OCCURENCES AND PROPERTIES OF ZEOLITIC TUFFS IN SERBIA

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ABSTRACT

The most significant Serbian deposits or appears of natural zeolites are: Zlatokop (Vranjanski basin), Igroš (mountain of Kopaonik), Beočin (area Fruška gora), Toponica (Sud of Serbia) and Slanci (Danube key, near Belgrade). Serbian zeolite deposits are spatially and genetically associated with volcanic-sedimentary rocks. On the basis of mineralogical, crystallographic, chemical and thermal analyses, can generally be ranked in two mineral groups: Ca-clinoptilolite and Ca-heulandite Due to a steadily growing interest, researches of this raw material have constantly been increasing for the last few decades. In this paper are presented the mineralogical research of Serbian deposits of natural zeolites.

Key words: deposit, zeolite tuffs, mineralogy, Ca -clinoptilolite, XRPD analysis.

INTRODUCTION

Zeolites are tecto-aluminosilicates with open framework structures, which enable almost complete ion-exchange [1]. Clinoptilolite, one of the most commonly observed zeolite, is a member of the heulandite group (HEU type zeolite) [2]. Zeolite minerals series clinoptilolite and heulandite, could be distinguished either by thermal analysis, by Si/Al ratio or by presence and arrangement of extra-framework cations (Ca^{+2}, Mg^{+2}, K^{+1}, and Na^{+1}) in structure of these minerals [3]. Zeolite tuffs can contain various accessory minerals clay, mica or feldspars minerals. The most significant Serbian deposits of natural zeolites are: Beočin, Slanci, Zlatokop, Igroš and Toponica. These deposits were formed in marine and lake environment, the Senonian and Neogene age, originated mostly by devitrification of volcanic glass. This paper presents basic mineralogical, crystallographic and chemical properties of zeolite minerals from Serbian deposits

EXPERIMENTAL

There major aspects in mineralogical research on zeolite tuffs are: chemical, optical, structural and physical characterization. Chemical analyses were done like classic wet-silicate analyses. Qualitative mineralogical analyses were made by polarisation microscope in transmitted light. Scanning-electron microscopy (using a JEOL JSM-6610LV scanning electron microscope (SEM) connected with an INCA energy-dispersion X-ray analysis unit (EDX), an acceleration voltage of 20 kV was used. The analyzed samples were coated with carbon (15 nm thick layer, density 2.25 g/cm^3). XRPD analyses were performed on a "Philips PW 1710" difractometer in the range from 4^o to 65^o 2θ. Analyses of cation exchange capacity (CEC) were made to determine the concentration of the extra-framework, exchangeable compensation cations, using Ming & Dixon method [4].

RESULTS AND DISCUSSION

Serbian zeolite tuffs deposits are spatially and genetically associated with volcanic-sedimentary rocks. These deposits were formed in marine and lake environment, the Senonian and Neogene age, originated mostly by devitrification of volcanic glass. In such rock, zeolite minerals are present in form of very small crystals (0.1-10μm) in mineral paragenesis with quartz, feldspar, mica, volcanic glass, and clay minerals, Table 1.

Table 1. Mineralogical properties of the observed samples from Serbian deposit.

Deposit	Rock type	Mineralogical composition	
Beocin	holocrystalline-porphyric	zeolite Heu-type (HEU), clay minerals	carbonates, plagioclase, quartz (Q), biotite
Slanci	**hypo**crystalline -porphyry	zeolite Heu-type (HEU), clay minerals	carbonates, plagioclase, quartz (Q), biotite op..
Zlatokop	**hypo**crystalline -porphyry	zeolite Heu-type (HEU)	plagioclase, quartz (Q), biotite, pyrite, op.,
Igros	**hypo**crystalline -porphyry	zeolite Heu-type (HEU)	plagioclase, quartz (Q), biotite., op.
Toponica	holocrystalline -porphyric	zeolite Heu-type (HEU)	plagioclase, quartz (Q), biotite, op.

op. - opaque minerals.

