

## **Zeolitized pyroclastic rocks from Oaxaca (southern Mexico): Mineralogy, ion-exchange properties, and use**

*Yotzo Yanev, Nikolai Popov, Tzvetoslav Iliev, Todorka Popova*

**Abstract.** Two quarries for construction material, situated in the southernmost parts of the Mexican Mid-Tertiary pyroclastic complex (in Sierra Madre del Sur), 7–8 km SE of Oaxaca City are sampled. They have rhyolitic composition and consist of glass shards, pumice and few plagioclase, quartz, biotite, magnetite phenocrysts and lithic clasts (probably andesites). Clinoptilolite, mordenite and light-green clay minerals replace all shards and pumice fragments but the original shape of the clasts is preserved. Clinoptilolite forms bands of microcrystalline mass, alternating with bands of clay minerals, or forms short-platy crystals in the central cavities of the shards. Mordenite needles and ribbons cover the platy clinoptilolite crystals. According to its chemistry clinoptilolite is sodic in one of the quarries and potassic to K-Ca-Na in the other. The mineral composition of the samples is estimated by semiquantitative X-ray analysis (49-52 wt.% clinoptilolite, 12-13 wt.% mordenite, 18-19 wt.% clays, 5-7 wt.% cristobalite + tridymite, 3-5% adularia, and pyrogenic minerals). The CEC, measured according to the method of Ming et al. (1993) vary from 94 to 135 meq/100g. These properties indicate a possible utilization of Oaxaca zeolitized pyroclastics as sorbents and substrate for direct growth of plants and improvement of soil structure in view of a possible decrease of the imported chemical fertilizers.

*Key words:* Mexico, Oaxaca, clinoptilolite, zeolitized pyroclastic rocks, CEC, liophilization, zeolite substrate

*Addresses:* Y. Yanev, Tz. Iliev - Geological Institute, Bulgarian Academy of Sciences; Sofia 1113, Bulgaria; E-mail: yotzo@geology.bas.bg; N. Popov, T. Popova - Institute of Cryobiology and Food Technologies, Sofia 1407, Bulgaria

**Йоцо Янев, Николай Попов, Цветослав Илиев, Тодорка Попова. Зеолитизирани пирокластични от Оахака (южно Мексико): минералогия, йонообменни свойства и приложение**

**Резюме.** Опробвани са две кариери за строителен камък, разположени в най-южната част на среднотерциерния пирокластичен комплекс в Мексико (в Сиера Мадре дел Сур), 7–8 km ЮИ от гр. Оахака. Те са с риолитов състав и се състоят от стъклени и пемзови късчета, малко плагиоклазови, кварцови, биотитови и магнетитови фенокристали, както и скални късчета (вероятно андезити). Всички стъклени и пемзови късчета са напълно заместени от клиноптилолит, морденит и бледозелен глинест минерал, но оригиналната им форма е напълно запазена. Клиноптилолитът формира ивици от микрокристални маси, редуващи се с глинести такива, а в центъра на кухините образува плочести кристали. Морденитови иглички и лентовидни кристали покриват плочестите клиноптилолитови кристали. Според състава на йонообменните катиони клиноптилолитът е натриев в една от кариерите

и калиев до К-Са-На – в другата. Минералният състав, оценен с полуколичествен рентгенов анализ е: 49-52 тегл. % клиноптилолит, 12-13% морденит, 18-19% глини, 5-7% кристобалит + тридимит, 3-5% адулар, както и пирогенни минерали. СЕС (йонобменният коефициент), измерен по метода на Ming et al. (1993) е 94-135 meq/100g. Тези свойства на зеолитизираните пирокластични сочат, че те могат да се използват като сорбенти, като материал за субстрат за директно отглеждане на растения и като подобрители на почвената структура с цел намаляване на използваните торове.

## Introduction

The largely zeolitized complexes of Mid-Tertiary pyroclastic rocks of Sierra Madre Occidental in northern Mexico and Sierra Madre del Sur in southern Mexico (the state of Oaxaca) are the most important sources of zeolitic raw material in Mexico. They have been subjects of many studies over the years (e.g. de Pablo Galán, 1986; de Pablo Galán et al., 1996; Ostrooumov, 2002). Mumpton (1973) was the first who discovered zeolites in

altered pyroclastic rocks from Mexico (SW of Oaxaca City). Now several zeolite deposits are known and the largest one, with 15 120 000 tons of zeolite material, is located in Oaxaca, Laollaga Municipality (Ostrooumov, Ostrooumova, 2006).

