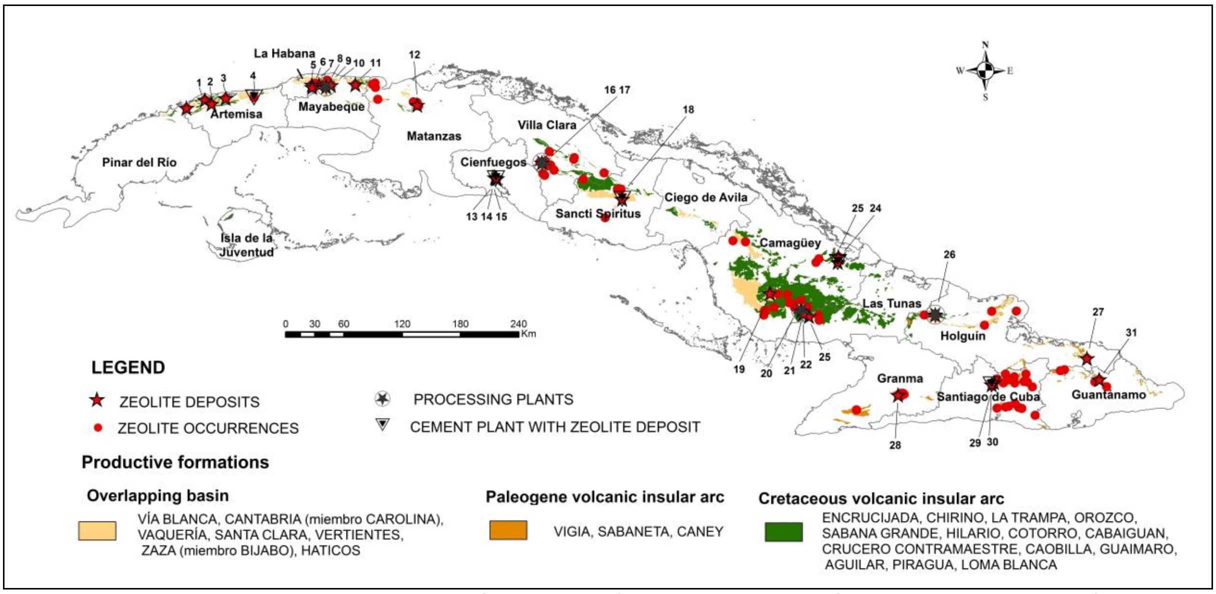
Sedimentary Zeolite Deposits in Cuba



(Map made by A. Brito, D.P. Coutín and D. Martín. Modified by G. Rodríguez-Fuentes with authors´ permission)

Introduction:

In Cuba, the first occurrences and deposits of natural zeolite rocks or *zeolitites** were discovered by B. Alexiev, A.D. Brito Rojas and D.P. Coutín Correa in 1970 [2, 3]. Since then more than a hundred occurrences of zeolite rocks of industrial significance have been studied in different degrees of details. The zeolite deposits in Cuba are located in different productive formations in Cretaceous and Paleogene volcanic insular arcs, and in overlapping basins of both arcs. Most of the occurrences contain clinoptilolite and mordenite in different proportions, save for the Las Margaritas and El Rubio analcime deposits, and Guaicanamar with heulandite, but in the Eastern region, the Paleogene deposits are mainly mordenite.

**Zeolitites are all rocks containing more than 50% of zeolites* [1].

Geology:

The range of ages of Cuban zeolite rocks is from Albian (Cretaceous) to Eocene (Paleogene), the most significant intervals being the Cenomanian to Campanian and the Lower Eocene to Middle Eocene. The zeolitisation process in all the above-mentioned volcanogenic-sedimentary sequences resulted from the transformation of volcanic glass contained in tuffaceous rocks. The composition of these rocks was andesitic, dacitic and rarely rhyodacitic. The alteration occurred during diagenesis and later due to hydrothermal activity or contact metamorphism. The resulting products (zeolites and accompanying minerals) are dependent on: 1) the chemical and aggregated mineral composition of the original rocks; 2) the content of the vitreous component; 3) the acting solutions such as seawater and hydrothermal fluids; 4) the temperature and pressure conditions.

The productive Cretaceous Formations are Encrucijada, Cabaiguán, Chirino, La Trampa, Orozco, Crucero Contramaestre, Caobilla, Guáimaro, Aguilar, Piragua, Hilario, Cotorro and Loma Blanca. Furthermore, in overlapping basins the productive formations are Vía Blanca, the Carolina member in Cantabria, Santa Clara, Vaquería. Vertientes and the Bijabo member of the Zaza Formation. Among the Paleogene formations, the productive ones are Sabaneta, Vigía, Caney, and eventually, in an overlapping basin, Haticos.

In addition, the potentially prospective Cretaceous Formations Sabana Grande in the Isla de la Juventud, and Provincial, Seibabo, Dagamal, Camujiro and Santo Domingo in the Central-eastern region increase the possibility of discovering new zeolite deposits in other territories.

The zeolitic rocks linked to the volcanogenic-sedimentary complex of the Cretaceous volcanic arc are massive, compact, hygroscopic, lightweight, greenish-coloured and whitish, sometimes with bluish and yellowish tonalities. In many places, it is possible to distinguish different cycles of sedimentation.

In the rocks of the Cretaceous complex, the zeolite content ranges between 50 % and more than 90 %, with clinoptilolite prevailing over mordenite. The greatest degree of zeolitisation occurs in the finely granular tuff variety. Locally**,** where hydrothermal and tectonic effects are observed, and near the contact with little intrusive bodies, the colour of the rocks becomes creamy yellow and the mordenite content increases.