The SEM images of zeolitic tuff from different deposit are presented in Figure 1(a-e). In all zeolitic tuffs the quartz grains are well preserved with typical angle-like forms and sharp edges. The zeolite minerals that are needle-like forms and very small dimensions are mainly distributed in matrix (up to 10μ). In deposit Beocin the carbonate minerals are visible in matrix, Figure 1a. In deposit Slanci the accessory minerals, apatite and zircon are regularly breezy and without any marks of alteration. Presence of plant fossils was also determined, Figure 1b. Pyrite is mostly altered with clearly visible effects of limonitisation in zeolitic tuff from deposit Zlatokop, Figure 1d.

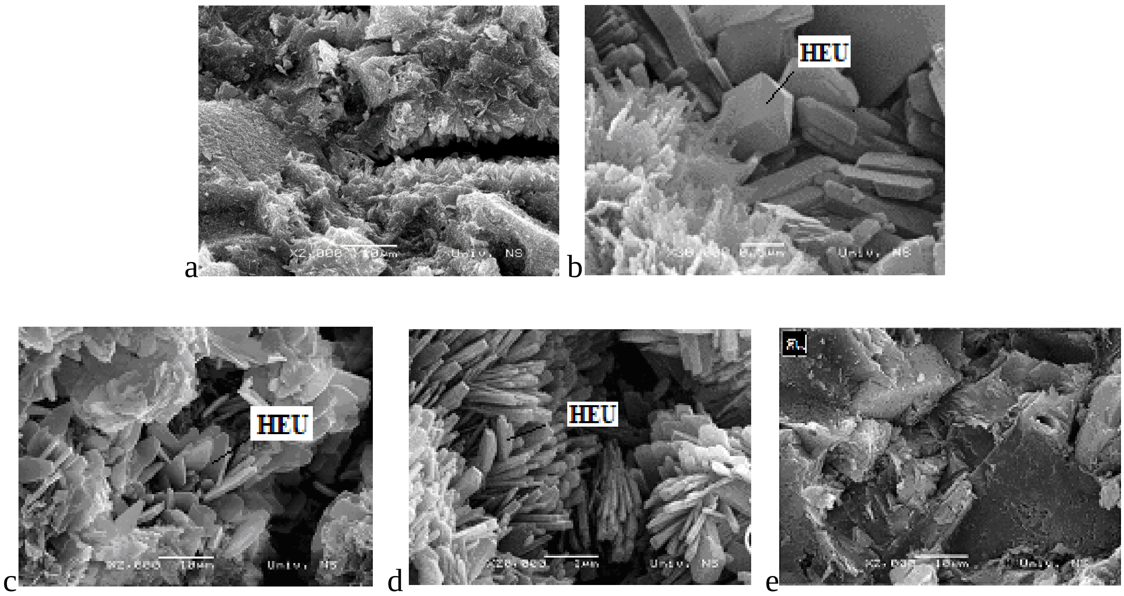

Figure 1. The SEM images of zeolitic tuff from deposite (a) Beocin; (b) Slanci; (c) Igros; (d) Zlatokop; (e) Toponica.

The chemical composition, Si/Al ratio, and overall CEC of various zeolite tuffs (average values) are presented in Table 2. Overall CEC is calculated as a sum of amounts of exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}).

Table 2. The chemical composition (wt. %), Si/Al ratio, and overall CEC (mmolM^{+}/100 g) of zeolite tuffs from Serbian deposits.

