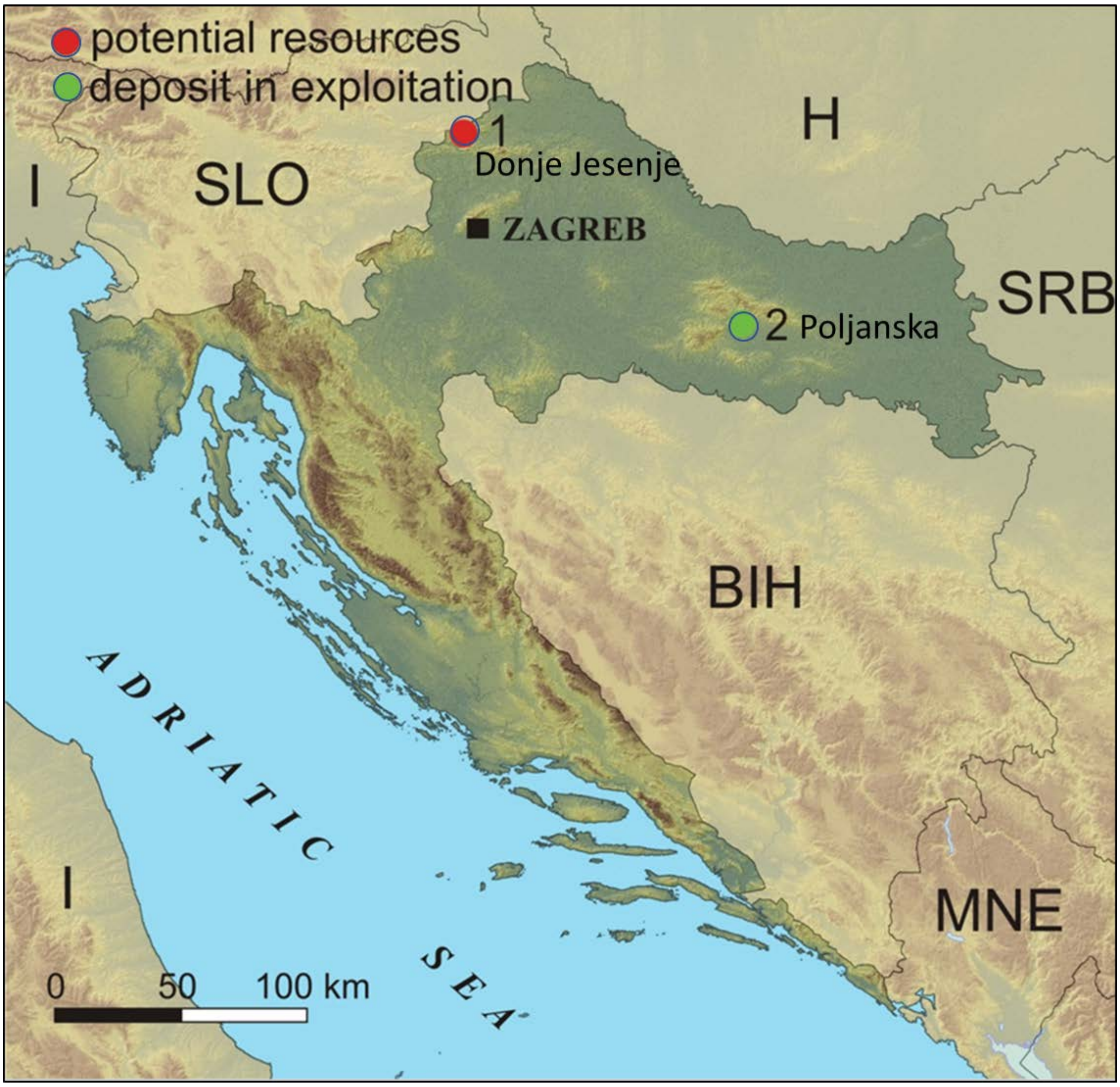
Sedimentary Zeolite Deposits in Croatia



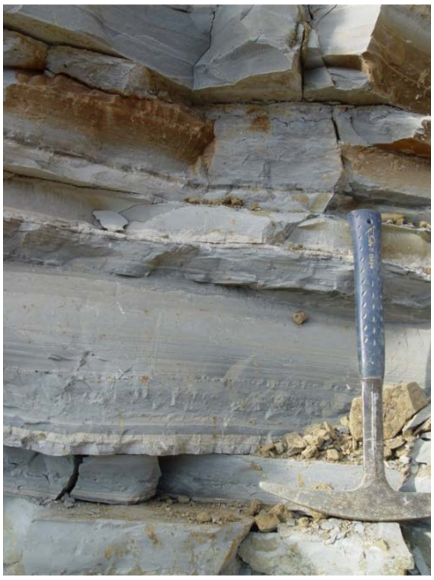
I = Italy; SLO = Slovenia; H = Hungary; SRB = Serbia; BIH = Bosnia and Herzegovina; MNE = Montenegro

