

NON-METALLIC MINERAL DEPOSITS OF THE TOKAJ MOUNTAINS NEOGENE VOLCANIC AREA

by

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Introduction: The Tokaj Mountains are of outstanding importance in the extraction and beneficiation of non-metallic mineral raw materials. This role is similar to that of the Transdanubian Central Range in the bauxite mining (Fig. 1).

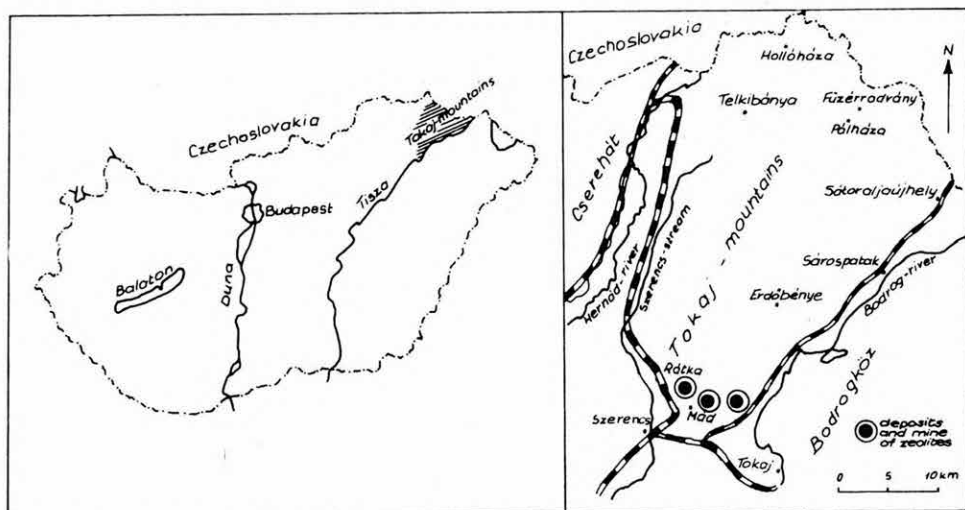


Fig. 1. Geographic situation. Map of the region

The 70×35 km area of the mountains, genetically belonging to the inner Carpathian volcanic zone, accommodates 13 mineral types deserving a special rank among the other volcanic aluminium-silicate rocks not for their metal or energy content but for their advantageous features due to their mineral composition (Fig. 2).

The exploration, mining and utilization of mineral deposits in the area of the mountains started in the historical past. At present, the raw materials from the mountains are exploited in 13 mines and processed and beneficiated in four dressing plants. The annual production is over 300 thousand tons. The semi-products or products manufactured from the raw material are delivered to about 1200 users in 45 main directions, to be utilized in remote areas of the country or to cross the border as exported goods (Fig. 3).

Among the mined minerals there are raw materials, like quartzite, used by prehistoric man for his tools which find their application in the industry of today as

Serial number	Denomination	Sign	Raw material		Useful mineral components	Main cation of the useful mineral	Relative degree of change of the parents rocks	Beginning of using or mining		in Tokaj	
			Useful quality					in the world	in Tokaj	Number of types of raw material	Number of deposits
1.	Quartzite		hardness, solidity		quartz, opal	Si		prehistoric age		2	7
2.	Kaoline		whiteness, fire-resisting plasticity		kaolinite	Si, Al, K		antiquity	1569. Sárospatak	5	15
3.	Potash tuff		low melting point, whiteness		kaolinite, adulara sanidine	Si, Al, K		xx century in Europe	1960. Szarvas	2	2
4.	colouring earth		colouring material		hydrohematite limonite	Si, Al, Fe		prehistoric age	1944. Mád	2	2
5.	Bentonite		plasticity, ion exchange swelling		montmorillonite	Si, Al, Ca, Mg		1925 Fort Benton USA	1940. Kamibaska	5	9
6.	illite fine clay		whiteness, plasticity melting		illite	Si, Al, K		xix century in Europe	1920. Füzér-madány	2	2
7.	zeolite		whiteness, ion exchange absorption		clinoptilolite			1880. Japan	1960. Mád	1	2
8.	Trass		building material		volcanic glass			Antiquity in Roma	1955. Rátka	2	4
9.	Pumicit		building material		pumice			1950 Italy	1940. Szegi	1	1
10.	perlite		therm. swelling, low density porosity		volcanic glass			1941. USA	1954. Pótláza	1	2
11.	kalitrochite		k-fertilizer		adulara			-	1980. Helyháza	1	1
12.	Diatomite		absorption, low density porosity		fragments of sil. algae	Si		Antiquity in Roma	1957. Erősbénye	2	4
13.	Loess		building material		quartz, kaolinite illite	Si, Al, K		Antiquity in Babylon	1569. Sárospatak	1	1
sum total 15 non-metallic raw material			quality of acidic volcanic rocks or minerals their alteration		volcanic or clay minerals			prehistorical or industrial minerals		17	47