Our study is also focused on the zeolitization in the state of Oaxaca, southern Mexico (Fig. 1). Here the pyroclastic rocks belong to the Mid-Miocene Suchilquitongo Formation with an age of 15.0-20.0 Ma (Ferrusquía-Villafranca, McDowell, 1991). The

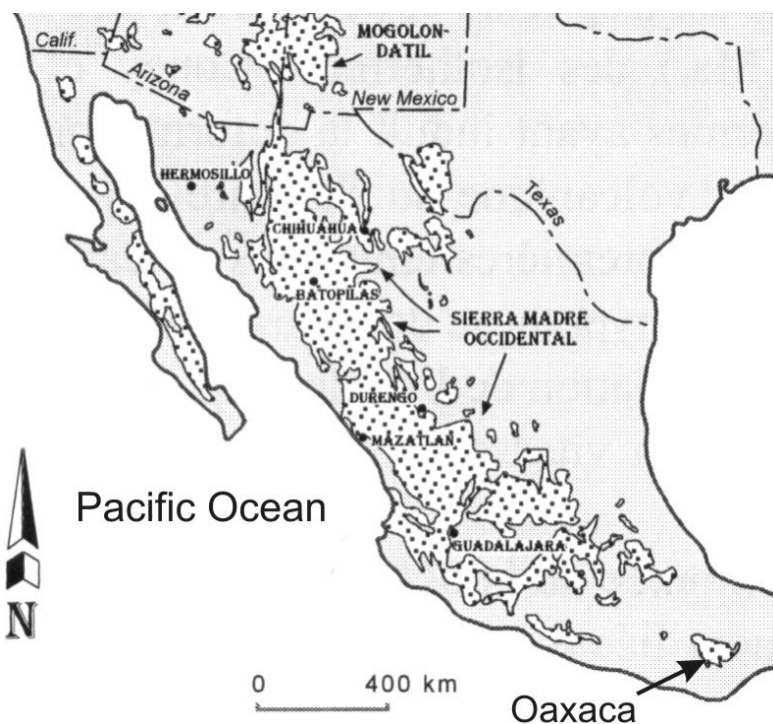


Fig. 1. Distribution of the Tertiary volcanic rocks in Mexico (after Ferrari et al., 1999)

aim of this paper is to provide new data on the petrographic, mineralogical, and chemical composition of the zeolitized pyroclastic rocks of two quarries for construction materials, located about 7-8 km SE of Oaxaca City, their sorption characteristics and possible utilization as zeolite material in agriculture.

This paper was presented on the 7<sup>th</sup> International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites (July 2006, Socorro, New Mexico, USA).

### Experimental methods

The samples have been studied under petrographic microscope Amplival-pol. The morphology and chemical composition of zeolites have been obtained by Jeol 733 Superprobe (WDS, using 15 kV acceleration voltage, 1 nA beam current and 5  $\mu\text{m}$  beam diameter) in the Geological Institute at Bulgarian Academy of Sciences.

The concentration of the mineral phases have been evaluated by semiquantitative X-ray diffraction analysis on a D500 Siemens diffractometer, also at the Geological Institute (analyst R. Pravchanska), according to the method of Peter and Kalman (1964) and Chang (1974, 1975). The operating conditions are monochromic  $\text{Cu}_{K\alpha}$  radiation, 40 kV, 30 mA,

continuous scanning at a velocity of 1-2<sup>o</sup>/min using an automatically changeable diaphragm. The concentration of each mineral has been obtained by measuring and calculation of its reference intensity ratio (RIR), the intensity of corundum peak at  $d_{113} = 2.085 \text{ \AA}$  being used for comparison. Especially for clinoptilolite the intensity of the peak  $d_{330} = 3.96 \text{ \AA}$  is measured.

The ion-exchange properties were studied according to the method of Chapman (1965) and the values of CEC (Cation Exchange Capacity) were measured according to the method of Ming et al. (1993). The sorption of Cs and Sr was obtained after mixing of the samples in Shootel apparatus for 4 hours.