In the volcanogenic-sedimentary complex of the Paleogene volcanic arc, andesitic rocks prevail, although there is a range in composition from basaltic to rhyolitic. This complex is constituted by sequences of well-defined sedimentary cycles or rhythms, mainly of tuffs and tuffites; the higher horizons are enriched in carbonate material. In the package of tuff rocks, the vitroclastic varieties of fine or large fragments predominate. In the zeolitisation of the tuffaceous Paleogene rocks, unlike that in the Cretaceous complexes hydrothermal solutions were involved.

In the provinces of eastern Cuba, the occurrence of zeolitite deposits is observed in places with deposits of manganese and intensive silicification, as well as bentonites. This is indicative of the action of hydrothermal processes in the region. There, the zeolitisation is abundant and widely developed although irregular, and the abundance of mordenite exceeds that of clinoptilolite.

In the overlapping basins formed over the Cretaceous and Paleogene volcanogenic-sedimentary complexes, zeolitic rocks also occur in sequences of mainly calcareous-terrigenous composition, with interposed beds of volcanogenic material linked to a remaining volcanic activity in the Late Cretaceous and in the Paleocene-Eocene. These deposits are more abundant and larger in the provinces of the central region. In some of the occurrences, tuffs and tuffites alternate with terrigenous rocks, without abrupt changes. In other places, the effects of tectonic displacements are observed. The zeolitisation processes that occurred in the overlapping basins are similar to those in rocks of the volcanic arcs.

The map reported above shows the geographical distribution of zeolitite deposits in Cuba in the Cretaceous and Paleogene insular arcs and in overlapping basins. Table 1 shows the list of deposits by provinces, their zeolite composition, dimension, and the type of industrial plant that processes the raw material.

Prior to field studies, the geologists carefully evaluated the aerial photographs and satellite images, at different scales, of the selected regions and zones. The field studies of the collected rocks from the occurrences were conducted using various analytical methods and techniques [1]. *Immersion heat (Δt)* is a practical discriminative method proposed by Culfaz, Keisling and Sand [19] for preliminary tests for the presence of zeolites in the rock. It also allows a semi-quantitative estimation of the zeolite abundance in the rock, based on the difference of temperature of the sample during the water adsorption process ($\Delta t > 11^{o}C$ zeolite content (ZC) > 60 %; $\Delta t = 8^{o}$-$11^{o}C$ ZC: 40-60 %; $\Delta t < 8^{o}C$ ZC: < 40 %). Other methods used were: *X ray diffraction analysis (XRD)* for the qualitative and quantitative determination of mineral phases; *optic microscopy* to study the aggregative composition of the components; *electron microscopy (transmission and scanning)* to establish the morphology and relationship of the zeolite and other minerals crystals; *differential thermal analysis* and *infrared spectrometry* to determine the non-zeolite mineral phases that cannot be observed by XRD; *chemical analysis* of macro and microelements using atomic absorption spectrometry and inductively coupled plasma spectrometry. Other techniques employed to complete the knowledge base were: *porosity, humidity, volumetric and specific weight, water absorption capacity, ion exchange capacity, abrasiveness* and *pozzolanic activity*.

Some of these analytical methods were carefully elaborated by Cuban analysts to be established as Cuban standards for the study of natural zeolites (see below). In Table 2 are reported the average values of the chemical and physical analysis of the zeolite rocks samples collected in the geological study of the deposits. The detailed results appear in the geological report of each zeolite deposit at the National Office of Mineral Resources (ONRM in Spanish) of Cuba.

The geologists Dr. Amelia Brito Rojas and Dr. Donis Coutín Correa have reported all their studies on Cuban zeolites in scientific papers and technical reports; some of them are the references 1-18. Recently, they wrote the book “Las zeolititas de Cuba: Resultados de 45 años dedicados a su estudio” (The zeolitites of Cuba: Results of 45 years dedicated to their study) published by Centro Nacional de Información Geológica of the Instituto de Geología y Paleontología (IGP) of Cuba, presented in the VII Earth Science Convention, La Habana, 4th April, 2017. All of their results have been confirmed by other authors [20-24] and by the geological prospecting surveys conducted in Cuba.

Table 1. Cuban zeolitite deposits, location, composition, industrial reserves, dimension and industrial processing plants.

No.	Deposit name	Province	Zeolite composition	Dimension and industrial reserves*	Type of processing plant
1	La Mulata	Pinar del Río	CLI-MOR	Small	
2	Harlem	Artemisa	CLI-MOR	Small	
3	La Granjita	Artemisa	MOR-CLI	Small	
4	Orozco	Artemisa	CLI-MOR	Medium	
5	Los Congos	Artemisa	CLI	Small	Cement
6	La Quebrada	La Habana	CLI	Small	
7	La Victoria	La Habana	CLI-MOR	Medium	
8	El Paso	La Habana	CLI-MOR	Small	
9	La Pita	Mayabeque	CLI-MOR	Small	
10	Castilla	Mayabeque	CLI-MOR	Small	Several uses
11	Galafate	Mayabeque	CLI-MOR	Small	
12	San Ignacio	Mayabeque	CLI-MOR	Small	
13	Olimpo	Matanzas	CLI-MOR	Small	
14	Carolinas (Puzolana)	Cienfuegos	CLI-MOR	Medium	Cement
15	Carolinas I	Cienfuegos	CLI	Small	
16	Carolinas II	Cienfuegos	CLI-MOR	medium	
17	Piojillo	Villa Clara	CLI-MOR	Small	Several uses
18	Tasajeras	Villa Clara	CLI	Large	
19	Siguaney (Puzolana)	Sancti Spíritus	CLI-MOR-ANA	Medium	Cement
20	San Cayetano	Camagüey	MOR>>CLI	Large	
21	El Chorrillo	Camagüey	CLI	Large	Several uses
22	Las Catalinas (Puzolana)	Camagüey	CLI-MOR	Large	
23	El Rubio (Puzolana)	Camagüey	ANA	Small	Cement
24	Las Margaritas (Puzolana)	Camagüey	ANA	Small	
25	Las Pulgas	Las Tunas	CLI-MOR	Large	
26	San Andrés	Holguín	CLI-MOR	Large	Several uses
27	Caimanes	Holguin	CLI-MOR-HEU	Large	
28	Bueycito	Granma	MOR-CLI	Medium	
29	Palmarito (Puzolana)	Santiago de Cuba	MOR	Medium	Cement
30	Palmarito de Cauto	Santiago de Cuba	MOR-CLI-HEU	Large	
31	Palenque	Guantánamo	CLI-MOR-HEU	Small	

