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COMPARATIVE MINERALOGICAL ANALYSIS OF TWO ZEOLITIC TUFF SLANCI AND ZLATOKOP

Katarina M. Mihajlović[1a], Jovica Stojanović[2a], Slavica Mihajlović[2b], Ivana Jelić[2c], Ana S. Radosavljević-Mihajlović[2d], Suzana Erić[2b]

[1] Mining and Geology faculty, University of Belgrade, Đušina 7, Serbia
[2] Institute for technology of nuclear and other raw materials, Franche d Eperea 86, 11000 Belgrade, Serbia
[1a] miha.katarina9@gmail.com, 0009-0007-2001-5794
[2a] j.stojanovic@itnms.ac.rs, 0000-0002-2752-6374
[2b] s.mihajlovic@itnms.ac.rs, 0000-0003-0904-3878
2[c]i.jelic@itnms.ac.rs, 0009-0000-9901-9323
[2d] a.radosavljevic@itnms.ac.rs, 0000-0003-1228-4058
[1b] suzana.eric@rgf.bg.ac.rs, 0000-0003-2303-2497

Abstract
The paper presents the comparative results of quantitative X-ray powder analysis and cation exchange capacity for zeolitic tuffs Slanci and Zlatokop. The basic mineral composition is represented by Ca-clinoptilolite (Zlatokop) and Ca-heulandite (Slanci), feldspars, quartz and clay appear as accompanying components. The X-ray powder diffraction method on a polycrystalline sample and the Sirquant software program were used to determine the quantitative composition.

Keywords*: zeolitic tuff, quantitative analysis, Siroquant software*

1. INTRODUCTION

The heulandite series of zeolites is represented by isostructural minerals clinoptilolite and heulandite, with a general crystalochemical formula $(Na,K,Ca,Mg)_6(Al_6Si_{30}O_{72})\cdot nH_2O$. Depending on the dominant extra-framework cation present in the zeolite structure, there are Ca-heulandite, Ba-heulandite, Ca-clinoptilolite, or K-clinoptilolite [1]. The minerals of heulandite series were formed as a product of devitrification of volcanic glass, and are related to lacustrine and marine sedimentary deposits [2]. In these sedimentary rocks, zeolites occur in the form of small crystals ranging in size from 0.1 to 100 µm, associated with other mineral components, such as clay minerals and other aluminosilicate and silicate forms of similar densities. The subject of this study was a comparative analysis of the quantitative mineral composition, and an analysis of the content of exchangeable cations in zeolitic tuffs.

2. EXPERIMENTAL

The samples used in this study are zeolitic tuffs from the Zlatokop and Slanci deposits, in a raw state with a grain size of +100% - 63 µm. Quantitative chemical analysis was performed by gravimetric method. To monitor the concentration of exchangeable inorganic cations Na^+, K^+, Ca^{2+}, and Mg^{2+}, the total cation exchange capacity (CEC) was determined by a standard method [3]. The XRD technique was used for identification of the crystalline phases in the powdered samples. The XRD patterns were obtained using a Philips PW-1710 automated diffractometer with a Cu tube operated at 40kV and 30mA. The instrument was equipped with a diffracted beam curved graphite monochromator and an Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angles from 4 to 65 ° with a step size of 0.02° counting for 1s. For quantitative analysis, the Siroquant V4.0 software was used [4].

3. RESULTS AND DISCUSSION

The chemical analyses of zeolitic tuffs show a high content of silicon, as well as the presence of oxides of alkali and alkaline earth metals. The SEM photomicrographs shown in Figure 1 provides the results of the chemical analyses and the morphological appearance of the zeolitic tuff from Slanci and Zlatokop.

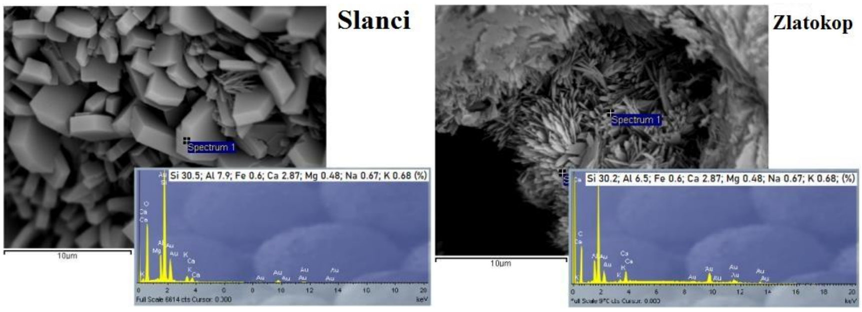

Figure 1. SEM photomicrographs of zeolitic tuff from Slanci and Zlatokop (magnification × 2.000).

Based on crystalochemical analysis, it was determined that the dominant cation for both tuffs is Ca, and the Si/Al ratio amounts to 3.86 (Slanci) and 4.64 (Zlatokop). It can be concluded that the zeolitic tuff from Slanci is rich in Ca-heulandite, while Zlatokop is rich in Ca-clinoptilolite, which is in accordance with previous studies [5-7]. The mineral composition of both zeolitic tuffs is uniform: heulandite, quartz, clay minerals (montmorillonite), and feldspar minerals (mainly plagioclase). The most dominant mineral in the samples is a zeolite mineral from the heulandite series, while contents of other accompanying minerals are lower. The zeolitic tuff from the Slanci locality (lacustrine Miocene formations located east of Belgrade in the Danube Ključ area, within the territories of Veliko Selo and Slanci) [2], rich in HEU minerals, is presented in the SEM photomicrographs in Figure 1. SEM photomicrograph of zeolitized dacitic tuffs from Zlatokop, which are interbedded in marlstone rocks of Middle Miocene to Pliocene age, is also shown in Figure 1. The zeolite minerals occur in the matrix as well developed crystals of monoclinic forms (pinacoids and monoclinic prisms), with sizes up to 10 µm. Comparative refined X-ray powder diffraction diffractograms of the zeolitic tuffs are given in Figure 2.