### Results

#### *Petrographic composition of the pyroclastic rocks*

The studied rocks are probably products of rhyolitic pyroclastic flows deposited in shallow, playa-like environment without evaporates (Mumpton, 1973). They consist of: shards average 0.1 mm in size, in single cases up to 0.5–0.6 mm; pumice fragments most commonly 0.5–0.7 mm, rarely up to 1 mm (with spherical or spindle-shaped bubbles, Fig. 2); few plagioclase ( $\text{An}_{20.8-22.1}\text{Or}_{5.3-5.7}$ )

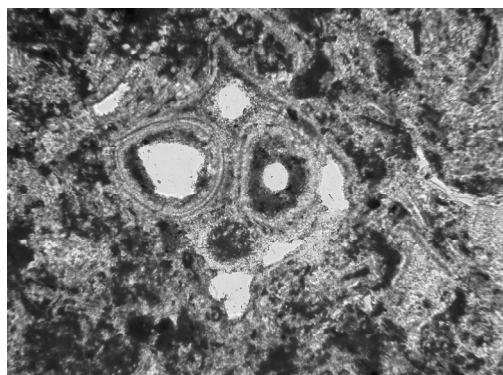


Fig. 2. Microphotographs of the zeolitized Oaxaca pyroclastic rocks showing perfectly preserved original shape of completely zeolitized glass shards (left) and zeolitized pumice clast with spherical bubbles (right). The light zones are zeolites, the dark ones are clays; plan-polarized light

phenocrysts up to 1 mm in size, quartz, biotite, magnetite, single zircon grains, and lithics (probably andesite and single clasts from the crystalline basement).

### *Zeolitization*

All shards and pumice fragments are replaced by zeolites and light-green clay minerals, but the original shape of the clasts is preserved (Fig. 2). Zeolites form bands of microcrystalline mass, alternating with bands of clay minerals (Fig. 3-3). Only on the walls of the central leached cavity of larger shards and in pumice bubbles short-platy crystals are formed (below 0.01 mm in size), rarely larger elongated-platy (up to 0.1 mm), all with heulandite habit (Fig. 3-2) and positioned parallel to the cavity walls. Representative microprobe analyses are given in Table 1. According to their Si/Al ratio (Coombs et al., 1997) and their position on the Mg+Ca/Na/K diagram (Fig. 4) all analyzed zeolites are alkaline clinoptilolites: sodic ( $\text{Na}_{4.53-5.27} \text{K}_{0.2-1.66} \text{Ca}_{0.27-0.42} \text{Al}_{5.7-6.89} \text{Si}_{29.06-30.16} \text{O}_{72} \cdot 24\text{H}_2\text{O}$ ) in the first quarry and potassic to K-Ca-Na ( $\text{K}_{1.57-2.92} \text{Na}_{0.81-1.5} \text{Ca}_{0.95-1.42} \text{Al}_{5.47-6.85} \text{Si}_{29.07-30.43} \text{O}_{72} \cdot 24\text{H}_2\text{O}$ ) in the second one. Small traces of Cl and/or S are detected in some clinoptilolites of the 1st quarry, grown on the walls of the pumice bubbles or in the central cavities of the shards (Table 1).

Mordenite forms needles or ribbon crystals up to 20–30  $\mu\text{m}$  long, often strongly twisted, overgrowing the platy clinoptilolite crystals (Fig. 3-2 and 3-4). Sometimes they are aggregated in spherulites (Fig. 3-1).

The estimation of the concentration of the different mineral phases (glass replacing and pyrogenic) is presented in Table 2. This analysis indicates also the presence of cristobalite-tridimite (probably opal-CT) and K-feldspar phase (probably adularia), also replacing shards and pumice together with the zeolites.

The clay minerals are deposited on the walls of the shards and bubbles in pumice

fragments, rarely filling them (Fig. 2). They are equally abundant in the two studied localities but differ in the proportion of the different clay minerals. Celadonite is sharply predominating clay mineral in the 2<sup>nd</sup> quarry and imparts the green color to the zeolitized pyroclastic rocks (Table 2). It forms small (below 0.1 mm) spheres irregularly scattered within the rock (Fig. 3-3).

### *Genetic remarks*

Several genetic hypotheses exist to explain the zeolitization of the thick pyroclastic series: burial diagenesis, open hydrologic systems, transformation in natural “autoclave”, low temperature hydrothermal alteration in the diagenetic *PT* field, summarized in many papers (e.g. Tsitsishvili et al., 1992; Sheppard, Hay, 2001; Utada, 2001, etc.). The studied zeolitized pyroclastic rocks do not provide any new facts to prove the existing genetic hypotheses. According to their geological and mineralogical characteristics they are very similar to the Eastern Rhodopes occurrences (Yanev et al., 2006 and references therein) and the same, low temperature hydrothermal alteration may be supposed.