Fig. 2. Non-metallic raw materials in the Sarmatian volcano-sedimentary formation on the Tokaj Mountains

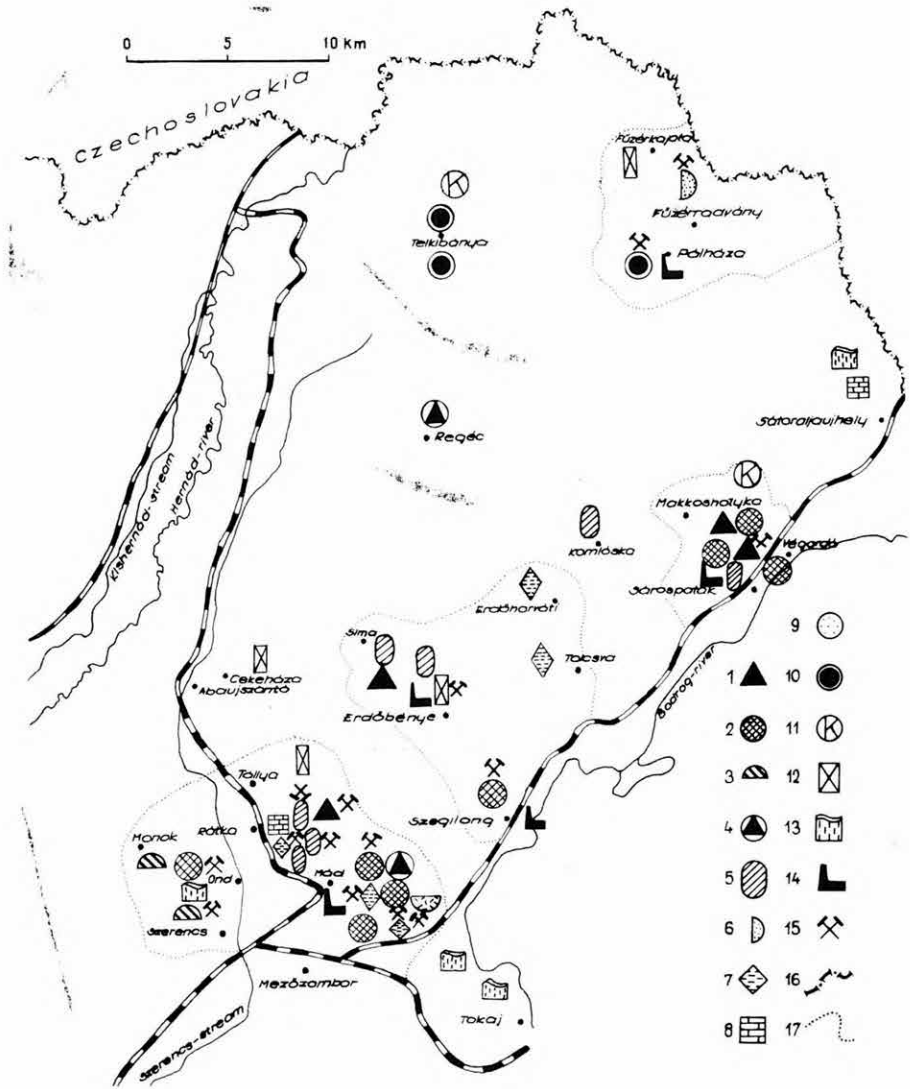


Fig. 3. Areal distribution of the mining works, explored mineral deposits and mineral-dressing plants in the Tokaj Mountains

1 Quartzite, 2 kaolite, 3 potash tuff, 4 bole, coloring earth, 5 bentonite, 6 illitic fine clay, 7 zeolitic rhyolite tuff, 8 trass, 9 pumicite, 10 perlite, 11 kalitrichite, 12 siliceous earth, 13 loess, 14 mineral-dressing plant, 15 operating mine, 16 national boundary, 17 boundary of the area of mineral resources for mining

drum mill lining and millstone in mills eliminating Fe contamination. There are also entirely new minerals owing their ranking as raw materials to the technological industrial needs of today. The rhyolitic tuffs with natural zeolite belong to this latter category.