Oxide	Zlatokop	Igros	Toponica	Beocin	Slanci
SiO_2	64.60	61.62	67.50	56.00	64.94
Al_2O_3	12.40	12.05	12.00	14.04	14.08
Fe_2O_3	1.84	2.02	1.00	1.85	1.72
CaO	4.02	5.44	4.91	6.20	4.72
MgO	0.80	1.37	0.34	2.64	0.78
K_2O	0.82	0,82	1,01	2,32	0,63
Na_2O	0.91	1.00	1.13	0.52	0.26
I. L.	14.00	15.00	12.65	15.50	12.65
Si/Al	4.71	4.42	4.40	3.93	3.91
CEC	142	123	140	166	130

The highest *Si/Al* ratio is present in zeolite tuff from Zlatokop deposit (4.71), while that ratio decreases among the rest zeolite tuffs (Toponica, Beocin, Igros, and Slanci). According to chemical analyses of zeolite crystals obtained from SEM EDX and thermal stability measurements [3, 5], it can be concluded that Zlatokop, Toponica, and Igros zeolite tuff deposits are mostly consisted of Ca-clinoptilolite, while Beocin, and Slanci zeolite tuff deposits are of Ca-heulandite.

XRPD analyses confirmed mineralogical composition of these zeolite tuffs. Matching X-ray patterns are given in Figure 2.

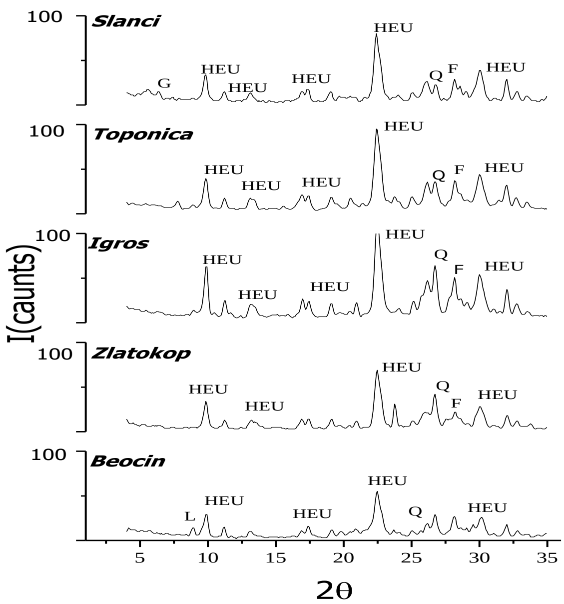

Figure 2. The X-ray powder patterns of observed zeolite tuff from Serbian deposits.

Minerals identified in XRPD analyses were marked as follows: HEU-zeolite minerals; Q – quartz; F – feldspar minerals; L – mica minerals; G – clay minerals.

Next reflections (*hkl*) were used for determination of unit-cell parameters (*a, b, c,* β and *V*): (200), (020), (-311), (111), (131), (400), (330), (240), (151). The results are presented in Table 3.

Table 3. The unit-cell parameters of HEU-type minerals of Serbian deposits.

Deposit	**a (Å)**	**b (Å)**	**c (Å)**	**ß (º)**	**V ($Å^3$)**
Zlatokop	17.67(5)	17.92(5)	7.41(5)	116.46(4)	2102
Igros	17.65(2)	17.94(2)	7.40(9)	116.46(9)	2096
Toponica	17.68(2)	17.95(2)	7.39(2)	116.30(9)	2103
Beocin	17.68(4)	17.86(4)	7.41(4)	116.47(3)	2097
Slanci	17.55(3)	17.95(2)	7.38(8)	116.45(9)	2084

Intensities of distinctive zeolite mineral reflections were approximately uniform for all deposits. Differences between reflection intensities were in function of type and the amount of extra-framework cations.

CONCLUSION

Based on complex mineralogical analyses, Zlatokop, Toponica, and Igros deposits were denoted as *Ca* -clinoptilolite type tuffs, and Beocin and Slanci deposits as *Ca* -heulandite type tuffs. *Si/Al* ratio is the highest in Zlatokop zeolite tuff deposit, and because of that it is the most stable zeolite mineral of all investigated tuffs.

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