### *Chemical and ion-exchange properties*

The chemical composition of the Oaxaca zeolitized rocks in comparison with other zeolitized pyroclastic rocks is presented in the Table 3. It reflects the difference in the chemistry of the clinoptilolite in the studied rocks (Table 1).

The ion-exchange properties (Table 4) are similar to those in other parts of the world, e.g. the Eastern Rhodopes zeolitized rocks in Bulgaria, especially those of Beli Plast deposit (Raynov et al., 1997) and other world known ones (Popov et al., 1992). These properties are directly related to the chemical composition of the clinoptilolite and indicate a possible utilization in technological fields, such as agriculture.

Table 1. Selected microprobe analyses of Oaxaca clinoptilolite and calculated formulae (based on the 72 oxigens)

Quarry 1	5b	8b	13b	17b	18b	19b	20b	5	7	15
SiO <sub>2</sub>	61.50	70.30	72.70	73.35	73.35	73.60	75.22	66.71	67.37	63.31
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	11.06	11.84	12.16	11.76	12.37	12.55	12.31	13.08	13.22	12.73
Fe <sub>2</sub> O <sub>3</sub> *	0.19	0.79	0.23	0.05	0.27	0.05	0.19	0.00	0.00	0.00
CaO	0.71	0.67	0.87	0.95	0.87	0.92	0.92	0.64	0.66	0.55
Na <sub>2</sub> O	5.04	6.03	6.60	6.38	6.53	6.44	6.28	6.08	6.18	5.09
K <sub>2</sub> O	0.65	1.38	0.79	0.55	0.61	0.54	0.40	2.65	2.81	2.84
BaO	0.22	0.16	0.04	-	0.20	0.22	-	0.60	0.54	-
SO <sub>3</sub>	0.29	0.15	-	0.20	-	-	0.17	-	-	-
Cl	0.18	0.12	0.04	-	-	-	-	-	-	-
Total	79.84	91.27	93.43	93.24	94.20	94.32	95.49	89.76	90.74	84.52
Si	29.75	29.78	29.91	30.16	29.92	29.94	30.13	29.13	29.12	29.06
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Al	6.31	5.93	5.90	5.70	5.95	6.02	5.81	6.73	6.73	6.89
Fe <sup>3+</sup>	0.07	0.25	0.07	0.02	0.08	0.02	0.06	0.00	0.00	0.00
Ca	0.37	0.31	0.38	0.42	0.38	0.40	0.39	0.30	0.31	0.27
Na	4.73	4.97	5.27	5.09	5.16	5.08	4.88	5.15	5.18	4.53
K	0.40	0.75	0.41	0.29	0.32	0.28	0.20	1.48	1.55	1.66
Total	41.62	41.98	41.94	41.67	41.81	41.72	41.48	42.80	42.88	42.41
Si/Al	4.72	5.03	5.07	5.29	5.03	4.98	5.19	4.33	4.32	4.22
E%	8.70	-2.28	-7.44	-8.02	-3.41	-2.11	-0.05	-6.81	-8.26	-2.68

Quarry 2	2	6	7	16	3b	4b	8b	10b	11b	13b
SiO <sub>2</sub>	64.04	68.33	62.81	67.65	67.39	70.02	60.91	70.38	69.67	71.41
TiO <sub>2</sub>	0.02	0.12	0.00	0.08	0.00	0.03	0.00	0.00	0.07	0.17
Al <sub>2</sub> O <sub>3</sub>	12.55	11.51	12.55	11.18	10.84	11.25	9.76	11.05	11.11	0.95
Fe <sub>2</sub> O <sub>3</sub> *	0.05	0.12	0.26	0.00	0.20	0.10	0.01	0.17	0.03	0.90
MgO	0.40	0.00	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	2.00	2.72	2.27	2.66	2.77	3.02	2.68	2.73	2.93	2.09
Na <sub>2</sub> O	0.91	1.64	1.11	1.42	1.12	1.67	1.20	1.52	1.78	1.43
K <sub>2</sub> O	4.99	3.12	5.41	3.17	3.20	2.94	3.34	2.55	2.84	4.37
BaO	-	-	-	-	0.15	0.10	0.16	0.05	-	-
Total	84.96	87.56	84.76	86.16	85.67	89.13	78.06	88.45	88.43	91.32
Si	29.34	30.03	29.07	30.17	30.27	30.22	30.19	30.43	30.26	30.27
Ti	0.07	0.04	0.00	0.03	0.00	0.01	0.00	0.00	0.02	0.05
Al	6.78	5.96	6.85	5.88	5.74	5.72	5.70	5.63	5.69	5.47
Fe <sup>3+</sup>	0.02	0.04	0.09	0.00	0.07	0.03	0.00	0.06	0.01	0.29
Mg	0.27	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.98	1.28	1.13	1.27	1.33	1.40	1.42	1.26	1.36	0.95
Na	0.81	1.40	1.00	1.23	0.98	1.40	1.15	1.27	1.50	1.17
K	2.92	1.75	3.19	1.80	1.83	1.62	2.11	1.41	1.57	2.36
Total	41.12	40.50	41.56	40.38	40.22	40.40	40.59	40.07	40.41	40.23
Si/Al	4.33	5.04	4.25	5.14	5.28	5.28	5.30	5.41	5.32	5.53
E%	8.96	5.13	0.16	5.43	6.04	-0.94	-6.66	9.13	-1.78	5.89