1920 illitic fine clay
1937 siliceous earth
1940 bentonite
1955 perlite
1965 trass
1972 potash tuff
1979 zeolitic rhyolite tuff

The pumiceous rhyolite tuff with relatively high content of natural zeolite (above 35%), referred to as zeolite in the industry, is one of the youngest mineral raw materials in the study area. Attracting the interest of potential users, the explored mineral reserves exceed 100 million t in this area. Further reserves of the same amount and similar quality are registered as prospective. The mineral base for the efforts aimed at the utilization of natural zeolitic minerals, the realization of their value and creation of natural zeolite based products was available as early as 1979.

The utilization of zeolitic minerals is based upon the large-scale distribution of the pure mineral and its useful qualities. The accumulation of relative knowledge and the development of the local zeolite industry based on this knowledge is the result of the research of the past 10 to 15 years.

Research of natural zeolites

In the 1960's Hungarian specialists, T. MÁNDY, E. NEMECZ, GY. VARJÚ and G. KLOPP, found that the cemented rhyolitic tuffs contained two characteristic zeolitic minerals, *mordenite* and clinoptilolite. Geological investigations indicated that the thickness of the rhyolitic tuffs containing at least 30% of *mordenite* or clinoptilolite amounted to 80 to 100 m. They are locally traced over several square km.

These large homogeneous masses are genetically related to subaquatic volcanic eruptions. They are distributed in flat lense-like accumulations of tuffs around sub-aquatic eruption centres. The commercial value of the rhyolitic tuffs is determined, besides their amount, by their advantageous characteristics.

These are determined by the structure of the chemical components rather than the composition. Thus the determination of the advantageous features was performed simultaneously with the development of investigations aimed at a determination of the structure of *silicates*, *aluminium silicates*. It was proved that other mineral components of natural zeolite-bearing rocks such as clay minerals and volcanic glass, did not influence negatively the main features of zeolite-bearing rocks such as biogenic gas absorption, ionic exchange and activable trace- and rare element content. On the contrary, these qualities did improve.

By the end of the 70s the "new mechanism" had been completely acquired in the industry as well. The agriculture switched over to industrial methods both in plant cultivation and stock-breeding. Town planning increased and the first threatening signs of pollution were registered. The resolution of the actual problems in the industrial plant growing, livestock breeding and environment protection could be the use of rhyolitic tuffs bearing the advantageous qualities of the natural zeolites after a suitable dressing procedure.

The zeolitic minerals of the Tokaj mountains and their occurrence

Only two of the 15 zeolitic minerals occurring in Hungary (Fig. 4) are found in the Tokaj Mts. These are clinoptilolite and mordenite. The other zeolite varieties occurring in the pores of basalts or andesites or in the fissures of these rocks and forming decorative crystals are insignificant in quantity. The concentration of zeolite as referred to the total rock mass does not exceed 1% even in the most enriched parts.

In the large-pored pumiceous pyroclasts, rhyolite tuffs of the Tokaj Mts, zeolite crystals are of rather small, microscopic or submicroscopic size. The phenocrysts, visible under microscope or even with the unaided eye formed, in this case too, in the micropores or fissures, but *zeolitization* in the tuff or tuffite material itself is also rather important. As opposed to the crystals of the pores and fissures here, xenomorphic crystals resembling zeolite in their internal lattice structure are characteristic. Zeolite formation in the Tokaj Mts followed the first subaquatic eruption periods of Pacific acidic volcanism with three intensive phases during the Neogene. The formation of zeolite crystals, as seen from laboratory and factory experience, requires the coincidence of the following parameters in time and space:

1 Parent rock forming the lattice of the natural zeolitic minerals with the main rockforming elements.

2 Energy necessary for the decomposition of the parent rock and zeolite formation.

3 External pressure required for the formation of the zeolitic lattice.

4 High humidity and the relative tension, due to water-vapour pressure.

The prerequisites for zeolite formation were provided in the subaquatic acidic volcanic environment of the Tokaj Mountains as follows:

1 *Parent rock*: Pacific or slightly alkaline, acidic volcanic glass.

