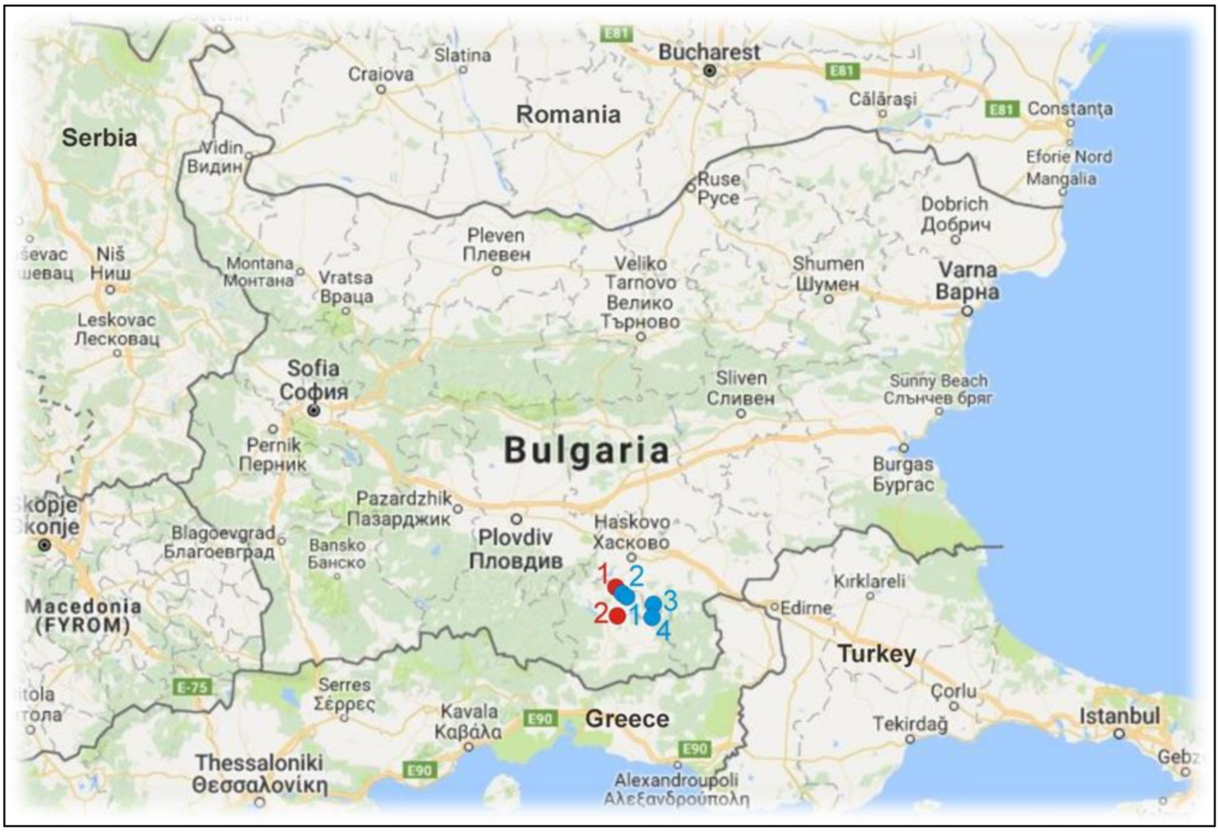
Sedimentary Zeolite Deposits in Bulgaria



Exploited deposits:

1. Beli Plast (Cpt);
2. Beliya Bair-Zhelezni Vrata (Cpt).

Unexploited but explored deposits:

1. Most (Cpt);
2. Gorna Krepost (Cpt);
3. Lyaskovets (Mor, Cpt);
4. Golobradovo (Cpt).

Geology:

Bulgarian zeolite deposits are genetically related to and hosted within the explosive products of volcanic activity that took place during Paleogene in the eastern parts of Rhodopes Mountain, South Bulgaria. The volcanism resulted from the continental collision between the south edge of Eurasian plate and parts of African plate (Yanev 1995, Yanev *et al.*, 1998). The volcanic activity was bimodal in composition (intermediate to basaltic and acid, mainly high-K Ca-alkaline and shoshonitic) and cyclic in character as four intermediate phases alternated with five acidic ones (Yanev et al., 1998 and the references therein). Volcanic activity took place in both marine and subaerial environment but wherever the vents were located, the larger part of the erupted tephra was deposited in marine environment where metastable volcanic glass was easily transformed to more stable phases. Secondary glass-replacing mineral associations are dominated mainly by zeolites (clinoptilolite, rarely mordenite and analcime), sometimes by clays or feldspar-quartz aggregate. Zeolites are the most abundant authigenic minerals especially in the acid in composition pyroclastic rocks (Aleksiev 1968; Aleksiev & Djourova 1976; 1982; Aleksiev *et al.* 1997; 2009; Djourova 1976; Djourova & Aleksiev 1983; 1989; 1990; 1995; Djourova & Ivchinova 1987; Djourova & Boyadjiev 1999; Kirov 1974; Ivanova *et al.* 2001; 2010a; 2010b; 2011; 2014; Ivanova & Gier 2006; Rens *et al.* 2010, Yanev *et al.* 2006, Yanev & Ivanova 2010). Perlite glass that is sometimes present in the periphery of lava domes can also be zeolitized (Kanazirski & Yanev 1983; Yanev *et al.* 1986, 1993).

Commercially potential zeolite deposits are genetically connected to the explosive products of 1st and 2nd Early Oligocene (Rupelian) acid phases as 5 clinoptilolite (Most, Gorna Krepost, Beli Plast, Golobradovo, Beliya Bair-Zhelezni Vrata) and 1 mordenite (Lyaskovets) deposits were identified and explored by drilling (Aleksiev & Djourova 1976; Aleksiev *et al.* 1997; Djourova & Aleksiev 1984, 1988, 1990, 1995, Raynov *et al.* 1997; Yanev *et al.* 2004, 2006, Yanev & Ivanova 2010).

First Rupelian acid phase (~34 Ma, Lilov *et al.* 1987) occurred in the beginning of the Oligocene. The explosive products are zonally arrangement around the vent: pyroclastic flows accompanied by fall-out tuffs dominate in the central zone, fall-out tuffs alternating with limestones occur in peripheral and pure sediments with dispersed pyroclastic material are exposed in distal zones (Yanev, 1995, Yanev *et al.* 2006). The flow products (weakly to moderately welded ignimbrites) and fall-out tuffs in the central zone crop out over an area of about 65 × 15-30 km. They are 110-120 m thick near the vent and 30-50 m – in the peripheral parts. These rocks host the largest zeolite deposits explored so far in Bulgaria: clinoptilolite deposits Beli Plast, Gorna Krepost, Most and Golobradvo and mordenite deposit Lyaskovets (Figs. 1-3).

Figure 1: The quarry of Beli Plast deposit (Cpt)

Figure 2: Zhelezni Vrata (trass) quarry, Belia Bair – Zhelezni Vrata deposit (Cpt)

Fig. 3. Golobradovo deposit

Second Rupelian acid phase (32–33 Ma) was even more paroxysmal. The resulting pyroclastics (also of flow and fall origin), erupted from several vents, were spread all over the Eastern Rhodopes covering an area of about 80 × 60 km. Many zeolite occurrences are related to these rocks but just one clinoptilolite deposit (Beliya Bair - Zhelezni Vrata) has been identified. The thickness of the zeolitized section varies from tens to 100-120 m in the deposit area where the section is composed by an alteration of non-welded ignimbrite units and fall-out tuffs (Djourova & Aleksiev 1990; Yanev *et al*., 2004, 2006).

