ZEOLITE DEPOSITS IN CROATIA

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ABSTRACT

In spite of the fact that zeolites have been found at several locations in Croatia, so far only two regions with economically interesting concentrations are known, both situated in northern part of the country.

The first one is located in the Macelj area in north-western part of Hrvatsko zagorje (NW Croatia) in which Lower Miocene (Egerian-Ottnangian) volcaniclastic rocks crop out on several localities. They have variable primary composition, and contain various alteration products of volcanic glass. The alteration products comprise zeolites (clinoptilolite as the most abundant zeolite, analcime and mordenite), clay minerals (smectite, authigenic mica), SiO_2 phases and authigenic feldspars. Performed investigations indicate that alteration products are the result of burial diagenesis.

In the other deposit, located in the vicinity of village Poljanska in Požega Valley, on the southern slopes of Mt. Papuk (Slavonian Mountains, N Croatia) analcime-bearing rocks can be found. Analcime was formed within closed hydrological system i.e. shallow saline alkaline lake which existed during early Miocene (Ottnangian) time.

Keywords: analcime, clinoptilolite, Croatia, mordenite, zeolite.

INTRODUCTION

So far zeolites have been found at several locations in Croatia, but mostly they are present in low concentrations. They were found in vugs and veins in altered volcanic rocks (ferrierite at Gotalovec [1], heulandite, mordenite, dachiardite at Lepoglava (Figure 1.)[2], laumontite at Hruškovec [3]), in altered pyroclastic rocks (analcime at Muć [4], clinoptilolite at Maovice [5] and Medvednica Mt. [6]), and cement in sandstone (laumontite and stilbite at Velešnja [7]).

Figure 1. SEM photograph of mordenite and opal-CT from vein in altered pyroclastic rock from Lepoglava [2]

According to present knowledge in Croatia only two regions with economically interesting concentrations of zeolites are known, one in situated in Hrvatsko zagorje (NW Croatia) and the other in Slavonia (N Croatia). Both belong to the Pannonian Basin. Due to diverse application of zeolites these deposits were investigated intensively during past thirty years e.g. [8], [9]. In this paper resume of these investigations will be given.

EXPERIMENTAL

Rocks were investigated in the field in order to determine their structures, spatial distribution and relation between different varieties. Laboratory investigations comprise optical microscopy (determination of textures, mineral composition and mineral reactions), scanning electron microscopy (Philips SEM 515 equipped with a PV 9900 energy-dispersive X-ray analyzer), X-ray powder diffraction (mainly) on whole rock samples (qualitative and semiquantitative phase analysis), chemical analyses of rocks (wet chemical analyses and X-ray fluorescence spectrometry - ARL 8410 spectrometer, Rh-tube, main elements were measured on glass beads, while trace elements were analyzed on pressed powder pellets [10]) and minerals (polished, carbon coated thin sections analysed by CAMECA/CAMEBAX and JEOL 8230 electron microprobes), CEC measurements [11] and IR-spectroscopy.

RESULTS, DISCUSSION AND CONCLUSIONS

In the Macelj area in north-western part of Hrvatsko zagorje (NW Croatia) Lower Miocene volcaniclastic rocks, up to 100 meters in thickness, have been described on several localities. They occur in two horizons, "older pyroclastic horizon" and "younger pyroclastic horizon" of Egerian and Ottnangian age respectively, interbedded with shallow-sea clastic sediments within the elongated syncline which gradually sinks towards the east (Figure 2A.) [12].