***Dimension and industrial reserves**
Small: thickness 1-10 m; length < 0.5 km; reserve 1-5 million tonnes
Medium: thickness 10-20 m; length 0.5-1 km; reserve 5-10 million tonnes
Large: thickness > 20 m; length 1-1.5 km; reserve more than 10 million tonnes

Deposits under exploitation:

Los Congos

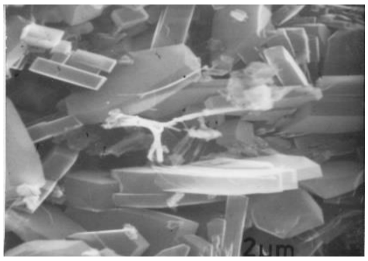
It is located 3.5 km southeast of the Mariel village, Artemisa province. The deposit is composed of tuffs containing varied vitro-, crystal- and lithoclastic components, calcareous tuffites and clays, all highly weathered and dark brown in colour. The deposit belongs to the Encrucijada Formation of the Albian-Cenomanian age, in the Cretaceous volcanic arc. The zeolitic body is in form of an elongated sub-horizontal bed. Tuffs of different aggregative compositions occur mixed with sandy-clay material, reddish in colour or with fragments of tuffites. The lithoclasts in the tuffs contain fragments of vitric rocks that are zeolitised, argillitised and chloritised as well as vitroclasts. The zeolite content, mainly clinoptilolite, is 40 % to 60 %. The deposit is small, and the two cement plants of the province exploit it as pozzolanic additive in cement production.

Other determinations
Chemical characteristics in Table 2
Mean values of SiO_2 = 55.45% and R_2O_3 = 21.2 %
Pozzolanic activity > 100%

Castilla-La Pita

The deposit is located near the village of Castilla, municipality of Jaruco, Mayabeque province. The zeolitic rocks are represented by tuffs of different structures; they belong to the La Trampa Formation of Cenomanian-Turonian age in the Cretaceous volcanic arc. They occur in lens-shaped bodies or in thin (1-10 m) packages a few hundred meters in length, sometimes more. These bodies are well stratified, generally dipping southeast, with variable layering. The zeolitised tuffs are from fine to coarse-grained, porous, lightweight, hygroscopic, easy breakable, and white coloured, sometimes with creamy and yellowish tonalities. Fine films of iron oxide and isolated manganese dendrites can be observed on the fracture planes of the zeolitised tuffs. The zeolite content of the rocks is 50 % to 90 %, and in some rocks close to 100 %. In the greater number of the analysed samples, the zeolite mineral is clinoptilolite. The rocks also contain as accompanying minerals plagioclase, quartz (minor quantities) and zircon, apatite and pyroxene (isolated grains). A large part of the deposit is ore type III (see Table 6). This deposit was exploited until the late 20th century.

Other determinations
Chemical characteristics in Table 2
Cationic specificity: Ca > Na > Mg > K
Density: 2.7 g/cm^3
Bulk density: 1.82 g/cm^3
Adsorption: 14.67 %
Porosity: 33.25 %

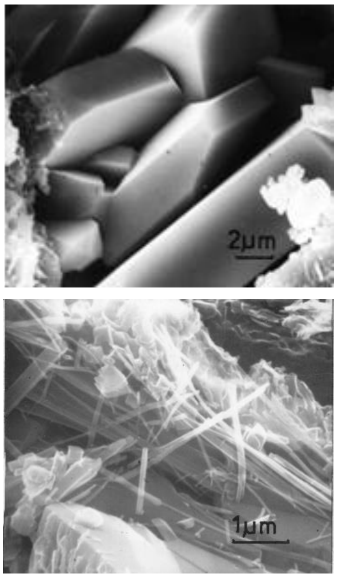


Clinoptilolite crystals with tabular morphology from Castilla deposit.
(Micrograph by G. Rodríguez-Fuentes [23, 24])

Piojillo-Tasajeras

This deposit is located at the village San Juan de los Yeras, municipality of Ranchuelo, Villa Clara province, in the central region of Cuba. The deposits of Piojillo and Tasajeras occurred at the surface as two separate but close bodies, with similar structural and lithological characteristics and mineralogical composition, but in depth, they make up only one body. For this reason during geological prospecting, it was studied as one deposit, although the reserves were calculated separately. Within the limits of the deposit, in an area about 3 km^2, the amount of zeolite in vertical and horizontal directions ranks above 70 %. The deposit is tectonically low in complexity. The outcrops are extensive. The general strike of the deposit is northwest-southeast and the dips vary from 25º to 30º northeast. The volcanogenic sequence containing the zeolitised tuffs is dated as Santonian-Campanian that belongs to Hilario Formation or to its facies analogue the Cotorro Formation, in the Cretaceous volcanic arc. The zeolitites are in several packages of different thickness, commonly greater than 20 meters. The zeolitic rocks are greenish in colour with some small spots in deeper green. They are lightweight, porous and hygroscopic rocks. This deposit was the first discovered in Cuba. It is the best-studied deposit in the country, and probably the largest. Its reserves are estimated in tens of millions of tonnes. The rocks of this deposit have been evaluated for their utilisation in different applications with successful results.