There are several ideas on the nature of the glass alteration and the main factors affecting this process in the area of Eastern Rhodopes (Aleksiev & Djourova 1975; Kirov *et al*. 1976; Kirov & Petrova 2009; Kirov *et al*., 2010; 2011; Ivanova 2016; Yanev *et al*. 2006). Aleksiev & Djourova (1975, 1988) proposed an original geoautoclave hypothesis to explain zeolitization of thick pyroclastic sections of flow origin. Yanev *et al*. (2006) argued that zeolitization in Eastern Rhodopes is a low-temperature hydrothermal process. The hydrothermal solutions are thought to consist of marine water heated by the anomalous geothermal gradient in active volcanic areas or/and by the hot pyroclastic rocks. Source area proximity and thickness of the deposits were also considered. The concept of Kirov *et al*. (2011) is based on the classic ideas of Hay and suggests closed system diagenetic alteration.

Mineralogy

Zeolite deposits-hosting pyroclastic sections in the Eastern Rhodopes are composite successions, built up by more than one depositional unit. Although all they are rich in glass particles there are always some magmatic crystals and non-glassy lithic fragments present. Their quantity is low but can vary even within the volume of one depositional unit. The most common magmatic minerals are quartz and feldspars, mainly plagioclase (Table 1). Secondary mineral associations appear as a result of volcanic glass alteration. The process of glass alteration involves all glass particles (shards, pumice and perlite fragments if present) but larger shards and ash-sized pumice seem to be the most suitable precursor material in the area for zeolites to grow. The alteration of larger pumice as well as tiniest ash shards result in clay-rich secondary mineral associations (Ivanova, 2016).

Clinoptilolite is the most abundant volcanic glass-replacing mineral in the Eastern Rhodopes. Mordenite and analcime are rarer. Clinoptilolite, as well as the other zeolites, always associate with some phillosillicates (montmorillonite, mixed-layered illite/smectite and pure 10Å varieties as celadonite), opal-CT, and feldspars (mainly adularia). Traces of calcite, commonly associated with fossil remnants, can be also present (Table 1 and Fig. 4).

Table 1. Mineral composition (%) of zeolite deposits, based on XRD and DTA data, and CEC values*

Deposits	Thickness [m]	Number of samples	Minerals[1]								CEC[2] meq/100g
			Hydrothermal						*Crystal clasts*		
			Cpt	Mont	10Å[2]	Ad+San	O-CT	Cal	*Q*	Pl+Ab	
Beli Plast	~70	56	80 52–95	6.2 2–16	2.9 1–9	4.3 0–22	1 0–5	0.6 0–9	0.7 0–2	4.9 0–7	106-166
Most	≤90	120	78 71–88	5.3 1–15	2.5 1–6	6.8 1–17	2.5 1–4	0.6 0–4	0.6 0–3	2.3 0–6	117-150
Gorna Krepost	≤90	101	84 73–90	4.5 2–13	1.4 0–5	4.7 1–13	1.9 0–3	0.2 0–1	1.1 0–2	1.7 0–4	75-153
Golobra-dovo	~80	33	75 54–93	5.4 0–10	2.9 2–7	5.1 1–14	1.6 0–2	4.1 0–11	1.2 0–5	3.8 0–6	146-159
Beliya Bair	~70	42	52.8 39–68	7.8 2–18	4 2–8	17.4 9–30	4.3 1–12	0.9 0–3	4.6 1–8	7.5 5–15	83-151

* Data from Raynov *et al*. 1997. Mineral composition: [$\frac{\text{average}}{\text{min-max}}$]; CEC: (min-max).

[1] Abbreviations: Cpt – clinoptilolite, Mont – montmorillonite, 10Å – Illite in Beli Plast, celadonite in Gorna Krepost and Golobradovo, Ad – adularia, San – sanidine, O-CT – opal-cristobalite/tridymite. Cal – calcite, Q – quartz, Pl – plagiolclase, Ab– albite (secondary albite was identified in Beliya Bair); [2]The method of CEC values estimation was not indicated.

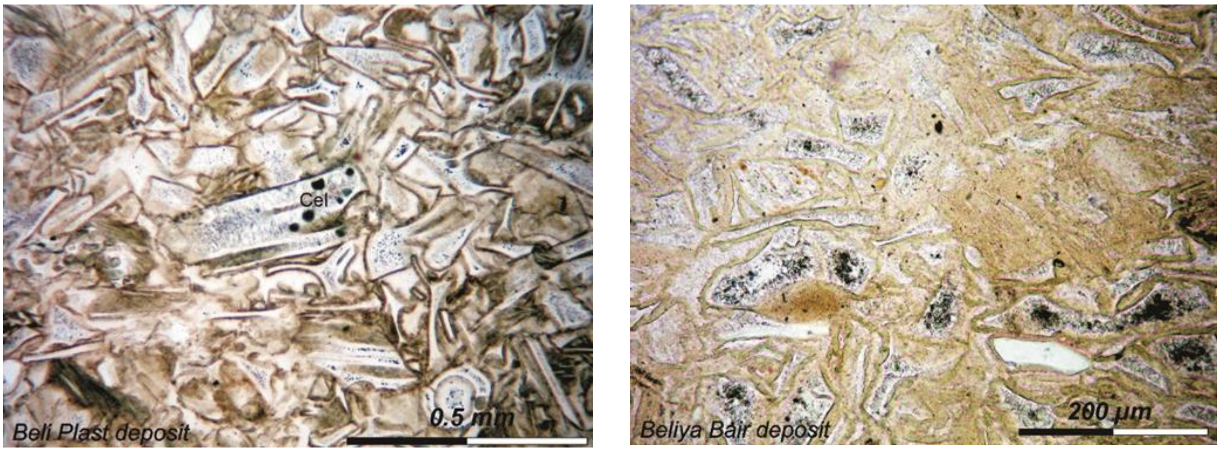


Fig. 4. Microphotographs of zeolitized ash tuffs from Beli Plast (I[st] Rupelian acid phase) and Beliya Bair - Zhelezni Vrata (II[nd] Rupelian acid phase) deposits; Cel – celadonite. Dark impurities visible in the central parts of the larger zeolitized shards on the right photo are from the polishing powder

The intense greenish colouration typical of all deposits, related to the first Rupelian acid phase, is due to the formation of green Fe-rich phyllosilicate mineral (celadonite, Fig. 3). Celadonite from Beli Plast deposit has the following composition (Burlet, 1997):

$$(Si_{3.98}Al_{0.02}O_{11})(Al_{0.44}Fe_{1.16}Mg_{0.42}Ti_{0.11}Mn_{0.01})\ K_{0.80}Na_{0.01}Ca_{0.03}.$$

Average clinoptilolite content for each of the clinoptilolite deposits varies between ~53 and 84% (Table 1, Raynov *et al*., 1997), being higher in Gorna Krepost and Beli Plast: 84% and 80%, respectively.

Although known as mordenite deposit, both clinoptilolite and mordenite were identified in the pyroclastic section near Lyaskovets village and according to Aleksiev *et al*. (1976) mordenite resulted from clinoptilolite alteration.

Rock Chemistry: The available data on whole-rock chemistry and cation exchange capacity of zeolitized pyroclastic rocks hosting largest Bulgarian zeolite deposits are given in Table 2. Some additional data can also be found in Djurova *et al*., 1989.

Table 2. Whole-rock composition of clinoptilolite-rich pyroclastics from different deposits (part I)

Oxides	Deposits							
	Beli Plast *(Djourova, Aleksiev, 1995)*	**Zhelezni Vrata** *(Yanev et al., 2004)*		**Beliya Bair** (*Yanev et al., 2004*)			**Gorna Krepost** *(Alexiev et al., 2009)*	
	Method: **WCA**[1]	**XRF**					**WCA**	
	Unit: –	Fall-out	Ignimbr.	Ignimbrite			Ash flow	Ignimbr.
	Samples: 9	–	–	–	–	–	3	3
SiO_2	65.73	70.91	70.62	73.30	73.32	73.46	66.27	65.88
TiO_2	0.13	0.10	0.15	0.14	0.13	0.10	0.22	0.22
Al_2O_3	11.04	10.72	11.56	11.14	11.53	10.14	11.02	11.46
Fe_2O_3	0.88	0.84	1.55	1.38	1.19	0.41	0.30	0.63
MnO	3.68	0.04	0.01	0.01	-	0.01	0.02	0.03
MgO	0.88	0.40	0.40	0.39	0.32	0.25	0.95	1.02
CaO	0.30	1.51	1.63	1.31	1.20	1.20	2.88	2.66
Na_2O	2.46	1.64	2.13	1.85	1.45	0.79	0.15	0.35
K_2O	2.69	2.44	2.94	3.66	3.56	4.21	3.65	4.48
P_2O_5	-	0.07	0.11	0.12	0.08	0.09	0.37	0.27
H_2O	-	-	-	-	-	-	4.89	4.62
H_2O^+	-	10.62	8.14	5.95	5.64	8.48	-	-
LOI	14.65	-	-	-	-	-	8.88	8.21

[1]WCA: wet chemical analysis.

