# PETROGRAPHIC STUDY OF BEOČIN ZEOLITE TUFF

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## ABSTRACT

Zeolite tuff in the Općište deposit has been subdivided into several varieties: mediumto coarse-grained, medium-grained and fine-grained zeolite-rich tuff, as well as mediumgrained and very fine-grained to fine-grained glass-rich zeolite tuff. Zeolite-rich and glassrich zeolite tuff varieties were already distinguished based on CEC values (> or <130 meq/100g respectively). Generally, very fine-grained to fine-grained tuff has lower, while medium-grained tuff has more zeolite content. Clinoptilolite is the dominant zeolite mineral.

Keywords: zeolite, tuff, SEM, Beočin, clinoptilolite

## **INTRODUCTION**

Due to their industrial significance zeolite tuffs were subject of many studies in Serbia [1-7]. All known tuff deposits in sedimentary basins in Serbia are related to Miocene volcanic activity.One of the most significant from the economic point of view is Općište zeolite. The Općište deposit is located near the Beočin Monastery, on the northern slopes of Fruška Gora. The zeolitized tuff is interstratified within Badenian marine marlstones. It occurs as one composite layer 8-25 m thick (~ 17 m in average). Overburden is 2-28 m thick, around 5.4 m in average [8]. The whole sedimentary series dips to the NNW at the angle of 15-25°. Previous exploration revealed three varieties of tuff: zeolite tuff, glass-rich zeolite tuff and glass-rich tuff (note that 'tuff' is here used in a non-genetic sense meaning that it delineates fine-grained material with volcanogenic particles irrespectively their fragmentation and depositional mechanism; see [9]). Total resources of all tuff varieties are ~2 Mt [9]. However, in 2006 only a part of the deposit with zeolitized tuff was explored in detail, and the measured and indicated resources were estimated at 364,000 t of zeolite tuff and 245,000 t of glass-rich zeolite tuff [10]. The aim of this study is petrographic characterization of zeolitic tuff in the Općište deposit.

#### SAMPLES AND METHODS

Eleven core samples of zeolite tuff from 4 boreholes drilled in 2006 have been collected. Samples were chosen in such a way to represent the vertical changes in tuff petrography. The petrographic study included optical and scanning electron microscopy. Scanning electron microscopy was used for imaging and collecting chemical data using a Jeol JSM – 6610 LV Scanning Electron Microscope fitted with energy-dispersive spectrometer (EDS). Analyses were run at an accelerating voltage of 20 kV, and working distance of 10 mm. Samples were pre-coated using the evaporated gold coating method to make the samples conductive. For quantitative chemical analysis, the microscope was calibrated for major elements using orthoclase (K), albite (Na), wollastonite (Ca), almandine (Si, Fe), MgF<sub>2</sub> (F), Ti 1 (Ti), GaP (P) and oxides (MgO, Al<sub>2</sub>O<sub>3</sub>) as standards.

#### **RESULTS AND DISCUSSION**

Tuff in Općište deposit is underlain by dark grey marlstone of Badenian age. Typical cross-section through the tuff sequence (bottom to top direction) is as follows:

- Marly tuff 0.6 m thick has been observed in one borehole;

- Economically important tuff sequence starts with medium- to coarse-grained zeolite tuff 1.0-1.6 m thick;

- Medium-grained zeolite tuff, occasionally with visible biotite flakes, occurs in all positive boreholes with thickness from 0.6 to 8.8 m;
- Fine-grained zeolite tuff 2.1-8.5 m thick is the last one in zeolite-rich tuff variety;
- Medium-grained glass-rich zeolite tuff 1.3 to 3.0 m thick has been detected in several boreholes;
- Fine-grained to very finegrained glass-rich zeolite tuff 1.0-16.0 m thick, is the most important variety of glass-rich zeolite tuff;
- Fine-grained zeolite tuff 2 m thick was observed in only one borehole so far;
- Tuff sequence finish with fragmented marly and clayey tuff.

Tuff is overlain by light grey Badenian marlstone 0.7-17.0 m thick, Quaternary loess up to 10 m thick, debris with clay up to 1.7 m thick, and soil up to 0.5 m thick.