Other determinations
Chemical characteristics in Table 2
Cationic specificity: Ca > Na > K > Mg
Bulk density: 1.49 g/cm^3
Adsorption: 22.25 %
Porosity: 31.84 %



Clinoptilolite crystals with tabular morphology (above) and mordenite crystals with acicular morphology over clinoptilolite crystals (below) in Tasajeras deposit.
(Micrographs by G. Rodríguez-Fuentes [23, 24])

Tasajeras deposit (left) and the plant of the zeolitic raw material (right) *(Photos by G. Rodríguez-Fuentes)*

Siguaney

The deposit is located 7 km west of the Taguasco village, in the Sancti Spiritus province. It is a small deposit of zeolitised tuffs. The Cement Plant of Siguaney exploits it as pozzolanic additive. The productive unit is quite homogeneous and well stratified, in nearly vertical position. The zeolitised and silicified tuffs are white, porous, lightweight and hygroscopic. The unit also contains intercalated sandstones, siltstones, argillites and calcareous tuffites, as part of a flysch belonging to Bijabo Member of the Zaza Formation in an overlapping basin of Lower to Middle Eocene age. Two other tuff units with similar characteristics are located near to the deposit. The chemical composition of the tuffs is very consistent (SiO_2 ≈ 67 %, R_2O_3 ≈ 14.2 %; CaO ≈ 4.6 %). The zeolite content is some 60 to 70 %, and it is mainly clinoptilolite.

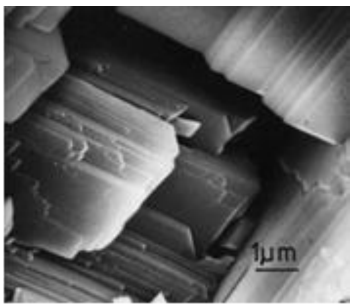
Las Carolinas

The deposit is located approximately 12 km northwest of the Cienfuegos city, capital of the province of the same name, close to the Carolina hamlet, in the earth-embankment of San Ignacio. It is of medium size. There are tuffs and tuffites of the Carolina Member of the Cantabria Formation in an overlapping basin of Maestrichtian (Upper Cretaceous) age. The productive unit has sub-horizontal thick beds of tuffs of light greenish colour with a psammitic fraction, where vitroclastic and crystal-vitroclastic varieties predominate. The pyroclasts are of diverse size, between 0.1 and 1.9 mm. In the volcanogenic-sedimentary packages, there are also tuffites, sandstones, limestones and clays. The alterations observed are zeolitisation, sericitisation, argilitisation and carbonisation. The zeolite content in the tuffs is more than 90 % clinoptilolite (main zeolite) and mordenite, accompanied by quartz, montmorillonite, plagioclase and chlorite. The raw material of this deposit has been used as pozzolanic additive in the cement produced by the Cienfuegos Plant. However, given the mineralogical characteristics and chemical properties of the zeolitic raw material, it could be used in water treatment, ion-exchange processes, additive to animal food, etc.

Other determinations
Chemical characteristics in Table 2
Cationic specificity: Ca > Na > K > Mg
Natural humidity: 20.02 %
Bulk density: 1.43 g/cm^3
Adsorption: 22.25 %
Porosity: 31.84 %
Dry compression resistance: 226 kg/cm^2
Saturated compression resistance: 109 kg/cm^2
Fratini essay: positive

El Chorrillo

The deposit is located at 20 km of the Najasa village and 50 km southeast of the Camagüey city, in the province of the same name. It has characteristics of a volcanogenic-sedimentary flysch, with a low carbonate content. The mineral raw material contains vitroclastic, vitro-crystal-clastic and crystal-vitroclastic zeolitised tuffs, with intercalations of sandstones and tuffites. The content of clinoptilolite and mordenite is 40 to 70 %; it also includes montmorillonite, plagioclase, quartz and metallic minerals. They are of light green colour, and the grains are fine to medium in size, and are mainly andesitic in chemical composition. The sedimentary rocks commonly contain volcanomictic material, and generally change gradually into pyroclastic rocks. This fact prevents an easy determination of the different lithologic types. The deposit is in the Crucero Contramaestre Formation in the Cenomanian-Campanian interval of the Cretaceous volcanic arc.



Clinoptilolite crystal with tabular morphology from the Chorrillo deposit.
(Micrograph by G. Rodríguez-Fuentes [23, 24])

Other determinations
Chemical characteristics in Table 2
Cationic specificity**:** Ca > Na > Mg > K
Density: 1.99 g/cm^3
Bulk density: 1.88 g/cm^3

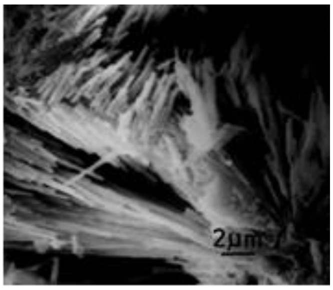
Las Margaritas y El Rubio

The Las Margaritas deposit is located 2 km northeast of the San Miguel de Bagá locality, south of the road to Nuevitas town, Camagüey province. The deposit is well stratified, and strikes in a northeast-southeast direction. Here the tuffs, sandstones and volcanoclastic conglomerates alternate. The zeolitites are rocks of different aggregative composition**,** generally occurring in fine grains of light green colour, sometimes almost white, with violet and brown-pinkish intercalations. They are relatively dense, and show low porosity; they contain dark coloured nodules, which have the same composition as the rest of the rock. These rocks belong to Caobilla Formation. Its age is Coniacian-Campanian in the Cretaceous volcanic arc. The main zeolite type is analcime (50 to 60 %), accompanied by quartz and montmorillonite. The zeolitic raw material has been exploited since the last century as a pozzolanic additive to cement**,** ignoring that it was zeolitic. At present, the cement plant of Nuevitas uses the zeolite raw material from El Rubio deposit located about 15 km southwest of Las Margaritas. These two deposits are very similar although the nodules of the El Rubio deposit are not so significant.