2 *Energy*: Heat energy from the volcanic eruption and hydration in the sludge belt.

3 *Water-vapour steam tension*: pressure of the water head above the volcanic channel and the internal pressure of the heated system.

These factors proceeded parallelly in time and space three times during the three intensive volcanic phases in the Neogene evolution of the Tokaj Mountains. Therefore, there are three volcanosedimentary horizons, especially rich in natural zeolites in the study area (Fig. 5). The mineable horizons on the surface and near it were formed in the Sarmatian as well as at the Sarmatian—Tortonian boundary. The uppermost, oldest zeolite horizon crops out only in a local spot and only in the NE. Commercial deposits are found mainly in the SW, the Mád—Rátka—Bodrogkeresztúr area, formed during the explosions of the Sarmatian volcanic megarhythm. In this area, detailed exploration discovered five explosive horizons. The 1st of these horizons is at several hundred metres below the surface. It is mainly due to argillization being, tuffitic character.

The several hundred metre thick pyroclastic rocks of the IInd and IIIrd horizons in the Rátka—Mád—Bodrogkeresztúr area bear the largest complex of zeolitic rhyolite tuff ever found in Central Europe. The Rátka area (Fig. 6) is characterized by cemented pyroclastic rocks with 35 to 55% clinoptilolite. The identified, categorized reserves are over 50 million ton.

The IIIrd explosive horizon in the Bodrogkeresztúr area is characterized by subaquatic explosions. The blanket-like eruption products locally exceed 500 m.

GROUP OF CRYSTALS TYPE	NAME OF MINERALS	CHEMICAL COMPOSITION OF MINERALS	CHARACTERISTIC MORPHOLOGY OF CRYSTALS	SI/Al value							Typical volcanic rock with natural zeolites				OCCURRENCE	CHARACTERISTIC DEPOSIT
				1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	tonalite	basaltite		
I.	thompsonite	$\text{Ca}_2\text{Na}(\text{Al}, \text{Si})_2\text{O}_5 \cdot 5 \text{H}_2\text{O}$	rhombic												in the hole of volcanic rocks	Mecsek-Balaton
	stieglite	$\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_6) \cdot 3 \text{H}_2\text{O}$	monoclinic												" "	Gülcis
	mezolite	$\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{30} \cdot 8 \text{H}_2\text{O}$	monoclinic												" "	Gülcis
	natrolite	$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 2 \text{H}_2\text{O}$	rhombic												" "	Mecsek
	phillipsite	$(\text{Ca}, \text{Na}, \text{K})_3(\text{Al}, \text{Si})_3\text{O}_{16} \cdot 16 \text{H}_2\text{O}$	monoclinic												" "	Mecsek
II.	analcime	$\text{NaAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$	cubic												on the surface of volcanic detritus	Somoskő - Tállya
	chabazite	$(\text{Ca}, \text{Na}_2)(\text{Al}_2\text{Si}_4\text{O}_{20} \cdot 6 \text{H}_2\text{O})$	trigonal												in the hole of volcanic rocks	Uzsa
	levyne	$\text{CaAl}_2\text{Si}_6\text{O}_{22} \cdot 6 \text{H}_2\text{O}$	trigonal												" "	Szab-Nadap-Dunabogáthy
	harmobome	$\text{Ba}(\text{Al}_2\text{Si}_6\text{O}_{26}) \cdot 6 \text{H}_2\text{O}$	monoclinic												on the surface of volcanic rocks	Nadap
	laumontite	$\text{Ca}(\text{Al}_2\text{Si}_9\text{O}_{44}) \cdot 3.5 \text{H}_2\text{O}$	monoclinic												" "	Somoskő
	epidzeimine	$\text{CaAl}_2\text{Si}_6\text{O}_{24} \cdot 5 \text{H}_2\text{O}$	monoclinic												in the hole of volcanic rocks	Mátra-Aszarlóhegy
III.	dezmine	$(\text{K}, \text{Ca}, \text{Na})_2(\text{Al}_3\text{Si}_7\text{O}_{41}) \cdot 7 \text{H}_2\text{O}$	monoclinic												" "	Nadap
	heulandite	$(\text{Ca}, \text{Na}_2)(\text{Al}_2\text{Si}_7\text{O}_{40}) \cdot 16 \text{H}_2\text{O}$	monoclinic												" "	Dunabogáthy-Csodáhegy
	kinoptilolite	$(\text{Ca}, \text{Na}_2)(\text{Al}_2\text{Si}_7\text{O}_{40}) \cdot 16 \text{H}_2\text{O}$	monoclinic												in the rhyolite tuff	Nadap
	mordenite	$(\text{Na}_4, \text{K}_2, \text{Ca})(\text{Al}_2\text{Si}_8\text{O}_{47}) \cdot 7 \text{H}_2\text{O}$	rhombic												" "	Rática
															" "	Bozsgyeresztúr