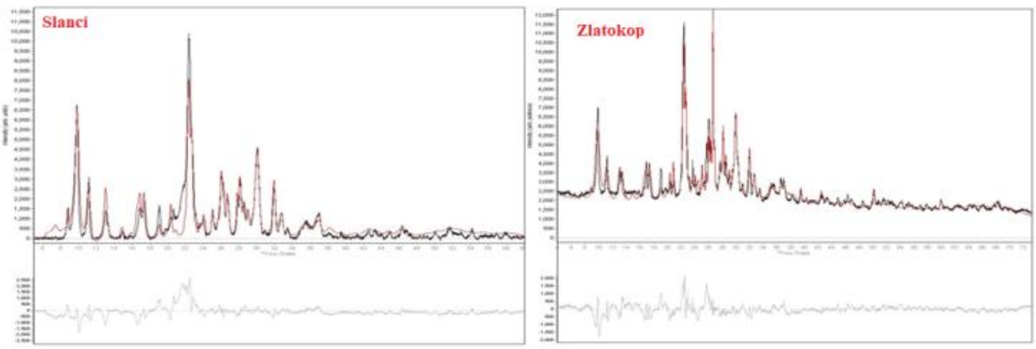

Figure 2. Comparative refined X-ray powder diffraction diffractograms of the zeolitic tuffs from Slanci i Zlatokop.

The main difference between these two tuffs lies in the quartz content. It is significantly more abundant in the zeolitic tuff from Zlatokop, indicating higher crystallinity, compared to the zeolitic tuff from Slanci which is characterized by the presence of amorphous matter of biogenic origin. Based on the X-ray powder diffraction diffractogram shown in Figure 2, the unit cell parameter are as follows: SLANCI (a = 17.55 Å (4), b = 17.94 Å (3), c = 7.38 Å (4), α = 90°, β = 116.48° (3), γ= 90°, V = 2078 (4) Å^3) and ZLATOKOP (a = 17.673 Å (4), b = 17.926 Å (3), c = 7.413 Å (4), α = 90°, β = 116.46° (3), γ= 90°, V = 2102 Å^3). It can be observed that the unit-cell of the zeolitic tuff from Slanci is smaller compared to that of the Zlatokop tuff. From quantitative X-ray diffraction analysis (Figure 2), the following phases were identified in Slanci: heulandite 85.1 %, quartz 1.9 %, muscovite 5.9%, albite 6.6 %, orthoclase 0.6% and calcite 0.21%. Quantitative X-ray analysis (Figure 2) of Zlatokop yielded following mineral composition: heulandite 77.2 %, quartz 8.8 %, pyrite 0.12%, muscovite 3.8 %, albite 6.3 %, orthoclase 3.2% and calcite 0.7%. The content of the zeolitic phase in Slanci is 10% higher, than in Zlatokop. All zeolites contain various monovalent, divalent, or trivalent cations in extra-framework positions. The types and contents of exchangeable cations in the starting clinoptilolitic tuffs are presented in Table 1. The total cation exchange capacity was determined as the sum of the exchangeable cation contents.

Table 1. Content of exchangeable cations in zeolitic tuff from Slanci and Zlatokop deposit.

	Exchangeable cations [MmolM$^+$/100g]				
Tuff	Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC
Slanci	145	3.0	4.1	8.0	160
Zlatokop	95	11.2	18.2	15.7	140.1

4. CONCLUSION

Based on the presented results, it can be concluded that there is a correlation between the cation exchange capacity and the content of the heulandite component in the zeolitic tuff. The heulandite phase is most abundant in the zeolitic tuff from the Slanci deposit, with 85% HEU minerals, while in the Zlatokop deposit it is at 77%. The total cation exchange capacity values for the examined zeolitic tuffs are in correlation with the content of the zeolitic phase.

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REFERENCES

[1] A. Radosavljević-Mihajlović, B. Matović., Tehnika., 13 (2) (2008) 107-119.
[2] J .Obradović, Geol anali Balkanskog poluostrva., XLI, (1977) 293-302.
[3] M. Pansu, J. Gautheyrou., Handbook of Soil Analysis. Mineralogical, Organic and Inorganic Methods, Springer-Verlag. Berlin, 2006, p. 709-754.
[4] J.C. Taylor, Powder Diffraction., 6 (1991) 2-9.
[5] J. Stojanović, A. Radosavljević-Mihajlović, V. Kašić. Zbornik radova VIII Simpozijuma JAM, Mineralogija Godišnjak JAM, Beograd, Srbija, 2003.
[6] A. Radosavljević-Mihajlović, J. Stojanović, V, Kašić, J. Lemić., Bull. Geoinstitute., 38 (2003) 149-155.
[7] A. Radosavljević-Mihajlović, J. Stojanović, V. Kašić., Radovi Geoinstituta., 40 (2005) 191-200.