Other determinations
Chemical characteristics in Table 2
Density: 1.99 g/cm^3
Bulk density: 2.08 g/cm^3
Porosity: 13.98 %

San Andrés (also known as **Loma Blanca de Tasajeras**)

The deposit is 3 km from the San Andrés village and 23 km northeast of Holguín city, in the homonymous province. It belongs to the Loma Blanca Formation, a volcanogenic-sedimentary tuffaceous sequence of medium acidic to andesitic composition. It is of Lower Cretaceous (Aptian) to Upper Cretaceous (Campian) age in the Cretaceous volcanic arc. The deposit outcrops as small-elongated hills. The zeolitic rocks constitute a unit of vitroclastic tuffs about 50 m in thickness, and extending one km in an east-west direction. The zeolitites here are similar to those of the Tasajeras deposit in Villa Clara province: lightweight, hygroscopic, and porous, of light greenish colour, bleached white in some places near the surface; numerous cracks cross the zeolitites and small pockets and veins of silica (chalcedony) are frequent. The rocks contain 85 to 97 % of clinoptilolite and mordenite (with predominance of the former) and rarely stilbite. In the rocks, there are also minor amounts of plagioclase, chalcedony, montmorillonite and calcite. The zeolitic raw material of this deposit has been evaluated as pozzolanic additive, for the filtration of liquid and gas, abrasives, concrete filler, carrier of nutrient for plants, carrier of pesticides, drug formulation, wastewater treatment and as a molecular sieve.



Clinoptilolite crystals with lath morphology from the San Andrés deposit. *(Micrograph by G. Rodríguez-Fuentes [23, 24])*

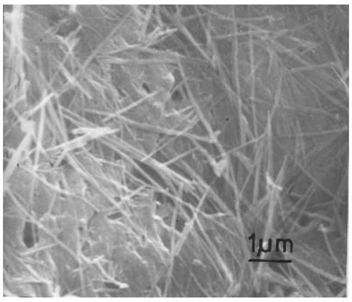
Other determinations
Chemical characteristics in Table 2
Cationic specificity: Na > Ca > K > Mg
Density: 2.35 g/cm^3
Bulk density: 1.65 g/cm^3
Porosity: 29.25 %

San Andrés deposit (left) and the plant of the zeolitic raw material (right) *(Photos by A. Caisés Ávalos)*

Palmarito

The deposit is located east of the Palmarito de Cauto village, in a large territory, that can be considered a mineral field, between the Guaninicum River, the Palmarito village, the Jagua River and La Almeida hamlet, in the Santiago de Cuba province. In this field, it is the sector known as Palmarito-Puzzolana or Tobas. From this sector a large amount of zeolitic rocks have been extracted for a long time as an hydraulic additive for the production of cement in the José Mercerón Cement

Plant of Santiago de Cuba. Moreover, in this deposit a Roman Cement Plant operated for some years with a production capacity of 120,000 tonne/year. Currently, dimension blocks are extracted for the production of flagstones used in the restoration of colonial palaces at the historical center of Old Havana. Volcanogenic-sedimentary rocks of the Sabaneta Formation (Paleocene-Middle Eocene) of the Volcanic Paleogene Arc occupy a large area here. These rocks are folded into domes whose long axis strikes northwest-southeast. In outcrop, several cycles of volcanoclastic rocks, with coarse-grained varieties at the base and fine-grained varieties in the upper levels, are evident. Both in the cycles and in the whole section, the content of vitric and calcareous components increases, upwards into tuffites and limestones. The zeolitised rocks have diverse particle sizes. They are gray or green in colour with green-yellowish hues, rarely white; the thickness of layers is 6 to 15 cm. The zeolite content is about 55 % to more than 90 %. The tuffs with the higher zeolite content also have the finest grain size, and generally, they are crystal-vitroclastic or vitroclastic rocks. The main characteristic of the deposit is the predominance of mordenite, commonly as the only zeolite in the rocks. However, clinoptilolite and heulandite are also present. Montmorillonite occurs in all of the analysed samples. In only one of the sectors of zeolitites in Palmarito, the resources evaluated for large-scale usage reach several tens of million tonnes.