Table 2. Whole-rock composition of clinoptilolite-rich pyroclastics from different deposits (part II)

Oxides	Deposits						
	Most			**Lyaskovets**		**Golobradovo**	
	Brunkin et al., 1984[1]	*Yanev et al., 2006*		*Konkin et al., 1988*[1]		*Yanev et al., 2006*	
	Method: **WCA**	**IPC-AES**		**WCA**		**IPC-AES**	
	Unit: –	Ash tuff	Ignimbr.	–	–[2]	Ignimbrite	
	Samples:	–	–	20	44	–	–
SiO_2	66.20	67.13	69.11	68.6	72.2	67.23	66.02
TiO_2	0.15	0.15	0.14	0.2	0.2	0.16	0.15
Al_2O_3	11.60	11.26	11.33	12.2	12.5	10.97	11.12
Fe_2O_3	0.89	0.83	0.83	1	1.4	0.81	1.02
MnO	-	0.01	0.01	0.5	0.2	0.03	0.04
MgO	0.80	0.91	0.98	0.1	0.1	0.85	0.67
CaO	3.10	2.94	2.35	0.6	0.1	2.91	3.20
Na_2O	0.53	0.25	0.20	2.1	2.2	1.12	2.04
K_2O	3.50	3.49	4.26	2.1	0.3	1.80	2.40
P_2O_5	-	-	-	0.05[3]	0.05	-	-
H_2O	-	0.71	2.27	-	-	2.47	2.69
H_2O^+	-	12.09	8.84	3.5[3]	5.0	12.10	10.89
LOI	6.70	-	-	-	-	-	-

[1] Unpublished geological records. [2] Mordenite-rich samples. [3] Average from 9 samples.

Zeolite Chemistry: The available data on the zeolite (clinoptilolite) chemistry are are listed in Table 3.

Table 3. Average microprobe analyses of clinoptilolite (Yanev *et al*., 2006)[1]

	Beli Plast	**Zhelezni Vrata** quarry	Beliya Bair				Gorna Krepost	Most			Golobradovo
SiO_2	68.14	64.43	66.84	62.31	62.38	64.95	68.33	67.03	67.61	66.24	67.84
Al_2O_3	11.98	11.95	12.22	11.45	11.85	12.31	11.89	11.50	11.90	11.74	11.80
Fe_2O_{3tot}	0.03	0.03	0.04	0.03	0.05	0.04	0.46	0.07	0.08	0.24	0.08
MgO	0.05	0.35	0.24	0.26	0.33	0.39	1.08	0.72	0.62	0.70	0.59
CaO	2.40	2.61	2.07	1.73	2.32	1.89	2.90	3.29	3.53	3.50	3.51
Na_2O	0.57	1.17	0.26	0.59	1.99	2.40	0.39	0.15	0.31	0.08	0.25
K_2O	4.61	3.44	6.04	5.78	2.71	2.80	2.59	2.67	2.56	3.02	2.65
H_2O_{tot}[2]	12.22	16.02	12.29	17.85	18.37	15.22	12.36	14.57	13.39	14.48	13.28
n[3]	*2*	*8*	*2*	*15*	*3*	*1*	*3*	*13*	*5*	*16*	*4*
Si	29.98	29.61	29.71	29.63	29.47	29.52	29.83	29.99	29.87	29.75	29.93
Al	6.21	6.47	6.40	6.42	6.60	6.59	6.13	6.06	6.20	6.22	6.14
Fe^{3+}	0.01	0.01	0.02	0.01	0.02	0.02	0.15	0.02	0.03	0.08	0.03
Mg	0.35	0.24	0.16	0.19	0.23	0.26	0.70	0.48	0.41	0.47	0.39
Ca	1.13	1.29	0.99	0.88	1.17	0.92	1.36	1.58	1.67	1.68	1.66
Na	0.49	1.04	0.23	0.55	1.82	2.11	0.33	0.13	0.27	0.07	0.22
K	2.59	2.02	3.34	3.51	1.63	1.62	1.44	1.53	1.45	1.73	1.49
Si/Al	4.83	4.57	4.64	4.62	4.47	4.48	4.87	4.95	4.82	4.79	4.88
E%	2.97	5.84	7.75	3.67	5.38	7.99	3.97	5.08	5.39	1.84	5.72

[1] The formulae are based on 72 oxigens. [2] Calculated by difference; [3] Number of analyses

Crystallography: Space group and unit cell parameters of clinoptilolite from Beli Plast deposit (BP) and its ion-exchanged forms are presented in Table 4 and illustrated below (Fig. 5)

Table 4. Space group and unit cell parameters of clinoptilolite from Beli Plast deposit

Sample	**Space group**	**a (Å)**	**b (Å)**	**c (Å)**	**β (º)**	**V (Å³)**
BP[1]	C2/m	17.686 (7)	17.934 (6)	7.413 (2)	116.40 (2)	2106 (2)
Ba-BP[2]	C2/m	17.670 (8)	17.922 (1)	7.391 (4)	116.12 (4)	2101 (2)
Ag-BP[3]	C2/m	17.656 (6)	17.945 (7)	7.402 (3)	116.13 (1)	2106 (1)
Zn-BP[4]	C2/m	17.668 (1)	17.973 (1)	7.414 (1)	116.24 (1)	2104 (1)
Tl-BP[5]	C2/m	17.696 (1)	17.949 (1)	7.412 (1)	116.224 (2)	2112.1 (2)

[1]Petrov *et al*., 1984; [2] Petrov *et al*., 1985; [3]Dimova *et al*., 2011; [4] Dimowa *et al*. 2015; [5] Dimowa *et al*., 2017.

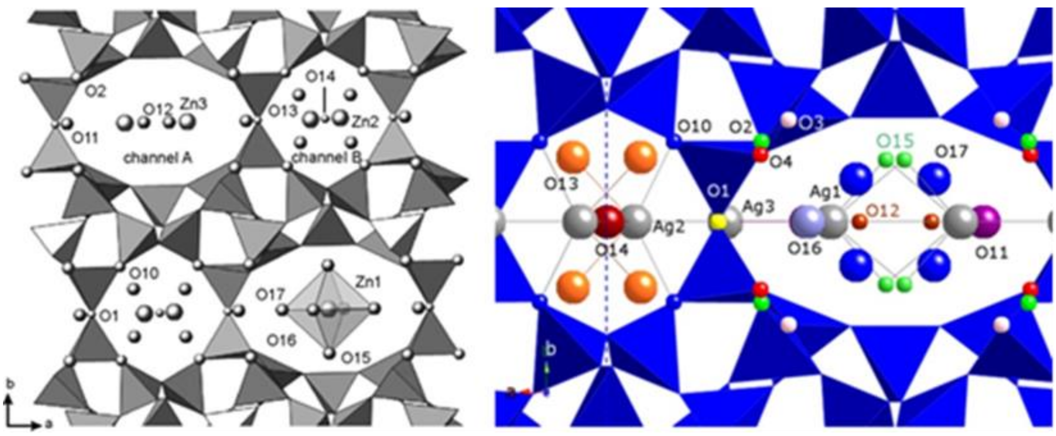


Fig. 5. Schematic structural representation of the positions in Zn- (left) and Ag-exchanged clinoptilolite (right) after Dimowa *et al*. (2011, 2015)

Some physical properties:

The available data on physical properties of zeolitized tuffs from some of the deposits are presented in Tables 5 and 6.