Introduction:

Both of the sedimentary zeolite deposits in Croatia (see map) are of Early Miocene Age. They are located in the northern part of Croatia, which geologically belongs to the Pannonian Basin System (PBS), extension structure formed at the beginning of the Miocene as a result of continental collision of Africa (Adriatic microplate) and Europe. The PBS is surrounded by mountain chains comprising the Alps, Carpathians and Dinarides, and palaeogeographically it occupies most of the Central Paratethys realm. Two basins with different depositional histories evolved in the area of north Croatia during the Early Miocene: the Hrvatsko Zagorje Basin (HZB), which occupied a small area in the north-westernmost part extending westwards into Slovenia, and the North Croatian Basin (NCB), that covered almost the entire area of north Croatia. Very important depositional differences occurred between the basins in the Early Miocene. The HZB was a part of the Central Paratethys characterized by brackish to marine deposition from the end of Oligocene/beginning of Miocene (Egerian and Eggenburgian) through almost the whole Miocene, except from the second part of Early Miocene (i.e. during late Ottnangian and Karpatian) till early Middle Miocene (i.e early Badenian). In the NCB deposition commenced later, in the Ottnangian, with the formation of continental environments after a long-lasting emersion. This was replaced by marine sedimentation in the Middle Miocene, i.e. in the middle Badenian (Pavelić and Kovačić, 2018 and references therein).

POLJANSKA

Zeolite occurrence: Analcime bearing sedimentary rocks.



Poljanska quarry: (left) general view; (right) typical laminated carbonate-analcime sedimentary rock.

Geology: The Early Miocene (Ottnangian) Poljanska deposit was formed in the NCB, an elongated rift-type basin generated by continental passive rifting that commenced in the Early Miocene, when normal listric faulting generated extension of the basin. The extensional tectonics formed four half-grabens as elongated subbasins that represented main depocentres. The Poljanska deposit is located in one of them, namely the Bjelovar Depression that continues into the Požega Depression. The basin evolved in two phases: the syn-rift phase which lasted from the Ottnangian until the middle Badenian, and the late Badenian to the Quaternary post-rift phase. The syn-rift phase was characterized by depositional environments that changed from continental to marine environments (Šćavničar *et al.*, 1983; Pavelić *et al.*, 2016; Kovačić *et al.*, 2017). The rocks exposed in the Poljanska quarry were deposited in shallow lacustrine environments which predate the Middle Miocene marine transgression of the Paratethys Sea. The lacustrine deposition most probably commenced in the Early Miocene and continued during the Middle Miocene. These geological periods are characterised by the alternation of warm and wet subtropical periods and periods of hot and arid climate, together with abundant volcanic activity. During the humid climate in fresh- or brackish-water lacustrine environments, pelites and marls were deposited. In contrast, during arid climate periods dolomites and hydrous Ca-bearing magnesium carbonate (HCMC) were deposited in a lake which had characteristics of an isolated salina-type lake. Dolomite layers alternate with analcimolite layers, which are a result of the alteration of tuff and/or clay minerals in an alkaline lake environment (Šćavničar *et al.*, 1983). Tuff and tuffite layers indicate abundant volcanic activity at the end of the Early Miocene and the beginning of the Middle Miocene in the area of the SW PBS. Such activity produced large quantities of pyroclastic material, which altered into smectite during humid periods or into analcime during more arid periods. Sandstone beds from the upper part of the succession indicate that metamorphic and granitoid basement rocks of the PBS were exposed on the surface, providing clastic material. The increased supply of the sandy material, along with the deposition of marly sediments, indicates a gradual establishment of more humid conditions and the formation of a large open lake in the Lower Badenian, which was later, during the Badenian, around 15 Ma ago replaced by a marine setting (Šćavničar *et al.*, 1983; Pavelić *et al.*, 2016; Kovačić *et al.*, 2017).