Mordenite crystals with acicular morphology from Palmarito deposit.
(Micrograph by G. Rodríguez-Fuentes [23, 24])

Other determinations
Chemical characteristics in Table 2
Cationic specificity: Ca > Na > K > Mg
Bulk density: 1.73 g/cm^3
Porosity: 40.08 %

Table 2. Chemical and physical characteristics of the deposits in production. All the values are of representatives samples; the analytical methods are described in the Cuban Standard 625: 2014 and authors´ papers [1]

Deposit		Los Congos	Castilla-La Pita	Piojillo-Tasajeras	Carolinas	Siguaney	El Chorrillo	Las Margaritas and El Rubio	San Andres	Palmarito
Oxide [% weight]	SiO_2	62.31	56.99	63.05	59.92	65.03	60.80	63.41	65.29	64.92
	Al_2O_3	14.96	13.30	11.54	12.59	13.46	12.60	12.12	11.50	14.30
	Fe_2O_3	4.20	3.66	1.66	2.77	2.79	3.59	2.53	2.64	4.38
	FeO	1.37	1.79	0.93	0.34			0.54	0.79	2.69
	MnO			traces	0.04			0.05		
	MgO	1.34	2.31	0.86	1.80	1.55	1.41	1.32	1.10	2.86
	CaO	3.94	5.02	3.96	3.95	3.10	5.60	4.63	3.44	8.91
	Na_2O	2.75	2.15	0.81	0.70		1.85	4.38	2.45	3.24
	K_2O	1.49	1.51	2.25	0.95		0.48	1.01	1.28	3.45
	H_2O	6.22	12.73	14.65	15.19	12.76	12.18	5.67	10.51	10.92
Zeolite type	Total[%]	40	74	80	64	55	66	52	87	94
	CLI	Predominant	Predominant	Predominant	Predominant		Predominant		Predominant	<20%
	MOR		<20%	<20%	<20%	<20%	<20%		<20%	Predominant
	HEU									<20%
	ANA					35%		Predominant		
CEC [meq/100g]	Total	75.25	97.69	128.00	96.73		96.20		134.10	129.75
	Ca		53.4	53.4	59.1		41.9		38.7	53.97
	Mg		3.87	4.67	7.64		3.9		3.5	3.54
	Na		31.9	51.9	21.24		24.4		55.8	53.68
	K		2.36	7.2	9.74		1.2		5.8	6.42
Δt [ºC]		3.8	8.8	12.8	7.9	8.9	10.2			9.9
Ore type		III	III, II	I, II, III	II, III	II	II	II	I, II, III	II, III

- **Chemical** analyses were carried out by atomic absorption spectrophotometry (AAS) after the acidic digestion of the sample.
- **Zeolite type** analysis was carried out by quantitative XRD analysis.
- **Total CEC** was determined using the *Ammonium chloride method*, measuring the quantity of ammonium exchanged by the sample, whereas the exchangeable cations content was determined in the exchange solution by AAS.
- **Δt** was measured using the method referred to in Ref. [19].
- **Ore type** was determined using the Cuban Standard NC 625:2014.

Cuban natural zeolite industry:

Origin

The first natural zeolite deposits in Cuba were discovered in 1970 by B. Alexiev, A. Brito Rojas and D. P. Coutín Correa [3]. Subsequently, other research groups from Cuban Universities and public research organizations joined the first group motivated by the study and possible applications of the zeolitised rocks. Based on the limited global experience and the few scientific reports available at the time, Cuban researchers embarked on the detailed geological study and characterization of the physical and chemical properties of the raw material. The objective was to identify, and eventually develop applications in response to specific problems in agriculture and manufacturing industries. Five research centres worked intensively in that initial phase:

- ✓ Instituto de Geología y Paleontología (IGP), Cuban Academy of Science (ACC);
- ✓ Centro Nacional de Investigaciones Científicas (CENIC), Ministry of High Education (MES);
- ✓ Instituto de Ciencia Animal (ICA), (MES);
- ✓ Centro de Investigaciones Químicas (CIQ), Ministry of Basic Industry (MIB);
- ✓ Centro de Investigaciones y Proyectos para la Industria Minero Metalúrgica (CIPIMM), (MIB).

As a result of the researchers' work, in 1982 a pilot plant with a capacity of 20,000 tonne/year was set up for the processing of zeolite minerals. The plant was built by Unión de Minería in Remedios, in the Villa Clara province, for the processing of raw material from the Piojillo-Tasajeras deposit. The raw material was dried, milled and packaged for animal feed and some agricultural uses.

In May 1988, the Cuban authorities approved the Zeolite Development Program designed and elaborated by Cuban researchers and technologists [25]. The main objective of the Program was *the rapid introduction of zeolite applications in agriculture, industry, services and medicine, with full material and productive support from the Cuban government*.

In the 1989-1991 period, four big plants were built for the processing of zeolitites. The placement of these plants took into consideration the location of the deposits, and the best geological-mineralogical and technical–mining conditions, with the purpose of distributing the product within a relatively short distance to the users of less than 200 km. The plants were built close to the deposits (5-9 km), with a total production capacity of 600,000 tonne/year. The plants are in the provinces of La Habana, Villa Clara, Camaguey and Holguin (Map and Table 3).

Table 3. Location of zeolite processing plants and proven industrial reserves in the deposits.

Deposit	**Region**	**Municipality, province**	**Proven reserve** [10^6 tonnes]
Castilla-La Pita	Western	Jaruco, Mayabeque	1,00
Piojillo-Tasajeras	Center	Ranchuelo, VillaClara	4,00
El Chorrillo	Center eastern	Najasa, Camagüey	2,30
San Andrés	North eastern	Holguín, Holguín	1,15

The evaluated reserves and resources of Cuban zeolite rocks are classified in four categories: calculated, indicated, inferred, and prognostic, for exploitation over short to medium time frames. According to the category of *deposit,* established by the National Office of Mineral Resources (ONRM in Spanish), Cuba has 31 investigated deposits of natural zeolite from where the zeolitic raw material was or is extracted (Table 1). The estimated industrial reserve in the 31 studied deposits is some 121 million tonnes with potential for applications in agriculture, livestock, building material, fertilizer and chemical industries, drinking water purification, treatment of industrial and nuclear wastewaters, environmental remediation, and for drug formulation for humans and animals.