Figure 1. Log of the B-XI/06 borehole with the position of studied samples (black circles), modified after [10]

LITHOLOGY	(h (m)	DESCRIPTION	CEC meq/100g				
LINIOLOGI	Dept		$Ca^{2+}$	$Mg^{2+}$	Na <sup>+</sup>	K <sup>+</sup>	Total
	0.0	Loess		B			
	8.5	Fragmented marly tuff					
		Beo-6 Light grey to white very fine- to fine-grained tuff, glass-rich Beo-14	72.5	10.2	3.3	11.0	97
	•		70.0	27.7	3.1	15.2	116
			65.0	27.9	3.0	16.1	112
	• 12.0		62.3	26.7	2.0	15.0	106
0 · 0 · 0 · 0 · 0 · 0 · 0 · 0 · 0 · 0 ·		<b>Beo-7</b> Light grey medium-grained tuff, glass-rich	62.0	28.5	1.4	14.1	106
0 · 0 . 0 · 0 . 0 · 0 . · 0 . · · · · · · · · · · · · · · · ·	•		62.3	29.6	2.4	18.3	86
0 · 0 . 0 · 0 . 0 · 0 . ~ .0 . ~ . 0 . ~ . 0 < 0 . 0 < 0 . 0 < 0 	15.0		63.8	24.2	2.0	17.0	107
	•	Beo-8 Light grey medium-grained tuff with biotite, zeolite-rich	72.5	20.8	1.6	25.1	120
일이 있는데 것이다. 같은 이 같은 이 같은 것			78.3	16.6	2.1	23.0	120
			87.5	20.4	1.1	27.0	136
탄하지 하지 않다. 지금 (지금 (지금 (지금 )			92.5	19.4	1.0	30.0	143
[아주아주아] [같이같이?	20.0		95.0	23.7	0.9	35.4	155
	• 21.0	Beo-9 Dark grey medium-grained tuff, zeolite-rich	102.5	20.4	1.2	38.0	162
	22.0	Dark grey marlstone					

Microscopic study revealed that altered volcanic glass (including zeolite minerals) predominantly occurs as glass shards. Detritus is made of phenocrysts and, rarely, larger pumice fragments. Quartz occurs as irregular angular grains, rarely in bipyramidal forms. Feldspars, represented mostly by sodic plagioclase, also occur as irregular grains with polysynthetic twinning lamellae. Biotite appears in the form of elongated flakes and is the most abundant mafic mineral, while amphiboles (hornblende) are quite rare. Carbonate minerals occasionally occur. Dimensions of mineral fragments vary according to the variety of tuff and, generally, become smaller upwards, which was also observed at outcrops in the open pit. Studied tuffs have either vitroclastic or vitrocrystalloclastic texture. In medium-

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grained tuff fossils were detected, indicating sedimentation in aqueous environment. Although the tuff is in general very pure, almost without any alochemic material, large cobbles and boulders of siltstone and fine-grained sandstone indicate a temporary input of terrigenous material into the basin.



Figure 2.Fine-grained zeolite tuff – typical texture formed by abundant glass shards in the matrix (Beo-8, ppl) - left; medium-grained zeolite tuff with fragments of quartz and plagioclase phenocrysts and fossil set in glassy matrix (Beo-9, xpl) -right.

ccording to SEM study, clinoptilolite is the dominant zeolite mineral. It differs in shape and grain size, from  $\sim 1\mu m$  flakes to  $\sim 5x7 \mu m$  tabular crystals (Fig. 3). Medium-grained tuff occasionally contains calcite. Glass shard relics are usually visible, displaying evidence of the initial stage of formation of clay and/or zeolite minerals (Fig. 3 C).



Figure 3. a) Typical texture of fine-grained clinoptilolite tuff (Beo-6); b) Different grain shape and size of clinoptilolite in fine-grained tuff (Beo-7); c) Clinoptilolite (cpt) formed by alteration of volcanic glass (Beo-6); d) Large calcite crystals in medium-grained tuff; calcite is associated with clinoptilolite (Beo-9).

# CONCLUSION

The Općište deposit is located near the Beočin Monastery, on the northern slopes of Fruška Gora. The zeolitized tuff is interstratified within Badenian marine marlstones. It occurs as one composite layer 8-25 m thick (~ 17 m in average). Eleven core samples of zeolite from 4 boreholes were studied by optical and scanning electron microscopy.

Tuff in the Općište deposit is underlain by dark grey marlstone of Badenian age. Typical cross-section through the tuff sequence (bottom to top direction) is as follows: marly tuff 0.6 m thick is the transition between marlstone and high-quality zeolite tuff. Economically important tuff sequence starts with medium- to coarse-grained zeolite tuff 1.0-1.6 m thick, followed by medium-grained zeolite tuff, occasionally with visible biotite flakes, with thickness from 0.6 to 8.8 m. Fine-grained zeolite tuff 2.1-8.5 m thick is the last one in zeolite-rich tuff variety. The lower quality tuff section starts either (but rarely) with medium-grained glass-rich zeolite tuff 1.0-16.0 m thick, or (usually) with fine-grained to very fine-grained glass-rich zeolite tuff 2 m thick was observed. The tuff section finishes with fragmented marly and clayey tuff. Zeolite rich and glass-rich zeolite tuff varieties were distinguished based on CEC values over 130 meq/100g for zeolite-rich tuff [10].

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