University of Belgrade
Technical Faculty in Bor and
Mining and Metallurgy Institue Bor

51st International October Conference on Mining and Metallurgy

PROCEEDINGS

Editors:

Prof. dr Srba Mladenović
Prof. dr Čedomir Maluckov

Bor Lake, Serbia,
October 16-19, 2019

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PREFACE

On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the 51st International October Conference on Mining and Metallurgy (IOC 2019) held at Bor Lake, Serbia, 16 – 19 October 2019.

The IOC 2019 has been organized by the University of Belgrade, Technical Faculty in Bor, in cooperation with Mining and Metallurgy Institute Bor. It is devoted to presenting recent research results and advances in the fields of geology, mining, metallurgy, materials science, technology, environmental protection, and related engineering topics. The primary goal of IOC is to bring together academics, researchers, and industry engineers to exchange their experiences, expertise and ideas, and also to consider possibilities for collaborative research.

These proceedings include 81 papers from authors coming from universities, research institutes and industries in 15 countries: Bosnia and Herzegovina, Croatia, Japan, Kazakhstan, México, Montenegro, Poland, Romania, Russia, Slovenia, Turkey, Ukraine, Switzerland, Brasil and Serbia.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged. The support of the sponsors and their willingness and ability to cooperate has been of great importance for the success of IOC 2019. The Organizing Committee would like to extend their appreciation and gratitude to all the donors and friends of the Conference for their donations and support.

We would like to thank all the authors who have contributed to these proceedings, and also to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to IOC 2019. Sincere thanks to all the people who have contributed to the successful organization of IOC 2019.

We look forward to welcoming you to the 52nd International October Conference on Mining and Metallurgy (IOC 2020), which will be held in October 2020.

On behalf of the 51st IOC Organizing Committee,
Prof. dr Srba Mladenović

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GEOLOGY CHARACTERISTICS OF ZEOLITIC TUFFS OF SERBIA

Vladan Kasic[1], Ana Radosavljevic-Mihajlovic[1], Jovica Stojanovic[1], Slavica Mihajlovic[1]
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ABSTRACT

Since about 50 years it is known that giant deposits of natural zeolites of pyroclastic origin are spread over all Miocene sediments of Serbia. Such rocks have often zeolite contents between 60 and 90%. The most significant Serbian deposits of natural zeolites are: Zlatokop, Igros, Beocin, Toponica, and Slanci. Based on obtained results of structural, chemical, physical, and thermal analyses, the investigated zeolite tuffs can be generally defined in two mineral series: clinoptilolite-Ca, and heulandite-Ca. The interest for these materials is in steady mass growth as they are of vital importance for Serbian economy. The oversights of perennial mineralogical research of Serbian giant deposits of natural zeolites were presented in this paper.

Key words: zeolite tuffs, clinoptilolite-Ca, heulandite-Ca, Zlatokop, Igros, Toponica, Beocin, Slanci, Serbia

INTRODUCTION

Zeolites are tecto-aluminosilicates with open framework structures, which enable almost complete ion-exchange [1]. Zeolite minerals have great economic interest found mainly in specific sedimentary rocks of pyroclastic origin. Zeolite minerals series clinoptilolite and heulandite, which are most common in Serbian tuff deposits, could be distinguished either 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. Zeolite tuffs can contain various accessory minerals that may have significant influence on zeolite component in them.

MINERALOGICAL CHARACTERISTICS

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 microscopic analyses were made by polarisation microscope in transmitted light. XRPD analyses were performed on a "Philips PW 1710" difractometer in the range from 4^{o} to 35^{o} 2θ. Unit-cell parameters were determined by using the LSUCRIPC software [2]. Analyses of cation exchange capacity (CEC) were made in aim of determination of concentration of extra-framework cations using Ming & Dixon method [3].

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 [4]. 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. The content of zeolite minerals is between 60 and 90%, with constant presence of accessory minerals.

Zlatokop zeolite tuff deposit - The matrix of this tuff is hyalclastic with clearly visible clasts of quartz and feldspar minerals as well as pyrite. Quartz grains are also well-preserved with typical angle-like forms and sharp edges. Feldspar minerals that are mainly preserved are mostly presented with plagioclase minerals. Among mica minerals that are mainly altered biotite is the most present. Zeolite minerals are clearly visible needle-like crystals. The crystal measurements are up to 10μ. Pyrite is mostly altered with clearly visible effects of limonitisation. Apatite and zircon are accessory minerals. Presence of well-preserved pant fossils is also determined.

Igros zeolite tuff deposit - The matrix of this tuff is hyalclastic with porous texture. Quartz grains are also well-preserved with typical angle-like forms and sharp edges. Feldspar minerals that are partially altered are mostly presented with plagioclase minerals. Zeolite minerals that are needle-like forms and very small dimensions are mainly distributed in matrix (up to 10µ). Biotite is dominant mica mineral, which is primary, while muscovite (sericite) is mainly as secondary mineral. Biotite is partially altered. Products of its alterations are iron-oxides and hydroxides (mostly limonite and goethite). Accessory minerals, apatite and zircon are regularly breezy and without any marks of alteration. Presence of plant fossils is quite frequent.