The plants are operated by the public companies Geominera Oeste, Geominera Centro and Geominera Oriente, members of the Grupo Empresarial GeoMinSal of the Ministry of Energy and Mines (MINEM). The mercantile society MITSA S.A. (see the brochure below) represents the Cuban zeolite enterprises for trade of zeolite products and other commercial interests [26]. The industrial processing of the Cuban zeolite mineral includes grinding, first particle size classification, drying, milling, second particle size classification, and packing with the trademark products Fertisol (1-3 mm), Zoad (< 0.8 mm), Zook (3-9 mm) and Microlit (< 0.074 mm) (see map). National and foreign clients of the Cuban zeolite industry buy these products for the applications reported in the following list:

Actual Cuban natural zeolites utilization

• Natural substrate for horticultural facilities	• Production of active ingredients for drug formulation
• Natural substrate to foster root growth	• Filter beds in water purification plants
• Production of mixed and granular fertilizers	• Construction and maintenance of roads and highways
• Compost production	• Maintenance of sport facilities
• Soil amendment	• Treatment of wastewaters
• Food additive for animal	• Additive for high resistance concretes
• Animal litter	• Flocculants for the clarification of sugarcane juice in sugar factories

MITSA
SOCIEDAD MERCANTIL

ZEOLITE

Zeolite is a mineral belonging to the group of natural aluminosilicates. Its use depends fundamentally on the granulometry of the product.

PRESENTATIONS AND RECOMMENDED USES OF OUR PRODUCTS

Natural Zeolite			
SiO_2	66-68 %	LOI	10.80-11.02%
Al_2O_3	11.8-12.7 %	Color	Green/Grey
Fe_2O_3	1.07-2.08 %	Poro volume	0.0189 cm^3/gr
Na_2O	1.34-1.57 %	Thermal Stability	400 ºC
K_2O	1.09-1.20 %	Cation exchange capacity (meq/100g)	Ca^{2+}: 83.0 Mg^{2+}: 1.2 Na^{+}: 1.2 K^{+}: 14.0
CaO	2.78-3.19 %		
MgO	0.77-0.95 %		
pH	< 10 %	Mineralogical composition	Alumino sodium-potassium silicate; Clinoptilolite-Modernite: >85 %
Humidity	< 12.0 %		
Specific Weight	2100-2240 Kg/m^3		

FERTISOL (Granulometry: 1-3 mm; + 3mm: 5%, -3 + 1mm: 85%, -1mm: 10%)
Improves the efficiency of chemical fertilizers, organic and the physical and chemical properties of soils. It reduces costs by 10-15% in formulations of chemical fertilizers. It retains gases, water and nutrients and releases them to be used by plants. It controls the acidity of the soil and improves its physical and chemical properties.

ZOAD (Granulometry: <0.8 mm; + 0.8 mm: 5%, -0.8 + 0mm: 95%)
Zoad affects the reduction of mortality of cattle and poultry. It increases the average egg weight for laying hens, the production of milk, fat and total solids in dairy cows, and reduces diarrhea and other digestive diseases in calves. It is a food supplement in animal feed.

ZOOK (Granulometry: 3-8 mm)
Zook is a granular complex, specially made for use as a bed for commercial breeding animals. It guarantees an adequate level of hygiene in all types of beds of pets and commercial. Widely used in cat litter.

MICROLIT (% retained on sieve 200 mesh (0.074mm) <7.6%)
It is used as an additive mineral in the elaboration of concentrated foods destined for animal feeding of different species, in the conservation of grains, in the purification of toxins in foods, manufacture of waterproofing of covers, of medicinal talcs and as substitute of compounds in the Powder detergents, to name a few of its various applications.

Five other crushing plants process the zeolitic rocks from deposits close to cement plants (Table 4 and map). The final product is used as pozzolanic additive to cement. A sixth plant was built in 1989 for the industrial production of Roman Cement (a mixture of zeolite and calcium oxide) in the Palmarito deposit, in Santiago de Cuba province, with a capacity of 120,000 tonnes/year. This plant operated until the beginning of the turn of this century. The Cuban Cement Industry of the Ministry of Construction operates all these plants. Its plans include a higher exploitation of the industrial reserves of the zeolite deposits.

Table 4. Location of the cement plants and their zeolite deposits.

Cement plant	Locality, province	Deposit
Cementos Curazao N.V.	Mariel, Artemisa	Los Congos
“Mártires de Artemisa”	Artemisa	Los Congos
Cementos Cienfuegos S.A.	Cienfuegos	Las Carolinas
Cementos Siguaney	Sancti Spíritus	Siguaney
“26 de Julio”	Nuevitas, Camagüey	Las Margaritas-El Rubio
“José Mercerón”	Santiago de Cuba	Palmarito (puzolana)

Quality management of zeolite products

The experience in Cuba with natural zeolites led to the elaboration and adoption of standards. The Cuban Standard NC 625: 2014 Natural Zeolite — Requirements [27], was approved in 2008 after 20 years of research, and validated the analytical methods specific to natural zeolites developed by the Cuban specialists. This standard is a set of strict regulations (Table 5) based on the experience of a group of Cuban specialists from the industry and research centres. In Cuba, all person related with natural zeolites, uses this standard as a tool to study, develop, produce and sale zeolite materials, with the certainty that the zeolite community can understand the results. Two other regulations are under investigation to establish methods for the determination of dioxins and fluoride.

Table 5. Standards contained in Cuban Standard NC 625: 2014 Natural Zeolite — Requirements [27].