Mineralogy:

In the quarry a more than 40 m thick sedimentary succession is exposed at the surface. The succession is divided in three parts. The lower part is characterised by the alternation of calcitic marls and tuffitic layers. Calcitic marls rich in fossil macro flora contain analcime. The tuffite layers, 10-30 cm thick, consist of altered vitroclasts, feldspar crystaloclasts, analcime, carbonate minerals, and detrital grains of quartz, feldspar, amphibole and mica. The thickest, middle part of the section is mostly composed of a few cm to several dm thick, massive, horizontally laminated or tectonically deformed carbonate-analcime sedimentary rocks. Carbonate minerals are crypto- to microcrystalline, concentrated in some lamina or homogeneously dispersed in rock. Dolomite is the most abundant carbonate mineral, but HCMC characteristic of playa environments is also detected in almost all samples. The analcime is cryptocrystalline and homogeneously dispersed within the rock or concentrated within the laminae in the up to 50 µm-sized isometric crystals. Minor natrolite, the other zeolite mineral characteristic of a saline environment, is also present. In the middle part of the succession sandstone layers (cm-2 m thick) occur beside the dominant analcime-carbonate layers. The sandstone is poorly sorted with grains derived from the locally uplifted metamorphic and granitoid basement rocks of the Pannonian basin. The upper part of the section, which is exposed laterally in the quarry, consists of thin layered fossiliferous marls (Kovačić *et al.*, 2017). Mineral composition of dominant rock types is shown in Table 1.

Table 1: Mineral composition (wt%) of representative samples of marls, dolomite- and analcime-rich rocks from Poljanska.

Phase	Marl	Dolomite with analcime	Dolomitic analcimolite
Analcime	18	15	50
Dolomite		45	30
Calcite	40		
HCMC		15	5
Plagioclase feldspar	10	5	5
K-feldspar	5	10	7
Illite/muscovite	14	3	1
Chlorite	2	1	2
Montmorillonite	2		
Pyrite	3	1	
Organic material	5	5	
Amorphous	1		

Chemistry
Sedimentary rocks:

Table 2: Chemical composition (wt%) of the representative samples of Table 1.

SiO_2	32.85	25.31	38.29
Al_2O_3	13.69	10.15	16.43
Fe_2O_3	4.72	5.06	3.73
MgO	3.02	11.25	5.98
CaO	18.03	12.99	7.73
Na_2O	2.37	2.06	7.23
K_2O	2.19	3.16	1.27
TiO_2	0.58	0.46	0.30
P_2O_5	0.10	0.04	0.19
MnO	0.09	0.11	0.08
Cr_2O_3	0.01	0.01	0.02
LOI	22.10	29.00	18.50

Analcime:

The chemical composition of analcime from Poljanska, analysed by microprobe, is shown in Table 3 (Jelavić, 2012). The corresponding crystal chemical formula of analcime is:

$(Na_{14.72}K_{0.08}Ca_{0.15}Mg_{0.23})[Si_{32.46}Al_{15.21}Fe_{0.28}Mn_{0.05}O_{96}]\cdot 19.65H_2O$.

Table 3: Chemical composition (wt%) of analcime from Poljanska.

SiO_2	54.44
Al_2O_3	21.64
Fe_2O_3	0.61
MgO	0.25
CaO	0.24
Na_2O	12.73
K_2O	2.19
TiO_2	n.d.
MnO	0.11
H_2O	9.88
Total	100.00
E%	-0.45

n.d. = not determined.
E% = balance error according to Gottardi and Galli (1985).

Crystallography:

The unit cell parameters of analcime from Poljanska are (Jelavić, 2012):

a [Å]	**V** [Å^3]
13.710(4)	2577

Physical and mechanical properties:

Table 4: Main physical properties of rocks from Poljanska.

Appearance (colour)	Greenish or brownish grey
Pozzolanic activity class	50-100
Density	2.46-2.68 g/cm^3
Bulk density	1.84-2.38 g/cm^3
Compressive strength	4.2-13.8 MPa
Bending strength	1.5-3.7 MPa

Reserves, production and main applications:

Estimated reserves in Poljanska quarry (at the end of 2016) are approximately 3,900,000 tonnes. Exploitation started in 1980, till 2018 approximately 730,000 tonnes were exploited, with average annual production in last years in the order of 10,000 tonnes. The material is used exclusively as a pozzolanic addition in the cement industry.

DONJE JESENJE

Zeolite occurrence:

Clinoptilolite-rich tuff.

Geology:

