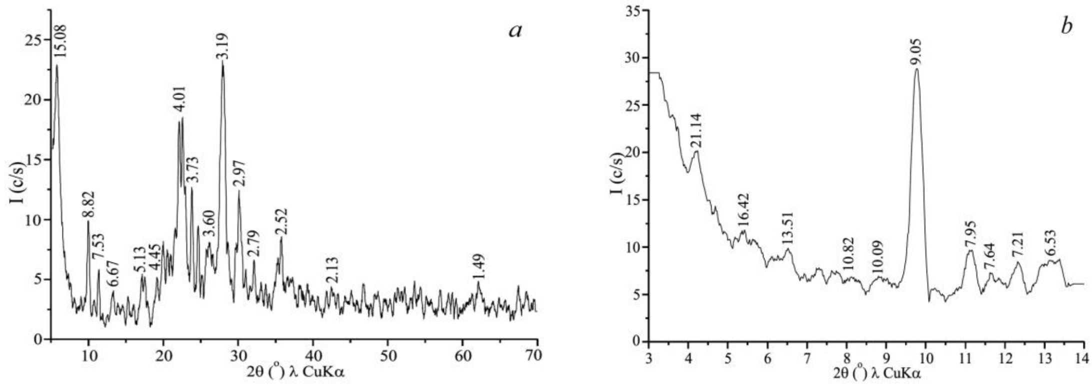
At the open cross section (Figure 1), clearly can be seen that almost sub-horizontal zeolite tuffs are covered with thin layer of humus (0.7-1 m), while beneath were located globular tuffs (partly weathered, with thickness of 0.5-1 m), below are located characteristic zeolite tuffs, which are compact, finegrained, layered and kaolinized at some places (Figure 1). The hiatus comes in the middle of the cross section (5-10 cm thick), while below it continue finelayered compact tuff. Their color varies from white, grey, pale yellow, pale pink to green. Very common occurrence, especially in the shallow parts, is the weathering of tuffs in form of regular concentric spheres, which dimensions are variable (5-50 cm). The spherical layers are composed of crystaloclastic andesite tuff with altered components. In the core of such spheres could be found completely fresh andesite with angular shapes. These tuffs are composed mainly of volcanic ashes, crushed grains of plagioclase and biotite while rarely occur pyroxene, amphibole and magnetite accompanied with andesite pieces. They are the most common in the area of Stracin (village close to ours area of study). Hyaloandesite tuff lie under the hyaloandesite while over them were deposited pliocene sands. They have similar mineral composition with impurities of terrigenous material. In this particular horizon occur level of diatomite earth composed up to 90% of opalized supstance, 2% of quartz, feldspar and biotite and 8% of other different hydrothermal silicates.

## Materials and Methods

The samples of finegrained layered volcanic tuff were taken from small open pit in the Vetunica deposit near the city of Kratovo. Major and trace elements were determined by an ICP–AES method. Dissolution of the sample was made by procedures described in (Radojevic and Baskin, 1999). Diffractometer PHILIPS Type PW 1051 in the region $2\theta = 5^{o}, 60^{o}$ was used for X-ray determination of mineral composition. Copper radiation was used CuK a = 1.54178 °A, the voltage of the generator "NORELCO" was 40 kV, and the current was 30 mA. $2\theta = 2^{o}$/min. Determination of clay minerals was made by two oriented thin sections (Blazev et al., 2012). One was taped untreated, then saturated with glycerine and taped, the other was annealed at 480 ◦C. Identification of the type of clay minerals was made in the area $2\theta = 3^{o}–14^{o}$. In the latest geochemical study, was performed with an atomic emission spectrometry with inductively coupled plasma, ICP-AES, Varian 715-ES, at the Institute of Chemistry, Faculty of Science in Skopje, R. Macedonia.

## Results and discussion

Optical and X-ray investigations confirmed that feldspar, quartz, stilbite and clay minerals are present in these rocks. The X-ray diagrams (Fig. 2a and b) show that in the Vetunica samples the most common clay minerals and feldspar are present but there is also stilbite (4 °A and 8.8 °A). Based on the height of the peak it can be assumed that stilbite is represented by about 27%.




a) b)

Figure 2. a) X-ray diagram of sample from Vetunica; d) X-ray diagram of sample from Vetunica annealed

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.