\* Total Fe as Fe<sub>2</sub>O<sub>3</sub>

E% - charge balance (Passaglia, 1970)

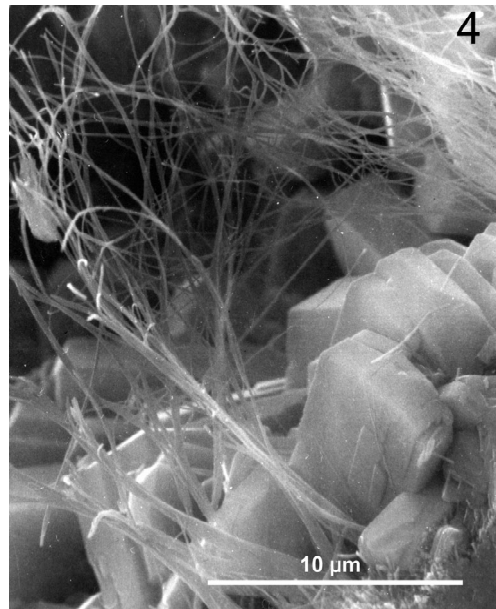
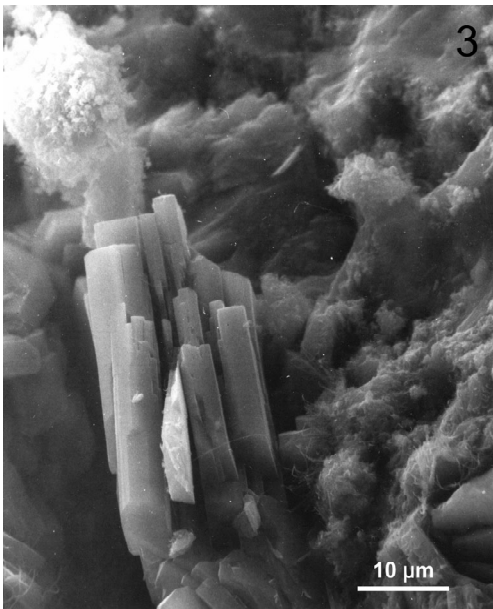
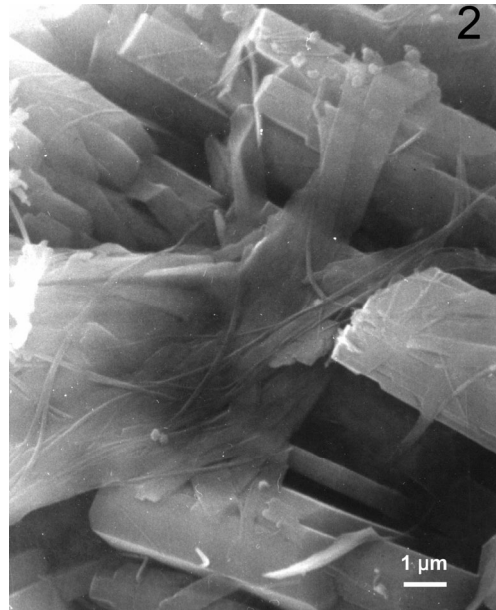
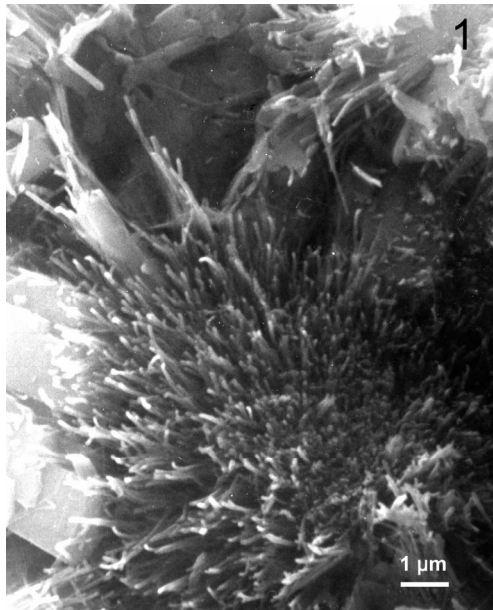