The Early Miocene (Eggenburgian) Donje Jesenje deposit was developed within the HZB. Due to the collision of the Adriatic microplate and the European foreland, the regional stress was characterized by a main NS compression axis with EW extension during the Oligocene and Miocene. Dextral strike slip fault systems were formed, representing the eastern continuation of the Periadriatic lineament. Associated with these fault systems is the occurrence of synsedimentary volcanism in the Egerian (andesite and pyroclastic rocks), Eggenburgian and Ottnangian (tuffs, tuffites and bentonites). The onset of the Eggenburgian was marked by a transgression and deposition of sands, glauconitic sands and pyroclastics in the coastal environment, coinciding with sea level rise in the Central Paratethys. Tuffs prevail among the Eggenburgian pyroclastics which were probably deposited in a marine environment. They are best exposed in the Donje Jesenje quarry, where vertical alternation of vitroclastic, vitrocrystalloclastic, crystalloclastic and crystallolithoclastic types is visible. Pyroclastic rocks have variable primary composition: the main constituents of vitroclastic and crystalloclastic tuffs are volcanic glass, plagioclase feldspars (andesine) and biotite, while amphibole and quartz are rare. Lithoclastic tuffs are composed of tuff and effusive rocks fragments, and in smaller quantities mineral fragments and glass. In the quarry SiO_2 content varies between 65 and 70 %, and therefore the tuff is dacitic. Alteration of volcanic glass is the result of burial diagenesis. Different alteration products are most probably due to temperature increase with increasing depth of burial. Clinoptilolite was 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. In some instances, the type of alteration product was also dependent on the grain size of the primary material (Avanić et al., 2018a, b and references therein).

Eggenburgian pyroclastic rocks in Donje Jesenje quarry

Typical tuff from Donje Jesenje.

Mineralogy

The pyroclastic rocks contain various alteration products of volcanic glass. The alteration products comprise zeolites, clay minerals (smectite, authigenic mica), SiO_2 phases and authigenic feldspars. Clinoptilolite (based on the Si/Al ratio) is the most abundant zeolite, however minor mordenite and analcime are also present (Table 5). The type of exchangeable cations in clinoptilolite is variable; therefore, clinoptilolites were divided into two subgroups: Ca-K- (present in the upper part of the quarry), and Na-rich (present in the lower part). Clinoptilolite content varies; the average content of clinoptilolite is approximately 50 wt% (Tibljaš, 1996; Tibljaš and Šćavničar, 2007).

Table 5: Mineral composition of representative tuff sample from Donje Jesenje (Hrenović et al., 2011).

Phase	Wt%
Clinoptilolite	50-55
Plagioclase feldspar	10-15
Opal-CT	10-15
Illite/celedonite	10-15
Quartz	traces
Analcime	traces

Chemistry:
Clinoptilolite

The following table (Table 6) reports the chemical composition (wt%) of the representative sample of clinoptilolite-bearing tuff from Donje Jesenje (Tibljaš, 1996).

SiO_2	70.09
Al_2O_3	11.03
TiO_2	0.09
Fe_2O_3	1.25
MnO	n.d.
CaO	2.43
MgO	0.88
K_2O	2.93
Na_2O	0.61
P_2O_5	0.04
H_2O	10.50

n.d. = not determined.

The cation exchange capacity (CEC), based on cation displacement by a NH_4^+ solution (Minato, 1997) followed by determination of NH_4^+ ions by an ion-selective electrode ranges from 40 to 160 mequiv/100 g.

The chemical composition of clinoptilolite from a representative Donje Jesenje sample, analysed by microprobe, is shown in Table 7 (Tibljaš, 1996). The corresponding crystal chemical formula of clinoptilolite is:

$$(Na_{0.25}K_{1.00}Ba_{0.01})(Ca_{1.58}Mg_{0.73})[Al_{6.24}Si_{29.85}O_{72}]\cdot 18.46H_2O.$$

Table 7: Chemical composition (wt%) of clinoptilolite from Donje Jesenje.

SiO_2	68.48
Al_2O_3	12.14
Fe_2O_3	<0.01
MgO	1.12
CaO	3.39
BaO	0.09
Na_2O	0.29
K_2O	1.79
H_2O	12.70
Total	100.00
E%	5.95

E% = balance error according to Gottardi and Galli (1985).

Crystallography:

The unit cell parameters of clinoptilolite from Donje Jesenje are as follows (Tibljaš and Šćavničar, 1988):

a [Å]	**b** [Å]	**c** [Å]	**β** [°]	**V** [Å^3]
17.647(6)	18.007(8)	7.396(3)	116.34(2)	2106

Physical and mechanical properties*:*

Table 8: Physical and mechanical properties of clinoptilolite-bearing tuffs from Donje Jesenje (Kruk *et al*., 2014; Tušek *et al*., 2017):.

Appearance (colour)	Mostly light-green
Pozzolanic activity class	Almost 150
Density	2.39g/cm^3
Surface area (3–60 µm powder)	12,055 m^2/g

Reserves, production and main applications*:*

In the Donje Jesenje quarry, abandoned in the first decade of 21st century, the thickness of the pyroclastic rocks as determined by exploration drilling is approximately 60 m (Golub and Brajdić, 1969; Marković, 2002). The material was first used as ornamental building stone, then as an additive in cement industry, and lately as a soil additive, litter additive and for wastewater and sewage water purification. Estimated zeolitized rock reserves are in the order of 3,000,000 tonnes (Kruk *et al*., 2014).

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