Table 5. Some properties of zeolitized tuffs measured on representative borehole samples (Raynov *et al*., 1995)

Deposit	Sorption of [mg/g]			Porometry			
	Sr^{2+}	Cs^{2+}	Sr+Cs	Specific surface m^2/g	Adsorption volume m^3/g	Pore volume cm^3/g	Average radius Å
Beli Plast	11-18	78-115	89-133	19.4-44.0	63-85	0.04-0.09	21-62
G. Krepost	8-21	94-115	102-135	24.7-40.2	72.3-86.2	0.04-0.06	22-50
Golobragovo	10-15	87-123	97-137	24.6-28.6	128.6-156.6	0.07-0.14	48-113
Most	2-13	104-137	106-150	23.6-28.9	60.5-79.6	0.06	42-48
Beliya Bair	9-19	67-110	76-128	28.6-49.1	115-196	0.09-0.15	49-86

Table 6. Some physical properties (measured on representative 10-kg samples) from zeolitized tuffs of Beli Plast and Beliya Bair - Zhelezni Vrata deposits (Popov *et al*., 2012).

Deposit	Pore volume, cm^3/g	Density, g/cm^3	Moisture equilibrium, %	Water absorption, %	Specific surface area, m^2/g	pH	CEC for NH_4^+, meq/100g
Beli Plast	0.10	1.16	6-7	24.0	35.26	6.9-7.0	110.61
Beliya Bair	0.12	1.06	7-8	26.0	38.83	6.8-7.0	107.0

In conclusion, the geological preconditions in the Eastern Rhodopes (two separate volcanic phases, highly explosive and voluminous eruptions of relatively crystals-poor magma, deposited as thick successions in submarine environments) resulted in the formation of a wide range and variation in properties (such as exchangeable cations, pore size, sorption, thermal- and tribomechanical activation capability, etc.), making the zeolite deposits suitable for a wide range of industrial applications.

Reserves and production:

The Intensive work on exploration and estimation on natural zeolite raw material in Bulgaria had been carried out in the period 1976-1986. As a result over 700 000 000 t of clinoptilolite raw material[1] (Most, Gorna Krepost, Beli Plast, Golobradovo and Beliya Bair deposits) and trass (Zhelezni Vrata) have been proven (Naydenova *et al*., 1994). There are also some reserves (thousands of tonnes) of mordenitized tuffs (Lyskovets deposit).

There are no official data available on the rate of current production.

Some applications:

Building stone in building industry – since antiquity (Figs. 6 and 7).

Cement production

Traditionally (since 1948) zeolitized tuff (trass) from Zhelezni Vrata is used in cement industry (Djourova & Aleksiev 1988, Yoleva *et al*., 2011). Details on the effect on Bulgarian natural zeolites on cement properties can be found in Lilkov *et al*., 2011a, b, c; 2016.

Agriculture and animal husbandry

Bulgarian natural zeolites are suitable for production of fodder mixtures (Sedloev *et al*., 1977; Abdel Baki *et al*., 1977; Nestorov *et al*., 1981), decontamination of livestock farms, soil conditioners fertilizer carriers, greenhouse production of flowers and vegetables, etc.

Their effect on soil properties is discussed in Filcheva *et al*., 1998; 1999, 2000a; Tsadilas *et al*., 1999; Filcheva & Chakalov, 2002; Chakalov *et al*., 2002; Filcheva & Tsadilas, 2002; Chakalov *et al*., 2003; etc.

[1] According to unpublished geological records as industrial resources of clinoptilolite only tuffs containing minimum 75% clinoptilolite and having CEC > 95 meq/100g are listed.

Fig. 6. The archaeological complex Perperikon: medieval fortress (right) built ontop of an ancient (5 000 BC) megalithic complex (left) near Gorna Krepost village

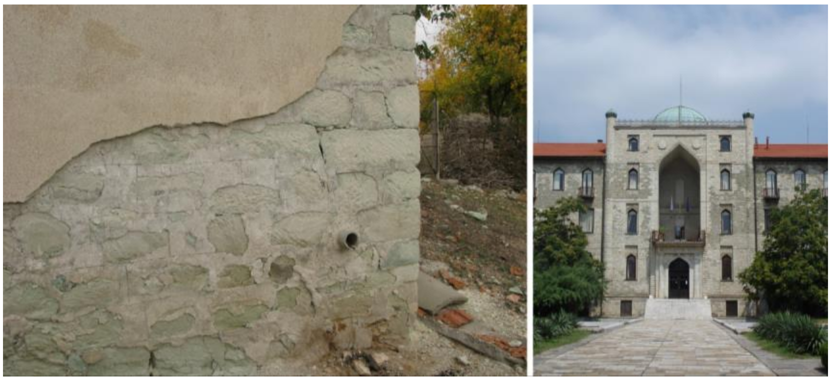


Fig. 7. House in the area of Eastern Rhodopes (photo courtesy of L. Machiels) and the hystory museum in Kardzhali, build in the period 1922-1930

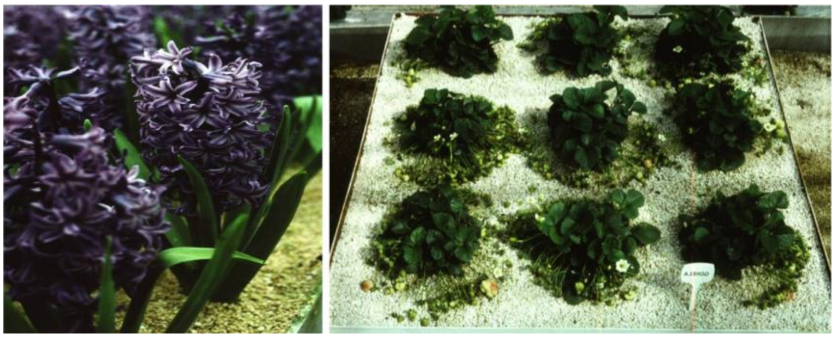


Fig. 8. Hyacinth and strawberries growing on “Balkanin”

Fig. 9. Tomato plants on “Balkanin”. The roof system of the plants is also visible

Mineral soil, containing 100% zeolite substrate, called BALKANIN was developed and used as substitute of standard soil. Natural zeolite (clinoptilolite), after thermal and chemical activation, serves as a feeding environment for growing plants in greenhouses and in open field: production of seedlings, vegetable and fruit cultures, flowers, leaf-decorative flowers (Figs. 8 and 9).

"Balkanin" is a long-lasting medium (minimum 5-6 yields), stocked up with macro- and microelements so there is no need to introduce additional food substances. It does not contain any nitrates or nitrites and guarantees ecologically clean products. Irrigation and phytosanitary protection are the same as with standard soils (Patent No. 40343, Stoilov et al., 1979). The product was awarded gold medals at exhibitions in Plovdiv (Bulgaria) and Leipzig (Germany). The product is authorized and patented in Russia, Hungary, USA, Japan, France, and Italy. Experiments with the product have been carried out in Greece, Italy, France, Spain, Malta, Cyprus and Libya. The “Balkanin” substrate was used to grow up so called “space vegetables” on board the MIR Space Station in 1990 (Ivanova et al., 1997).

Wastewater treatment

Bulgarian natural zeolites and their thermally and chemically (Fe^{3+} and Ag^{3+}) activated forms can be successfully used for the removal of heavy metals from wastewaters as they are effective at low concentration of the pollutants (Popov *et al*., 2010, 2012, Ivanova *et al*., 2010a). Some chemical aspects of the processes can be found in Mihalev *et al*., 2013a; b and Georgiev 2013.