Fig. 3. SEM image presenting the morphology of the zeolites from zeolitized Oaxaca pyroclastic rocks: 1 - mordenite spherulites; 2 - platy clinoptilolite crystals covered by mordenite ribbons; 3 - platy clinoptilolite crystals between clay bands and 4 - platy clinoptilolite crystals covered by mordenite needles

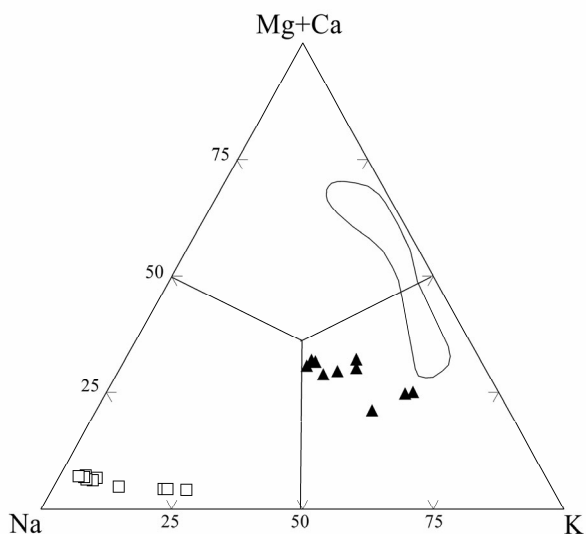


Fig. 4. Extra framework cations ratio of clinoptilolite from 1st (squares) and 2nd (triangles) quarries (source data from Table 1). The field of Beli Plast, Bulgaria, clinoptilolite (the black line) is given for comparison (data from Djourova, Ivchinova, 1987 and Yanev et al., 2006)

Table 2. Semiquantitative evaluation of mineral phases (wt.%) in Oaxaca zeolitized pyroclastic rocks (X-ray diffraction)

Quarry	Clinoptilolite	Mordenite	Smectites	Mixed layers I-S clays	10Å mica*	Cristobalite + tridymite	Adularia + sanidine (?)	Plagioclase	Quartz
Oaxaca 1	52	12	13	1	5	7	5	3	2
Oaxaca 2	49	13	3	5	10	5	3	4	8

\* Celadonite, or glauconite, or illite

Table 3. Chemical composition of zeolitized pyroclastic rocks (wt.%)

Provenance of the samples	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	LOI	Total
Oaxaca 1 (Mexico)	67.89	0.10	11.72	1.54	0.24	0.97	3.99	1.96	10.79	99.20
Oaxaca 2 (Mexico)	69.72	0.09	11.75	1.74	0.28	1.80	1.16	3.91	9.26	99.71
Beli Plast (Bulgaria)	68.80	0.17	11.90	0.80	1.20	3.55	0.65	2.42	10.20	99.69
Geoexplorers - New Mexico (USA)	68.50	0.09	11.33	1.48	0.46	2.07	0.63	4.09	10.88	99.53
New Zealand	71.12	0.12	12.89	1.67	0.04	1.77	1.77	1.90	7.73	99.01

Table 4. Ion-exchange properties (meq/100g) of zeolitized pyroclastic rocks

Provenance of the samples	CEC (method of Ming et al., 1993)	Ion-exchange property (method of Chapman, 1965)				
		K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Total
Oaxaca 1 (Mexico)	135.00	12.78	119.62	16.12	0.00	148.52
Oaxaca 2 (Mexico)	94.00	24.29	28.27	43.32	0.00	95.88
Beli Plast (Bulgaria)	137.50	32.20	9.05	107.50	1.00	149.75
Geoexplorers - New Mexico (USA)	94.50	59.46	5.98	29.94	0.50	95.88
New Zealand	66.50	12.15	33.71	15.12	0.00	70.98



Fig. 5. Plant root system cultivated on the mineral substrate prepared from the zeolitized rocks of quarry 2

#### Possible use of the Oaxaca zeolitized rocks

Mineral substrates for pot experiments and mineral sorbents for purification of wastewater from heavy and radioactive metals have been prepared in order to prove the possible utilization of Oaxaca zeolitic rocks.