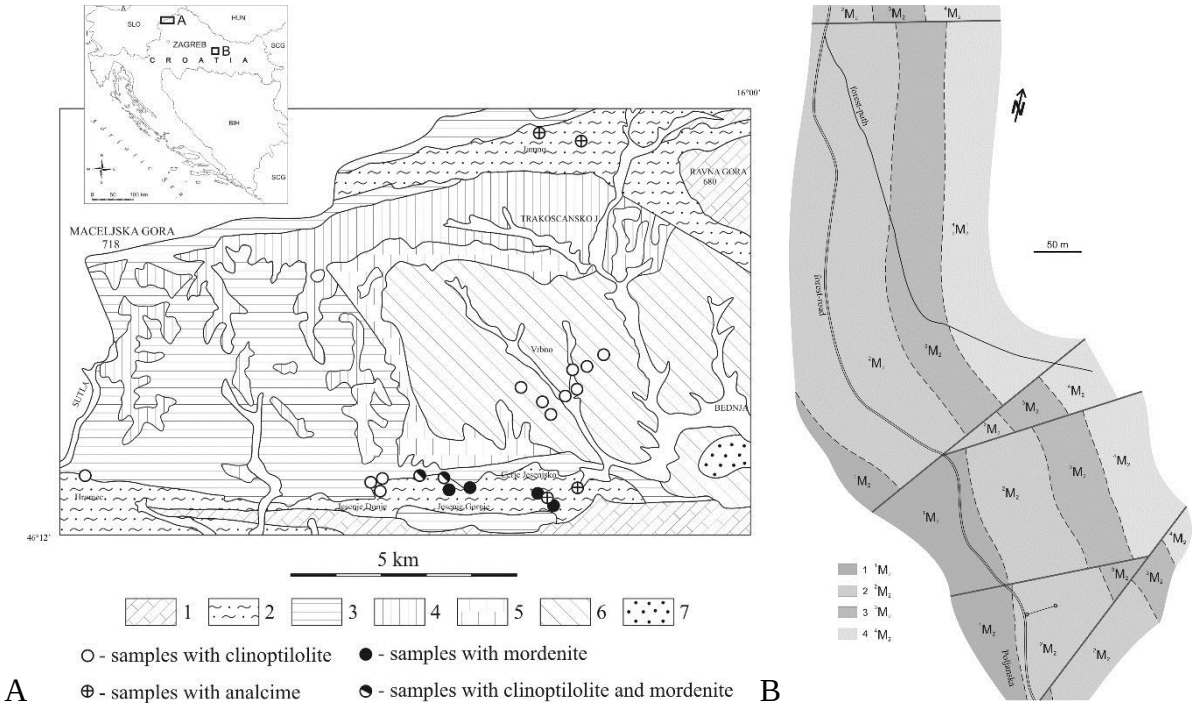
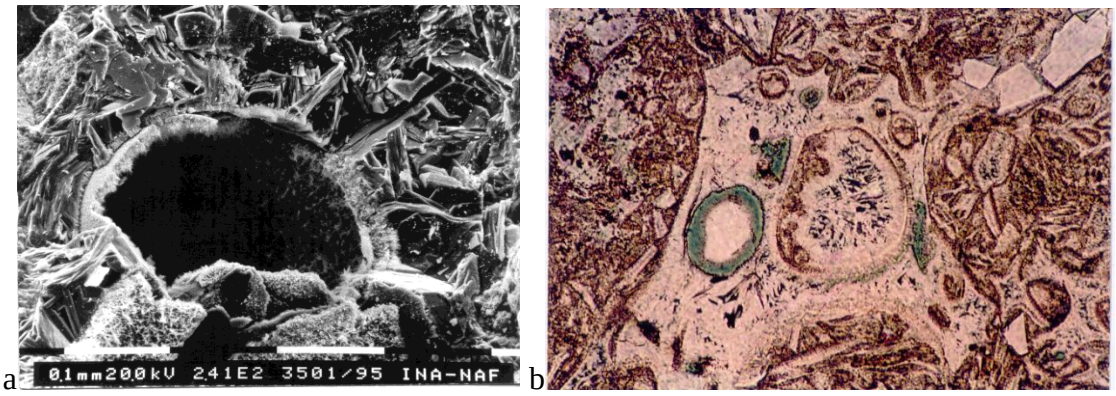