Geopolymers

The work on creation of zeolite-based geopolymer materials has long been classified. According to some recently published data activated natural zeolite (clinoptilolite) from Beli Plast deposit has been used (Nikolov *et al*., 2017).

Food supplements

The first food supplement (approved for human use) was developed in the early 90s in the Institute of Cryobiology and Food Technologies on the base of sorbent CLS-5 (Popov *et al*., 1993; Popov *et al*., 1997). 55 000 first aid kits containing 2×7 g sorbent in powder form for a two days use in case of radiation danger were produced and distributed among people in the area of the Nuclear Power Station “Kozloduy” and among the workers in the plant (Fig. 10).

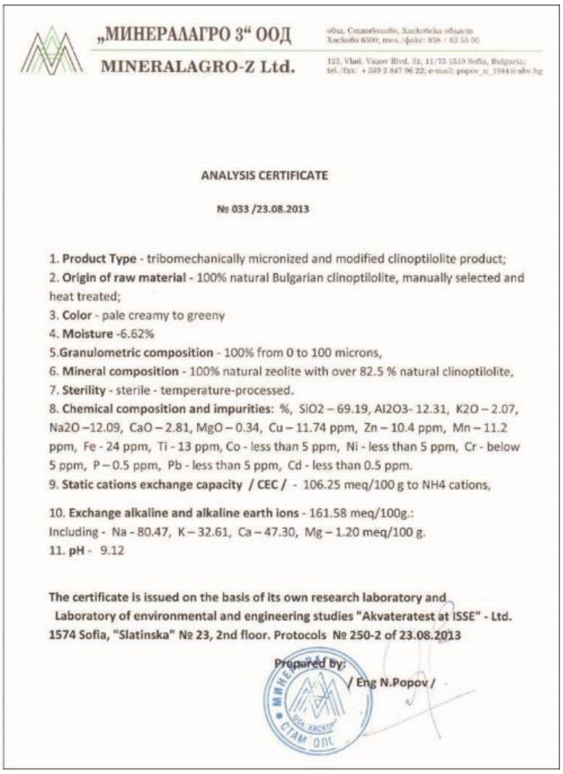
Fig. 10. CLS – powder (left); personal kit for radiological protection (right)

Later six modifications including food components have been developed on the basis of CLS – 5 (Fig. 11). The nutritional effect is achieved through the content of saccharides, pectin, vitamins and essence. In such a way the flavouring properties of the product improve and become suitable both for patients and healthy people.

In 2013 the CLS sorbent was used to produce two types of food supplements (www.natstim.eu). They are in the form of a 1 gram tablet in containers of 60 or 90 tablets each. Each tablet contains 0.6 g CLS-5 (first variant – “Clinodetox”) and second variant – Clinodetox-Vita + 200 mg vitamin premix of 7 vitamins, which are accepted in the European Community for daily intake (Fig. 12).

The clinosorbent is produced from selected hand-picked rock pieces of Bulgarian zeolites containing a minimum of 82 % clinoptilolite. The material was subjected to sterilization and tribo- and chemical activation following a special certified technology.

Fig. 11. Clinotablets



„МИНЕРАЛАГРО 3“ ООД

MINERALAGRO-Z Ltd.

ANALYSIS CERTIFICATE

№ 033 /23.08.2013

1. **Product Type** - tribomechanically micronized and modified clinoptilolite product;
2. **Origin of raw material** - 100% natural Bulgarian clinoptilolite, manually selected and heat treated;
3. **Color** - pale creamy to greeny
4. **Moisture** -6.62%
5. **Granulometric composition** - 100% from 0 to 100 microns,
6. **Mineral composition** - 100% natural zeolite with over 82.5 % natural clinoptilolite,
7. **Sterility** - sterile - temperature-processed.
8. **Chemical composition and impurities**: %, SiO_2 – 69.19, Al_2O_3- 12.31, K_2O – 2.07, Na_2O –12.09, CaO – 2.81, MgO – 0.34, Cu – 11.74 ppm, Zn – 10.4 ppm, Mn – 11.2 ppm, Fe - 24 ppm, Ti - 13 ppm, Co - less than 5 ppm, Ni - less than 5 ppm, Cr - below 5 ppm, P – 0.5 ppm, Pb - less than 5 ppm, Cd - less than 0.5 ppm.
9. **Static cations exchange capacity / CEC /** - 106.25 meq/100 g to NH_4 cations,
10. **Exchange alkaline and alkaline earth ions** - 161.58 meq/100g.: Including - Na - 80.47, K – 32.61, Ca – 47.30, Mg – 1.20 meq/100 g.
11. **pH** - 9.12

The certificate is issued on the basis of its own research laboratory and Laboratory of environmental and engineering studies "Akvateratest at ISSE" - Ltd. 1574 Sofia, "Slatinska" № 23, 2nd floor. Protocols № 250-2 of 23.08.2013

Prepared by:

/ Eng N.Popov /

Fig. 12. “Clinodetox” (left) and Certificate of the CLS-5 sorbent (right)

There is also a sorbent (CLS-10AM) specially developed and designed for animals that can be applied in cases of chronic heavy metal intoxication (Beltcheva *et al*., 2012; 2014; Topashka-Ancheva *et al*. 2012).

Table 7. Properties of CLS-5 and CLS-10 compared to the natural zeolites from Beli Plast and Beliya Bair deposits (unpublished data of Popov *et al.*[2]).

Index	Natural		Modified	
	Beli Plast	**Beliya Bair**	**CLS-5**	**CLS-10AM**
1.Chemical composition, %				
SiO_2	68.90	70.99	65.03	66.09
Al_2O_3	11.50	11.78	10.61	10.62
Fe_2O_3	0,76	0.83	0.72	0.76
TiO_2	0.10	0.14	0.12	0.12
CaO	2.05	1.55	2.20	3.03
MgO	0.90	0.55	0.80	0.33
K_2O	3.26	4.25	3.25	3.11
Na_2O	0.61	2.00	2.86	4.49
+ H_2O	11.57	7.14	13.56	11.57
2. Cation exchange capacity, CEC, meq/100g (NH_4^+)	110.61	107.00	103.50	139.50
3.Exchangeable cations, meq/100g				
Total	113.67	112.73	168.70	196.30
K^+	39.26	28.13	33.73	36.08
Na^+	14.53	45.99	82.56	133.14
Ca^{+2}	59.48	37.61	49.45	24.68
Mg^{+2}	0.40	1.00	2.96	2.41
4. pH , water solution 1:5	6.70	6.80	8.90	9.60
5. Sorption of: (mg/g)				
Sr^{+2}	13,21	14.15	21.40	33.75
Cs^+	89.30	105.00	105.00	162.50
$Cs^+ + Sr^{+2}$	100.46	106.74	119.32	129.44
Pb^{+2}	29.30	46.60	58.30	65.60
Cd^{+2}	9.10	10.40	24.00	32.70
6. Porometry				
Specific surface cm^2/g	35.26	38.83	25.28	30.80
Adsorption volume cm^3/g	105.63	162.65	101.90	93.53
Pore volume cm^3/g	0.10	0.12	0.11	0.08

Mining area reclamation and lands rehabilitation

Natural zeolites are currently used for land reclamation in the areas affected by extensive open-pit mining in Bulgaria (Filcheva *et al*., 2000b; Chakalov *et al*., 2002; Hristov *et al*., 2003). Industrial experiments on reclamation of ore waste and drained terrains of an old tailings pond using natural zeolites have been carried out since 2014 in the copper and copper-concentrate producing company “Asarel-Medet (Fig. 13).

[2] Popov, N., T. Popova, I. Denev, R. Shekerdjiisky, L. Balabansky, Iv. Timev, E. Dimitrova. 2014. “Clinodetox” - Effective detoxicant of heavy metals and radionuclides. 8th meeting of Hasumi International Research Foundation - Bulgaria: “Together in Cancer Control: Immunology, Viruses and Natural Remedies”, co-organizers: Medical University-Pleven and the Medical Section of the Bulgarian Academy of Sciences (October 24-25, 2014, Pleven), Session 4: Natural Remedies for Cancer Prevention, poster presentation.