The mineral substrate prepared (according to the Patent № 4.337.078 of Petrov et al., 1982) from sample 2, irrespective of its lower CEC, shows better agricultural indices due to its more favourable cation composition. The substrate characteristics are (wt.%): total N – 0.08, total P – 0.06, K – 0.5; pH – 5.8; electric conductivity – 840  $\mu$ S/cm. Results of the pot experiment with plants on this substrate are shown on Figure 5.

The mineral sorbents have been prepared following the next procedure: 10 g of alkaline salt, 100 g zeolite sample and 550 ml distilled water have been placed in 1l ball mill and activated by mixing for 6 h at 25-30°C. After

Table 5. Ion-exchange properties (mg/g) of the mineral sorbents prepared from the zeolitized pyroclastic rocks

Provenance of the samples used for mineral sorbent production	Sr <sup>2+</sup>	Cs <sup>+</sup>
Oaxaca 1 (Mexico)	10.45	112.55
Oaxaca 2 (Mexico)	12.26	116.53
Beli Plast (Bulgaria)	16.50	113.08
Geoexplorers - New Mexico (USA)	12.72	108.84
New Zealand	9.60	114.51



that they have been dried by liophilization. The moisture of the product after liophilization is 2.5 to 4%. The measured sorption of Cs and Sr (Table 5) indicates that the samples from Oaxaca can be successfully used for purification of industrial wastewaters and non-productive soils (the so-called “dead fields” of Oaxaca).

## Conclusion

The studied zeolitized samples from the state of Oaxaca display good ion exchange and sorption properties and can be successfully used for production of zeolite sorbents and substrates for direct growth of plants and improvement of soil structure in respect of possible decrease of the imported chemical fertilizers.

*Acknowledgments:* The authors thank R. Pravchanska (Geological Institute “Strashimir Dimitrov”, Bulgarian Academy of Sciences) for the powder XRD measurements, E. Tarassova for the microscope photographs and Y. Tzvetanova (the both from Central Laboratory for Mineralogy and Crystallography “Ivan Kostov”, Bulgarian Academy of Sciences) for computerizing of some figures. We thanks also R. Ivanova (from the Geological Institute) for the critic remarks and improvement of the text.

## References

- Chang, F. 1974. Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix-flushing method for quantitative multi component analysis. *J. Appl. Cryst.*, **7**, 519–525.
- Chang, F. 1975. Quantitative interpretation of X-ray diffraction patterns of mixtures. II. Simultaneous determination of set of reference intensities. *J. Appl. Cryst.*, **8**, 17–19.
- Chapman, H.D. 1965. Cation-exchange capacity. In: *Methods of Soil Analysis – Chemical and Microbiological Properties. Agronomy*, **9**, 891-901.
- Coombs, D.S., A. Alberti, T. Armbruster, G. Artioli, C. Colella, E. Galli, J.D. Grice, F. Liebau, J.A. Mandarino, H. Minato, E.H. Nickel, E. Passaglia, D.R. Peacor, S. Quartieri, R. Rinaldi, M. Ross, R.A. Sheppard, E. Tillmanns, G. Vezzalini. 1997. Recommended nomenclature for zeolite minerals: Report of the subcommittee on zeolites of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *Canad. Mineral.*, **35**, 1571-1606.
- Djourova, E., L. Ivchinova. 1987. Distribution of K, Na, Rb and Ca in the clinoptilolitic rocks of some zeolitic deposits in the North-Eastern Rhodopes. *Ann. Univ. Sofia “St. Kl. Ohridski”, Fac. Géol. et Géogr.*, **81**, 1 - Géol., 75-89 (in Bulgarian with English abstract).
- Ferrari, L., M. López-Martínez, G. Aquirre-Díaz, G. Carrasco-Núñez. 1999. Space-time patterns of Cenozoic arc volcanism in Central Mexico: from the Sierra-Madre Occidental to the Mexican Volcanic Belt. *Geology*, **27**, 303-306.
- Ferrusquía-Villafranca, I. McDowell, F.W. 1991. The Cenozoic sequence of selected areas in southeastern Mexico: its bearing in understand regional basin development there. In: *Convención sobre la evolución geológica de México. Primer Congreso Mexicano de Mineralogía*, Pachuca, Hgo., México, Memoria, 45-50.
- Ming, D.W., E.R. Allen, C. Galindo Jr., D.L. Henninger. 1993. Methods for determining cation exchange capacities and compositions of native cations for clinoptilolite. In: G.R. Fuentes, J.A. Gonzales (Eds.), *Memoirs of the 3rd International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites*, **2**, 31-35.
- Mumpton, F.A. 1973. First reported occurrence of zeolites in sedimentary rocks of Mexico. *Amer. Mineral.*, **58**, 287-290.
- Ostrooumov, M. 2002. Zeolitas de México: Diversidad mineralógica y aplicaciones. *Sociedad Mexicana de Mineralogía*, <http://www.geocities.com/smexmoneralogia/zeolitas.htm>.
- Ostrooumov, M., Ostrooumova, I. 2006. First reported occurrence of clinoptilolite-rich tuff deposits in the Mexican Volcanic Belt (state of Michoacan, southwestern Mexico). In: *Zeolite '06 “7<sup>th</sup> International Conference on the Occurrence, Properties, and Utilization of Naturel Zeolites”*, Socorro, N. Mexico, 199-200.
- de Pablo Galán, L. 1986. Geochemical trends in the alteration of Miocene vitric tuffs to economic zeolite deposits, Oaxaca, Mexico. *Appl. Geochem.*, **1**, 273-285.
- de Pablo Galán, L., M. Chávez-García, M. Cruz Sanchez. 1996. Sedimentary zeolites in the Sierra Madre del Sur and Sierra Madre