Toponica zeolite tuff deposit – The matrix of this tuff is hyalclastic. Quartz grains are well-preserved with typical angle-like forms and sharp edges. Feldspar minerals that are mainly altered are mostly presented with plagioclase minerals. Among mica minerals that are partially altered biotite is the most present. Zeolite minerals are clearly visible needle-like crystals. The crystal measurements are above 10μ. Accessory minerals are regularly breezy and without any marks of alteration. Presence of plant fossils was also determined.

Beocin zeolite tuff deposit - The matrix of this tuff is hyalclastic. Quartz grains are well-preserved with typical angle-like forms and sharp edges. Feldspar minerals that are mainly altered are mostly presented with plagioclase minerals. Among mica minerals that are partially altered biotite is the most present. Among mica minerals that are mainly altered biotite is the most present. Products of its alterations are iron oxides and hydroxides (mostly limonite and goethite). Zeolite minerals are clearly visible needle-like crystals. The crystal measurements are up to 10μ. Accessory minerals are regularly breezy and without any marks of alteration. Carbonate minerals are visible in matrix. Presence of plant fossils was also determined.

Slanci zeolite tuff deposit - The matrix of this tuff is hyalclastic with porous texture. Quartz grains are also well-preserved with typical angle-like forms and sharp edges. Feldspar minerals that are mainly altered (kaolinized and sericitized) are mostly presented with plagioclase minerals. Zeolite minerals that are needle-like forms and very small dimensions are mainly distributed in matrix. Biotite is dominant mica mineral, which is primary, while muscovite (sericite) is mainly as secondary mineral. Biotite is partially altered. Products of its alterations are iron oxides and hydroxides (mostly limonite). Accessory minerals, apatite and zircon are regularly breezy and without any marks of alteration. Presence of plant fossils was also determined.

The chemical composition, Si/Al ratio, and overall CEC of various zeolite tuffs (average values) are presented in Table 1.

Table 1. Chemical composition (in wt.%), Si/Al ratio, and overall CEC (mmolM⁺/100 g) of zeolite tuffs from different 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). Based on results of chemical analyses, it can be concluded that Zlatokop, Toponica, and Igros zeolite tuff deposits are mostly consisted of clinoptilolite-*Ca*, while in Beocin, and Slanci zeolite tuff deposits it is heulandite-*Ca* [5, 6]. Overall CEC is calculated as a sum of amounts of exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+).

XRPD analyses confirmed mineralogical composition of these zeolite tuffs. Matching X-ray patterns are given in Figure 1. Minerals identified in XRPPD analyses were marked as follows: HEU-zeolite minerals; E – erionite; 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 2.

Table 2. Unit-cell parameter values of zeolite minerals from different zeolite deposits

Deposit	**a (Å)**	**b (Å)**	**c (Å)**	**ß (º)**	**V (Å³)**
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.

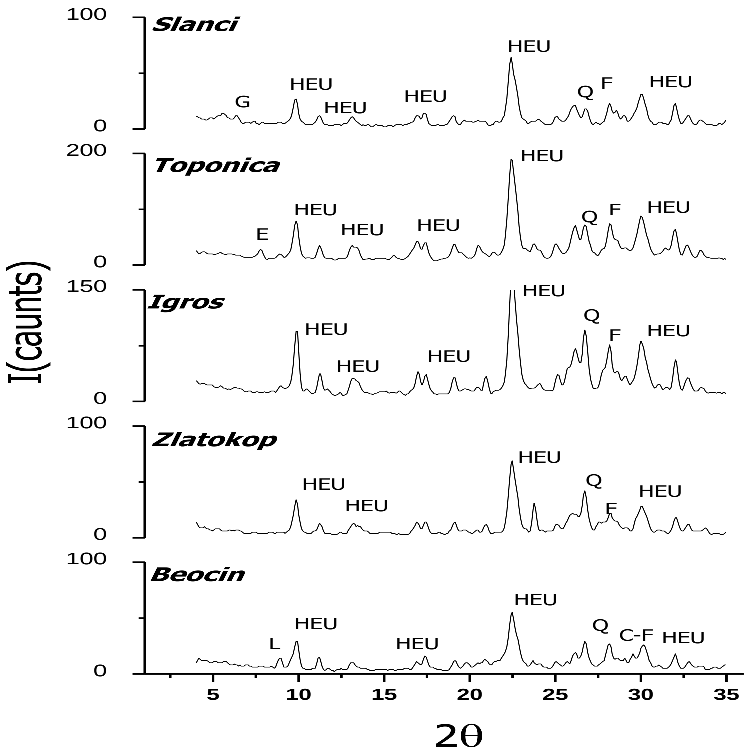

Figure 1. Matching X-ray patterns of tested zeolite tuffs

CONCLUSION

Based on complex mineralogical analyses, Zlatokop, Toponica, and Igros deposits were denoted as clinoptilolite-*Ca* type tuffs, and Beocin and Slanci deposits as heulandite-*Ca* 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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