Fig. 13. Development of grass turf on ore heap + Balkanin N (upper left). On the other photos - turf and mini roses on a support of activated zeolite and tailings waste

References

Abdel Baki, S., N. Nestorov, N. Sedloev. 1977. Studies on some biochemical indices of the rumen content and blood of male weaned lambs fed high doses of urea, urea-zeolite, and STAREA". *Meat Industry Bulletin*, **6**, 7-11 (in Bulgarian with an English abstract).

Aleksiev, B. 1968. Clinoptilolite des Rhodopes du nordest. *C. R. Acad. bulg. Sci*., **21**, 1093–1095.

Aleksiev, B., E. Djourova, Z. Milakovska-Vergilova. 1997. Geology of the Oligocene zeolitic rocks in NE Rhodopes, Bulgaria: a review and new data. In: G. Kirov, L. Filizova, O. Petrov (Eds.), *Natural Zeolites, Sofia'95*, Pensoft, Sofia-Moscow, pp. 249–262.

Aleksiev, B., E. Djourova. 1975. On the origin of zeolite rocks. *C. R. Acad. bulg. Sci*., **28**, 517-520.

Aleksiev, B., E. Djourova. 1976. Mordenite zeolitites from the Northeastern Rhodopes. *C. R. Acad. bulg. Sci.*, **29**, 865-867.

Aleksiev, B., E. Djourova. 1982. Zeolitic rocks in the region between the villages of Golobradovo and Moryantsi, district of Haskovo. *Annuaire de l'Universite de Sofia "St. Kliment Ohridski", Faculte de Géologie et Géographie, Livre 1 – Géologie*, **76**, 3–15 (in Bulgarian with an English abstract).

Aleksiev, B., Z. Milakovska, E. Djourova. 2009. The rocks of "Perperikon", NE Rhodopes, Bulgaria. *C. R. Acad. bulg. Sci*., **62**, 1423–1430.

Alexiev B., E. Djourova. 1988. Genetic features of zeolitic rocks in Bulgaria. In: D. Kallo, H. S. Sherry (Eds.). *Occurrence, Properties and Utilization of Natural Zeolites*, Budapest, Acad. Kiado, 77-86.

Beltcheva, M, R. Metcheva, M. Topashka-Ancheva, N. Popov, S. Teodorova S, J.A. Heredia-Rojas, A. O. Rodriguez de la Fuente, L. E. Rodríguez-Flores. 2014. Zeolites versus Lead Toxicity. *J. Bioequiv. Availab.,* **6**, 223–240.

Beltcheva, M., R. Metcheva, N. Popov, S. Teodorova, J. A. Heredia-Rojas, A. O. Rodríguez-de la Fuente, L. E. Rodríguez-Flores, M. Topashka-Ancheva. 2012. Modified natural clinoptilolite detoxifies small mammal's organism loaded with lead I. Lead Disposition and Kinetic Model for Lead Bioaccumulation. *Biol. Trace Elem. Res.,* **147**, 180-188.

Burlet, E. 1997. Les tufs volcaniques zéolitisés des Rhodopes (Bulgarie) caractérisation, propriétés physico-chimiques, origine. MSc thesis, Univ. Aix-Marseille 111, France.

Chakalov K., T. Popova, E. Filcheva. 2002. Soil fertility management with zeolite amendments. II. Zeolite effect on the maintaining the soil Eh. In: J. Kimble, R. Lal, R. Follet (Eds.): *Agricultural Practices and Policies for Carbon Sequestration in Soil*, Lewis Publishers, CRC Press LLC, Chapter 21, 229-235.

Chakalov K., T. Popova, K. Mitov, E. Filcheva. 2003. Influence of natural and modified zeolites on the mobility of some heavy metals in soil and model experiments. In: L. Kuzev, I. Nishkov, A. Boteva, D. Mochev (Eds.), Proceedings of X Balkan Mineral Processing Congress, 15-20 June, 2003, Varna, Bulgaria, 780-786.

Chakalov, K., T. Popova, E. Filcheva, K. Dimitrov, M. Koleva. 2002. Reclamation of damaged lands in the Maritza East region using zeolite products. *Mining and Geology*, **6**, 54-58 (in Bulgarian).

Dimova, L., O. Petrov, N. Lihareva, A. Stoyanova-Ivanova, V. Mikli. 2011. Preparation and Rietveld refinement of Ag-exchanged clinoptilolite. *Clay Minerals*, **46**, 197-204.

Dimowa, L. T., O. E. Petrov, M. P. Tarasov, M. K. Kadiyski. 2017. Structural study of Tl-exchanged natural clinoptilolite using Rietveld refinement, *Bulgarian Chemical Communications*, **49**, Special Issue A, 46–52.

Dimowa, L. T., O. E. Petrov, N. I. Djourelovand, B. L. Shivachev. 2015. Structural study of Zn exchanged natural clinoptilolite using powder XRD and positron annihilation data. *Clay Minerals*, **50** (1), 41-54.

Djourova, E. 1976. Analcime zeolitites from the North-Eastern Rhodopes. *C. R. Acad. bulg. Sci*., **29**, 1023–1025.

Djourova, E., B Aleksiev. 1989. Zeolitic rocks in the East Rhodope Paleogene depression. *Geologica Rhodopica*, **1**, 199-211.

Djourova, E., B. Aleksiev. 1983. Zeolitic rocks to the south-east of the village of Kralevo, Haskovo district. *Annuaire de l'Universite de Sofia "St. Kliment Ohridski", Faculte de Géologie et Géographie, Livre 1 – Géologie*, **77**, 165–175 (in Bulgarian with an English abstract).

Djourova, E., B. Aleksiev. 1984. Zeolitic rocks deposits of economic value in North-Eastern Rhodopes. – *Annuaire de l'Universite de Sofia "St. Kliment Ohridski", Faculte de Géologie et Géographie, Livre 1 – Géologie*, **78**, 256–263 (in Bulgarian with an English abstract).

Djourova, E., B. Aleksiev. 1988. Zeolitic Rocks. In: S. Trashliev (Ed.), *Non-metallic mineral deposits. Volume 1. Exogenic industrial minerals and rocks*, Technika Publ. House, Sofia, pp. 233-347.

Djourova, E., B. Aleksiev. 1990. Zeolitic rocks related to the second acid Paleogene volcanism to the east of the town of Kardzhali. In: Konstantinos, S. (Ed.), *Geologica Rhodopica 2,* Aristotel University, Thessaloniki, pp. 489-499.

Djourova, E., B. Aleksiev. 1995. Zeolitic rocks in the Northeastern Rhodopes. In: B. Aleksiev, (Ed.), *Sofia zeolite meeting '95*, *Guide to the post-meeting field trip*, pp. 20-48.

Djourova, E., L. Ivchinova. 1987. Distribution of K, Na, Rb and Ca in the clinoptilolitic rocks of some zeolitic deposits in the North–Eastern Rhodope. *Annuaire de l'Universite de Sofia "St. Kliment Ohridski", Faculte de Géologie et Géographie, Livre 1 – Géologie*, **81**, 75–89 (in Bulgarian with an English abstract).

Djurova E., I. Stefanova, G. Gradev G. 1989 Geological, mineralogical, and ion exchange characteristics of zeolite rocks from Bulgaria. *J. Radioanal. Nucl. Ch.*, **130**, 425–432.

Djurova, E., S. Boyadjiev. 1999. The zeolitic rocks in the vicinity of Karamfil village, Haskovo district – mineralopetrographic and geochemical characteristics. *Geology and Mineral Resources*, **7**, 18–23 (in Bulgarian with an English abstract).