Figure 2. Simplified geological maps: A - of the northwestern part of Hrvatsko zagorje [12] showing outcrops of volcaniclastic rocks containing zeolites. Legend: 1. Triassic: dolomite and limestone; 2. Egerian: sand, gravel, marl, clay and older volcaniclastics; 3.-5. Eggenburgian (different members of the Macelj formation): conglomerate, sandstone, siltstone, marl, clay; 6. Ottnangian: conglomerate, sandstone, marl, clay and younger volcaniclastics 7. Karpatian-Badenian: gravel, sand, limestone, marl; B – of the Poljanska deposit in Slavonia opened in Ottnangian sediments. Legend: 1. footwall: calcareous shales; 2. I productive horizon: dolomites;

dolomitic marls, analcime-bearing rocks; 3. marly interhorizon; 4. II productive horizon: dolomites; dolomitic marls, analcime-bearing rocks.

Volcaniclastic rocks have variable primary composition, and contain various alteration products of volcanic glass (Figure 3). The alteration products comprise zeolites, clay minerals (smectite, authigenic mica), SiO_2 phases and authigenic feldspars. Clinoptilolite (according to the Si/Al ratio [13]) is the most abundant zeolite, however analcime and mordenite are also present. The type of exchangeable cations in clinoptilolite is variable; therefore clinoptilolites were divided into three subgroups: Ca-, Ca-K-, and Na-rich. Clinoptilolite content in the volcaniclastic rocks discovered in Macelj area varies significantly, in some rocks it is the dominant component, in others it is present only in traces. In Donje Jesenje quarry, in which due to exploitation the best outcrops of these rocks can be found, the variations, although present, are not so conspicuous, and the average content of clinoptilolite is approximately 50 wt. %. Alteration of volcanic glass is the result of burial diagenesis. Different alteration products are most probably due to different temperatures to which sediments were exposed, with increasing depth of burial clinoptilolite transformed to mordenite and analcime, while opal-CT changed to opal-C and recrystallized to quartz. However different immobile element content of rocks containing different alteration products indicates that alteration was probably also dependent on chemical composition of the rocks. Sometimes type of alteration product was also dependent on chemical composition of primary material and its granulometric characteristics. Huge reserves of volcaniclastic rocks make them economically interesting, nevertheless it will be necessary to take care about raw material properties i.e. zeolite content and its chemical composition, when planning its particular application.



a b

Figure 3. SEM microphotograph of volcanic glass shard altered to platy clinoptilolite. Vesicle within the shard is lined by laths of authigenic mica (a), Microphotograph of tuff from Donje Jesenje quarry (b) showing glass shard altered to platy clinoptiloite and authigenic mica (celadonite) present as lining of vesicle (diameter of the vesicle is ca. 0.1 mm).

The other zeolite deposit is located in Slavonian Mountains, on the southern slopes of Mt. Papuk in the vicinity of village Poljanska in Požega Valley. In the deposit four horizons that are results of changes in climate and related variations in sedimentary basin characteristics can be differentiated; two with analcime-bearing rocks (used in cement industry for improving pozzolanic properties) which are underlain by sandy calcareous shales and separated by marly horizon (Figure 2B.).

The analcime-bearing rocks are of hybrid composition. They contain, in layered or laminar alternation or mixed together, in various proportions, authigenic dolomite, volcaniclastic, and pyroclastic particles from neighbouring ancient volcanoes as well as terrigenous psamitic and pelitic material. The analcime, that is present as dispersed grains or in monomineral laminae and thin layers, was formed by alteration of pyroclastic material (and

possibly detrital clays) within closed hydrological system i.e. shallow saline alkaline lake which existed during early Miocene (Ottnangian) time due to arid and semiarid climates. Depositional environment was determined on the basis of mineral parageneses (analcime, dolomite, and hydrous Ca-bearing magnesium carbonate [14]) sedimentary textures e.g. salt crystal prints, desiccation cracks etc. The conditions in such lake were also favourable for formation of dolomicrites. On the contrary calcareous footwall and marly interhorizon were deposited during more humid climates in a deeper lake characterized by fresh to brakish water in which montmorillonite and minor clinoptilolite were formed as alteration products.

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