Table 1. Chemical and CEC/AEC values (a) and geochemical composition (b) of the Vetunica deposit tuffs

*a)*

| | Kl | K2 | K3 | K4 |
|---|---|---|---|---|
| $SiO_2$ (%) | 57,27 | 54,84 | 52,82 | 53,73 |
| $Al_2O_3$ (%) | 19,24 | 19,94 | 20,89 | 20,56 |
| FeO (%) | 3,3 | 3,97 | 4,66 | 3,98 |
| CaO (%) | 4,23 | 4,85 | 4,94 | 5,4 |
| MgO (%) | 0,93 | 1,26 | 1,01 | 1,13 |
| $Na_2O$ (%) | 2,67 | 1,55 | 1,87 | 1,78 |
| $K_2O$ (%) | 2,23 | 2,39 | 2,55 | 2,41 |
| $TiO_2$ (%) | 0,6 | 0,35 | 0,41 | 0,42 |
| MnO (%) | 0,06 | 0,05 | 0,06 | 0,06 |
| $P_2O_5$ (%) | 0,2 | 0,22 | 0,25 | 0,27 |
| LOI | 9,15 | 11,32 | 10,51 | 10,01 |
| Sum | 99,88 | 99,93 | 99,97 | 99,75 |
| Sr (ppm) | 1367 | 1088 | 1128 | 1302 |
| Ba (ppm) | 1876 | 1531 | 1534 | 1756 |
| Zn (ppm) | 87,6 | 106 | 119 | 116 |
| Pb (ppm) | 171,2 | 87 | 104,3 | 132,3 |
| Ni (ppm) | 7,7 | 6 | 8,1 | 7,8 |
| Cu (ppm) | 44,6 | 33,8 | 39,9 | 39,4 |
| Co (ppm) | 15,4 | 10 | 12,3 | 11,5 |
| Cd (ppm) | 0,7 | 0,9 | 1 | 0,9 |
| As (ppm) | 1,03 | 2,6 | 1,08 | 1,3 |
| Data on CEC /AEC values of Vetunica samples | | | | |
| Ca | 0,21 | 0,21 | 0,22 | 0,22 |
| Mg | 0,08 | 0,09 | 0,09 | 0,08 |
| Na | 0,04 | 0,03 | 0,04 | 0,03 |
| K | 0,73 | 0,61 | 0,67 | 0,65 |
| CEC meq/100 g | 107 | 94 | 102 | 104 |
| CEC NH4+ meq/100 g | 112 | 109 | 114 | 111 |

*b)*

| (ppm) | **S-1** | **S-2** | **S-3** | **S-4** |
|---|---|---|---|---|
| Ag | 1.02 | 1.04 | 0.9486 | 0.9672 |
| Al | 41008.6 | 46464.5 | 40188.4 | 45070.6 |
| As | 37.01 | 27.47 | 35.899 | 30.22 |
| B | 17.89 | -0.52 uv | 16.638 | 17.21 |
| Ba | 735.88 | 2194.53 | 706.445 | 1470.3 |
| Ca | 21224.3 | 18265.5 | 19844.72 | 21918.6 |
| Cd | 1.17 | -0.68 uv | 1.1466 | 1.21 |
| Co | -11.3 uv | -5.33 uv | -10.13 uv | -6.47 uv |
| Cr | 11.19 | 13.04 | 10.4067 | 11.86 |
| Cu | 62.31 | 19.33 | 57.948 | 27.062 |
| Fe | 25808.9 | 10388.8 | 25034.63 | 11666.6 |
| K | 12799.3 | 6261.11 | 11903.35 | 5822.83 |
| Li | 6.17 | 18.8 | 5.7381 | 16.36 |
| Mg | 4393.02 | 7194.25 | 3997.65 | 6690.65 |
| Mn | 215.44 | 149.21 | 200.359 | 138.76 |
| Mo | 0.08 uv | -0.07 uv | -0.09 uv | -0.07 uv |
| Na | 6611.48 | 2869.28 | 6148.68 | 4590.85 |
| Ni | 8.16 | 10.67 | 7.589 | 9.923 |
| P | 709.29 | 365.97 | 659.6397 | 512.358 |
| Pb | 52.4 | 671.98 | 49.78 | 624.941 |
| Sr | 570.01 | 959.07 | 701.1123 | 891.94 |
| Tl | -6.78 uv | -7.51 uv | -6.93 uv | -7.22 uv |
| V | 127.7 | 25.72 | 123.869 | 29.06 |
| Zn | 70.86 | 35.52 | 69.4428 | 60.38 |

The units are units milliequivalents per 1 g zeolite meq/g (Helfferrich, 1962). 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 the Vetunica 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 (Blazev et al., 2012). Stilbite rich tuffs from the Vetunica 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 latest geochemical study of the Vetunica tuff (Table 1b) displayed standard values for most of the analyzed elements, followed with increased concentrations of the representative geochemical association for this type of volcanic rocks primarily strontium, barium and especially boron, silver, zinc and phosphorus, which is representative for water environments. Of major elements the highest values displayed calcium, magnesium, iron, manganese as well as alumina and silica.

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.

## Conclussion

Within the Vetunica deposit were calculated geological ore reserves of zeolite bearing tuff of 11 000 000 $m^3$. Zeolite bearing tuff are of shallow type and regularly at depth of approximately 10 meters below the surface they are characterized by clay hiatus (probably bentonite or Fe-enriched illite). The present study confirmed presence of stilbite and light enrichment with B, Pb, Ag, Sr, As etc., and high concentration of Ca in studied tuffs. Also, in zeolite bearing tuff was determined potassium enrichment within the finely stratified white to white-gray tuff.

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