Filcheva E., C. Tsadilas, V. Samaras, K. Chakalov. 1999. Soil amendment with sewage sludge and zeolite. I. Influence on soil organic matter. In: *6th International meeting on soils with Mediterranean type of climate*. July 4-9, 1999, Barcelona, Spain, 870-872.

Filcheva E., K. Chakalov, T. Popova. 1998. Model approach to improve soil quality using organo-zeolite compost. *J. Balkan Ecology*, **1**, 1, 72-78.

Filcheva E., K. Chakalov, T. Popova. 2000a. Clinoptilolite Impact on Humus Substances. In: *Entering the Third Millennium with Common Approach to Humic Substances and Organic Matter in Water, Soil and Sediments*. Proceedings of 10th International Meeting of the IHSS, vol. 1, Toulouse (France), pp. 659-663.

Filcheva E., K. Chakalov. 2002. Soil fertility management with zeolite amendments. I. Effect of zeolite on the carbon sequestration. A Review. In: J. Kimble, R. Lal, R. Follet (Eds.) *Agricultural Practices and Policies for Carbon Sequestration in Soil*, Lewis Publishers, CRC Press LLC, Chapter 20, 223-228.

Filcheva E., Tsadilas. 2002. Influence of clinoptilolite and compost on soil properties. *Communications in Soil Science and Plant Analysis*, **33**, 3-4, 595-607.

Filcheva, E., K. Chakalov, T. Popova, K. Dimitrov. 2000b. Soil forming processes in zeolite amended anthropogenic substrates in Maritza-Iztok region of Bulgaria. In: *Soils of Urban, Industrial, Traffic and Mining Areas (SUITMA)*, First Int. Conf. 12-18 July, University of Essen, Germany, 2000, v. III, 813-819.

Georgiev, G. 2013. Removal of lead and cadmium ions in aqueous solutions of natural zeolite (clinoptilolite): II. Kinetics. *University of Ruse*, *Conference Proceedings*, 52, book 10.1 Chemical Technologies, 230-234.

Hristov B., K. Chakalov, T. Popova, K. Mitov, E. Filcheva, K. Dimitrov, M. Koleva. 2003. A new method for reclamation of anthropogenic substrate using zeolite materials. In: L. Kuzev, I. Nishkov, A. Boteva, D. Mocheva (Eds.) Proc. X Balkan Mineral Processing Congress, 15-20 June, 2003, Varna, Bulgaria, 763-768.

Ivanova, R. 2016. Volcanic agents of zeolitization in the Eastern Rhodopes: V/S of volcanic glass particles. *Geosciences 2016*, *National Scientific Conference of the Bulgarian Geological Society with international participation, Short communications*, 61-62.

Ivanova, R., S. Gier. 2006. Zeolites and associated clay minerals from the altered Sheinovets caldera ignimbrites (eastern Rhodopes, southern Bulgaria). In: R. Bowman, S. Delap (Eds.), *Zeolite'06, 7th Int. Conf. on the Occurrence, Properties, and Utilization of Natural Zeolites (Book of Abstracts)* Socorro, New Mexico, USA,136-137.

Ivanova, R., I. Peytcheva, M. Kadiyski, A. Vlahov, N. Vucović. 2014. Zeolitization of 2nd Rupelian acid phase pyroclastics near Kostino village, Kardzhali District (E. Rhodopes, S. Bulgaria). In: A. Daković, M. Trgo, A. Langella (Eds.), *Zeolite 2014, 9th Int. Conf. on the Occurrence, Properties and Utilization of Natural Zeolites (Book of Abstracts),* Belgrade, Serbia, 99-100.

Ivanova, R., N. Popov, Y. Yanev, T. Popova, L. Machiels. 2010a. Mineralogy of zeolitized pyroclastics from Golobradovo deposit, (East Rhodopes) and their application for industrial waste water treatment. In: O. Petrov, Y. Tzvetanova (Eds.), *Zeolite 2010, 8th Int. Conf. on the Occurrence, Properties, and Utilization of Natural Zeolites (Book of Abstracts),* Sofia, Bulgaria, 115-116.

Ivanova, R., Y. Yanev, E. Vasilieva, L. Machiels, J. Elsen. 2010b. Zeolitization of acid pyroclastic deposits from northern parts of Dzhebel depression, E. Rhodopes, S. Bulgaria. In: O. Petrov, Y. Tzvetanova (Eds.), *Zeolite'10, 8th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites (Sofia, Bulgaria), Book of Abstracts*, 117-118.

Ivanova, R., Y. Yanev, Tz. Iliev, E. Koleva, T. Popova, N. Popov. 2001. Mineralogy, chemistry and ion-exchange properties of the zeolitized tuffs from the Sheinovets caldera, Eastern Rhodopes (South Bulgaria). In: A. Galarneau, F. di Renzo, F. Fajula, J. Vedrine (Eds.), *Stud. Surf. Sci. Catal., 135*, Proceedings of the 13th IZC, Elsevier, Amsterdam (full text on CD).

Ivanova, R., Y. Yanev, E. Vasilieva, L. Machiels, J. Elsen, Tz. Iliev. 2011. Zeolitized volcaniclastics from northern part of Dzhebel depression, E. Rhodopes: stratigraphy, petrography and mineralogy. *Geosciences 2011*, *National Scientific Conference of the Bulgarian Geological Society with international participation, Proceedings,* 63-64.

Ivanova, T., I. Stoyanov, G. Stoilov, P. Kostov, S. Sapunova. 1997. Zeolite gardens in space. In: G. Kirov, L. Filizova, O. Petrov (Eds.) *Natural Zeolites – Sofia'95*, 3-10.

Kanazirski, M., Y. Yanev. 1983. Physicochemical analysis of mineral parageneses of zeolitized perlites in the Borovicka area in the Eastern Rhodope Mts. *C. R. Acad. bulg. Sci*., **36**, 1571-1574.

Kirov, G. 1974. Zeolites in sedimentary rocks from Bulgaria. *Annuaire de l'Universite de Sofia "St. Kliment Ohridski", Faculte de Géologie et Géographie, Livre 1 – Géologie*, **66**, 171–184 (in Bulgarian with an English abstract).

Kirov, G., E. Šamajova, R. Nedialkov, Ts. Stanimirova. 2011. Alteration processes and products of acid pyroclastic rocks in Bulgaria and Slovakia. *Clay Minerals*, **46**, 279-294.

Kirov, G., N. Petrova. 2009. Volcanic ash-thermal interaction. Experimental observation. *Compt. rend. Acad. bulg. Sci*., **62**, 1289-1298.

Kirov, G., R. Nedialkov, Ts. Stanimirova. 2010. Alteration processes in acid pyroclastic rocks in Eastern Rhodopes, Bulgaria. *Geosciences 2010*, *Proceedings of the National Scientific Conference of the Bulgarian Geological Society with international participation,* 25-26.

Kirov, G., V. Pechigargov, E. Chelebiev. 1976. Effect of the grain size of volcanic glass on the mineral composition of its alteration products. *Geochemistry, Mineralogy and Petrology*, **4**, 83-90.

Lilkov, V., I. Rostovsky, O. Petrov. 2011a. Physical and mechanical characteristics of cement mortars and concretes with addition of clinoptilolite from Beli Plast deposit (Bulgaria), silica fume and fly ash. *Clay Minerals*, **46**, 213–223.

Lilkov, V., O. Petrov, V. Petkova, N. Petrova, Y. Tzvetanova. 2011b. Study of the pozzolanic activity and hydration products of cement pastes with addition of natural zeolites. Hydration products in cement-zeolite pastes. *Clay Minerals*, **46**, 241–250.

Lilkov, V., O. Petrov, Y. Tzvetanova. 2011c. Rheological, porosimetric, and SEM studies of cements with additions of natural zeolites. *Clay minerals*, **46**, 225–232.

Lilkov, V., O. Petrov, D. Kovacheva, I. Rostovsky, Y. Tzvetanova, V. Petkova, N. Petrova. 2016. Carbonation process in cement with mineral additions of natural zeolite and silica fume – early hydration period (minutes) up to 24 hours. *Construction and Building Materials*, **124**, 838–845.