- Occidental, Mexico. *Revista Mexicana de Ciencias Geológicas*, **13**, 2, 188-200.
- Passaglia, E. 1970. The crystal chemistry of chabazites. *Amer. Mineral.*, **55**, 1278–1301.
- Peter, E., A. Kalman. 1964. Quantitative X-ray analysis of crystalline multicomponent systems. *Acta Chimica Hungar.*, **41**, 413–422.
- Petrov, G., I. Petkov, Ch. Etropolski, D. Dimitrov, N. Popov, N. Uzonov. 1982. *Substrate for the Cultivation of Agricultural Crops and Rooting of Green Cutting in Greenhouses and in Open Air*. US Patent 4.337.078.
- Popov, N., T. Popova, A. Zlatev, Ph. Stanchev, V. Marinov. 1992. Ion-exchange and sorption properties of clinoptilolite from Bulgarian deposits in respect to fractional and chemical composition. In: I. Belokonski (Ed.), *Proceedings of the Scientific-practical Conference on People Prevention During Disasters and Accidents*, **2**, Sofia, 151-156 (in Bulgarian).
- 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) tuffs deposits in the Eastern Rhodopes, Bulgaria. In: G. Kirov, L. Filizova, O. Petrov, (Eds.), *Natural Zeolites, Sofia '95*. Sofia-Moscow, Pensoft, 263-275.
- Sheppard, R.A., R.L. Hay. 2001. Formation of zeolites in open hydrologic systems. In: D.L. Bish, D.W. Ming (Eds.), *Natural Zeolites: Occurrence, Properties, Applications. Reviews of Mineralogy and Geochemistry*, **45**, Mineral. Soc. of America, Geochem. Soc., 261–275.
- Tsitsishvili, G.V., T.G. Andronikashvili, G.N. Kirov, L.D. Filizova, 1992. *Natural Zeolites*. Ellis Horwood, Chichester.
- Utada, M. 2001. Zeolites in burial diagenesis and low-grade metamorphic rocks. In: D.L. Bish, D.W. Ming (Eds.), *Natural Zeolites: Occurrence, Properties, Applications. Reviews of Mineralogy and Geochemistry*, **45**, Mineral. Soc. of America, Geochem. Soc., 277–304.
- Yanev, Y., J.-J. Cochemé, R. Ivanova, O. Grauby, E. Bulet, R. Pravchanska, 2006. Zeolites and zeolitization of acid pyroclastic rocks from paroxysmal Paleogene volcanism, Eastern Rhodopes, Bulgaria. *N. Jb. Mineral. Abh.*, **182**/3, Stuttgart, 265-283.

Accepted February 12, 2007  
 Пpуема на 12. 02. 2007 г.