Standard number	Name
NC 626: 2014	Natural Zeolites – Determination of total cation exchange capacity — Ammonium chloride method
NC 627: 2014	Natural Zeolites – Samples preparation for laboratory tests
NC 628-1: 2014	Natural Zeolites – Determination of noxious elements — Part 1: Determination of mercury content – Cold vapour method
NC 628-2: 2014	Natural Zeolites – Determination of noxious elements — Part 2: Determination of arsenic, cadmium and lead by inductively couple plasma atomic emission
NC 629: 2014	Natural Zeolites – Determination of zeolite, clay and calcite contents by thermal analysis
NC 630: 2014	Natural Zeolites – Determination of zeolite contents by X-ray diffraction
NC 631: 2014	Natural Zeolites – Particle size determination

The Annex A (normative) of the standard establishes the requirements of natural zeolite for its use in human and animal health and nutrition:

a) Mineral phase composition: clinoptilolite-heulandite (>65 %), mordenite (<5 %) and calcite (<5 %).

b) Noxious elements composition (g/tonne): F (<200), Pb (<10), As (<3), Cd (<2), Hg (<5) and dioxins (<1).

Other requirements are also regulated: green-gray colour, odourless, particle size (depending on the application), real density (1.4 - 1.6 g/cm^3), apparent density (0.6 - 0.8 g/cm^3), and humidity (<10 %).

The standard NC 625: 2014 also establishes three types of natural zeolite ores (TNM in Spanish) according to zeolite content determined by X-ray diffraction following the standard NC 630: 2014, and the total cation-exchange capacity following the standard NC 626: 2014 determined by the method of ammonium chloride. Table 6 shows the classification of zeolite ores according to their zeolite content and CEC.

Table 6. Zeolite ore types established by Cuban Standard NC 625: 2014

Physical and chemical property	Unit	Ore type		
		I	II	III
Zeolite content (minimum)	%	80	60	40
Total cation exchange capacity (minimum)	meq/100g	120	80	55

Products and technologies of high value-added

The concept of Natural Zeolite Engineering can be expressed as the adequate combination of chemical treatment with substances selected for their own characteristics, and physical treatment of the selected zeolitic mineral, according to the preconceived design of the new zeolite and its properties for a given purpose [28]. Based on the previous experience of Rodríguez-Fuentes circa 1980 [24] to obtain new materials, using technological procedures that not only modify the pore size of the zeolite, the specialists of the Laboratory of Zeolite Engineering (LIZ, in Spanish) of the Universidad de La Habana (UH), heading by G. Rodríguez-Fuentes have pursued this line of Research & Development + Technological Innovation with Cuban natural zeolites since 1989. The LIZ is the leader of innovation in the processing of zeolites [29-31]. This laboratory received crucial support from the UH's Tech-transfer unit (OTRI, in Spanish), including contract management work, a process that can be characterized as entrepreneurial [32]. The LIZ has designed, developed and introduced new materials based on Cuban zeolites (Table 7). Various technologies developed by LIZ (NEREA® substrates, NEREA® fertilizers, zeoponic technology, NZ, ZZ®, Enterex®, Neutacid®) were transferred to Cuban public companies since 1988, taking into account international regulations for the process of technological innovation. OTRI has signed contracts to export LIZ's zeolite products of high value-added produced in pharmaceutical plants and others with available production capacity. Sales of LIZ's product ZZ to Mexico began in 1994. Export of the purified natural zeolite NZ started in 2004. Through OTRI, LIZ began the transfer of technology to foreign companies in 2006. In 2011, innovation activities at the LIZ were transformed by a joint-production contract signed with a Cuban public company. Under the agreement, the LIZ provides technology, equipment and product quality management, while the company provides financial support, industrial facilities, technical workers and the market. The agreement allowed the construction of an experimental plant for the production of ZZ® microbicide (capacity 200 tonne/year) and the assembling drinking water purification systems using ZZ as purifier. The plant has a sanitary permit for production since it meets Good Manufacturing Practice (GMP) requirements. This plant also produces ZNPmed® (NZ), Colestina® and FZ®. The Cuban zeolite company Geominera Oriente and the UH are developing an association agreement for the joint production of LIZ products ZZ and NEREA substrates and fertilizers; the two industrial plants will be commissioned in early 2018.

NatZEng® Natural Zeolite Engineering, the consulting service firm [33] created in 2016 by the incubator project of the University of Havana and the University Von Humboldt, offers all the technologies for production of the zeolite products developed by LIZ, and the experience accumulated by the Cuban natural zeolite specialists, and their colleagues from other countries. Recently, Rodríguez-Fuentes *et al.* published a comprehensive analysis of the creation of Cuban natural zeolite industry as a technological innovation process of the Cuban universities and public research centres along the last 47 years [34].

Table 7. Products and technologies developed by LIZ-UH.

Product and technology	Field of application
NEREA® substrates for soilless culture	Agriculture
NEREA® zeoponic technology	Agriculture
NEREA® fertilizers	Agriculture
Colestina®, additive for animal diets	Agriculture
ZNPmed®, purified natural zeolite NZ additive for diets	Human health
Enterex®, antidiarrheal tablets	Human health
Neutacid®, antacid chewing tablets	Human health
Colestina®, hipo-cholesterolemic	Human health
FZ®, anti-hyperglycaemic	Human health
ZZ®, microbicide for formulation of antiseptic drugs	Human health
ZZ®, microbicide for drinking water purification	Human health
Cream ZZ® dermic cicatrizer of pressure ulcer, burns and scratch	Human health
Elimination of ammonia, Ni and Co of wastewaters of the hydrometallurgy of nickel	Environmental remediation
Immobilization of heavy metals of industrial wastewaters	Environmental remediation
Monoliths for purification of fluids	Environmental remediation
Acid catalyst for ethanol dehydration to produce ethylene	Industry
OPAZ® opacifier of glass, ceramic and paint	Industry
Paints for walls	Industry

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