Lilov, P., Y. Yanev, P. Marchev. 1987. K/Ar dating of the Eastern Rhodopes Paleogene magmatism. *Geologica Balc.*, **17**, 49–58.

Mihalev, T., I. Petrov, I. Chomakov. 2013. Removal of copper and nickel ions in aqueous solutions of natural zeolite. Technical Studies, III, 4, 51-55 (in Bulgarian with an English abstract).

Mihalev, T., I. Petrov, I. Peychev. 2013. Removal of lead and cadmium ions in aqueous solutions of natural zeolite (clinoptilolite): I. Thermodynamics. *University of Ruse*, *Conference Proceedings*, 52, book 10.1 Chemical Technologies, 225-229.

Naydenova, S., G. Darakchiev, A. Vlahov. 1994. Non-metallic mineral resources - trends in consumption and markets (part I*). Mining and Geology*, **8**, 28-31 (in Bulgarian).

Nestorov, N., N. Sedloev, F. Stanchev, G. Ialov, N. Popov. 1981. Studies on the effect of dietary zeolite on some physiological indices of fattening lambs. *Meat Industry Bulletin*, **1**, 1-4 (in Bulgarian with an English abstract).

Nikolov, A., I. Rostovsky, H. Nugteren. 2017. Geopolymer materials based on natural zeolite. *Case Studies in Construction Materials*, 6, 198-205.

Petrov, O. E., L.D. Filizova, G.N. Kirov. 1985. Cation distribution in clinoptilolite structure: Ba-exchanged sample. *Compt. Rend. Acad. Bulg. Sci*., **38**, 5, 603-606.

Petrov, O.E., T.A. Karamaneva, G.N. Kirov. 1984. Cation distribution in clinoptilolite structure: Natural samples. *Compt. Rend. Acad. Bulg. Sci.*, **37**, 6, 785-788.

Popov, N., G. Jilov, T. Popova. 1997. Study of the use of natural clinoptilolites and their modifications as effective sorbents of Sr and Cs and heavy metals from water solutions and drinking waters. *5th International Conference of Natural Zeolites "Zeolite–97",* September 21–29, Ischia (Naples), Italy.

Popov, N., D. Mochev, I. Grigorova, I. Nishkov, K. Atanasova. 2010. Zeolites for purification of flotation wastewater. *Mining and Geology*, **3-4**, 52-56 (in Bulgarian with an English abstract).

Popov, N., L. Georgieva, Ts. Tsvetkov, T. Popova. 1993. "Clinosorbent-5" – a new remedy having radioprotective effect. In: *Proceedings of the 2nd Scientific and Practical Conference on the Protection of the Population from Disasters and Accidents*, September 28-29, 1993, Sofia, pp. 133-134.

Popov, N., T. Popova, J. Rubio, S.R. Taffarel. 2012. Use of natural and modified zeolites from Bulgarian and Chilian deposits to improve adsorption of heavy metals from aqueous solutions. *Geochem., Mineral., Petrol*., **49**, 83-93.

Raynov, N., N. Popov, Y. Yanev, P. Petrova, T. Popova, V. Hristova, R. Atanasova, R. Zankarska. 1997. Geological, Mineralogical and Technological Characteristics of Zeolitized (Clinoptilolitized) Tuff Deposits in the Eastern Rhodopes, Bulgaria. In: G. Kirov, L. Filizova, O. Petrov (Eds.) *Natural Zeolites – Sofia '95*, 263-275.

Rens, M., R. Ivanova, J. Elsen, Y. Yanev, L. Machiels. 2010. Petrography, composition and CEC of the zeolitized Paleogene pyroclastic rocks to the south of the town of Dzhebel, SE Rhodopes, Bulgaria. In: Petrov O., Y. Tzvetanova (Eds.) *Zeolite'10, 8th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites (Sofia, Bulgaria), Book of Abstracts,* 220-221.

Sedloev, N., S. Abdel Baki, N. Nestorov. 1977. Studying the influence of rations containing urea, urea and zeolite, and urea preparation "STAREA" on some indices of blood and rumen content when feeding male weaned lambs. *Meat Industry Bulletin*, **5**, 6-11 (in Bulgarian with an English abstract).

Stoilov, G., I. Petkov, D. Dimitrov. 1979. Patent No. 40343 Bulgaria.

Topashka-Ancheva, M., M. Beltcheva, R. Metcheva, J.A. Heredia-Rojas, A.O. Rodriguez de la Fuente, Ts. Gerasimova, L. E. Rodríguez-Flores, S. Teodorova. 2012. Modified natural clinoptilolite detoxifies small mammal's organism loaded with lead II. Genetic, cell, and physiological effects. *Biol. Trace Elem. Res.,* **147**, 206-216.

Tsadilas C., V. Samaras, E. Filcheva, K. Chakalov. 1999. Soil amendment with sewage sludge and zeolite. II. Influence on nutrient uptake by plants. In: *6th International meeting on soils with Mediterranean type of climate*. July 4-9, 1999, Barcelona, Spain, 357-359.

Yanev, Y. 1995. General characteristics of the Late Paleogene collision volcanism in the Rhodopes. In: B. Aleksiev (Ed.) *Guide to Post-meeting Field trip. Sofia Zeolite Meeting'95*, 3-19.

Yanev, Y., F. Innocenti, P. Manetti, G. Serri. 1998. Upper Eocene-Oligocene collision-related volcanism in Eastern Rhodopes (Bulgaria) – Western Thrace (Greece): Petrogenetic affinity and geodynamic significance. *Acta Vulcanol*., **10**, 279-291.

Yanev, Y., Ph. Ildefonse, D. Stefanov. 1993. Chemical characterization of clay minerals associated with zeolitization of perlites (East Rhodopes, Bulgaria). *Geol. Carpathica, Series Clays*, **44**, 35–42.

Yanev, Y., J.-J. Cochemé, R. Ivanova, O. Grauby, E. Burlet, R. Pravchanska. 2006. Zeolites and zeolitization of acid pyroclastic rocks from paroxysmal Paleogene volcanism, Eastern Rhodopes, Bulgaria. *N. Jb. Miner. Abh.*, **182**, 265-283.

Yanev, Y., N. Raynov, I. Tchechlarova, V. Tchuneva, M. Matanova, V. Lazarova. 1986. Zeolites in perlites from the eastern part of the Borovitza region, Eastern Rhodopes (Bulgaria). In: *Crystal Chemistry of Minerals*. *Proc. of 13th General Meeting of the IMA*, Varna, 1982, Sofia, Publ. House Bulg. Acad. Sci., 737– 748.

Yanev, Y., R. Ivanova, Tz. Iliev, S. Gier. 2004. Part I – Eastern Rhodopes. In: M. Fiticas, Y. Yanev (Eds.), *Guidebook for Post-congress Excursion P-36 Paleogene and Recent Volcanism in the Eastern Rhodopes (Bulgaria) and on Milos Island (Greece), and Related Industrial Minerals*, 32nd International Geological Congress, Florence, Italy, pp. 7-13.

Yanev, Y., R. Ivanova. 2010. *Zeolite 2010. Post-conference field trip guidebook, Eastern Rhodopes, South Bulgaria*. M. Drinov Academic Publishing House, Sofia Bulgaria, 34 pp.

Yoleva, A., S. Djambazov, G. Chernev. 2011. Influence of the pozzolanic additives trass and zeolite on cement properties. *JUCTM*, **46**, 261-266.

This report has been prepared by

Rositsa Ivanova, rossiv@geology.bas.bg
Geological Institute, Bulgarian Academy of Sciences

Ognyan Petrov, opetrov@dir.bg
Institute of Crystallography and Mineralogy, Bulgarian Academy of Sciences

Nikolay Popov, popov_n_1944@abv.bg
"Mineralagro – Z" Ltd.

Further information on exploited and unexploited deposits is available from the authors.