Fig. 4. The natural zeolites of Hungary

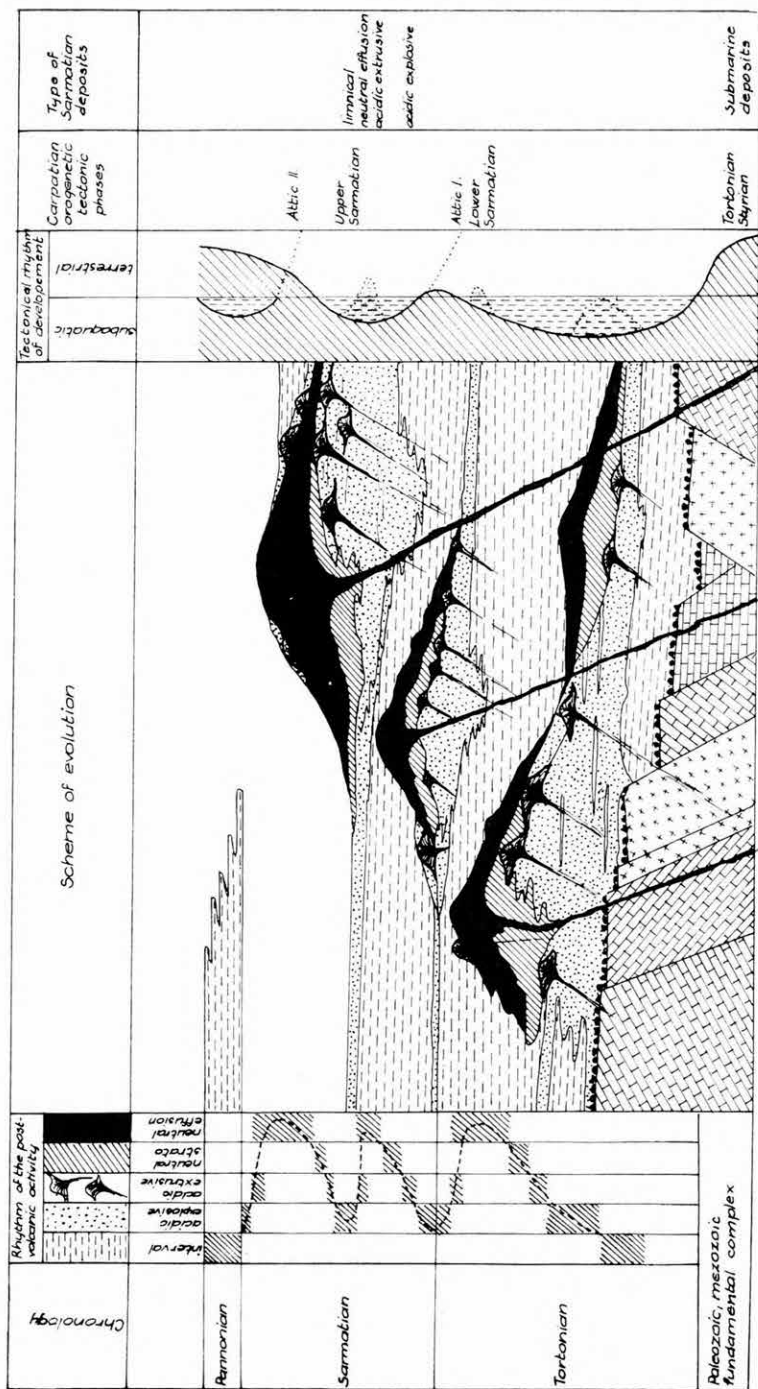


Fig. 5. Theoretical evolution scheme of the Neogene volcanic activity in the Tokaj Mountains

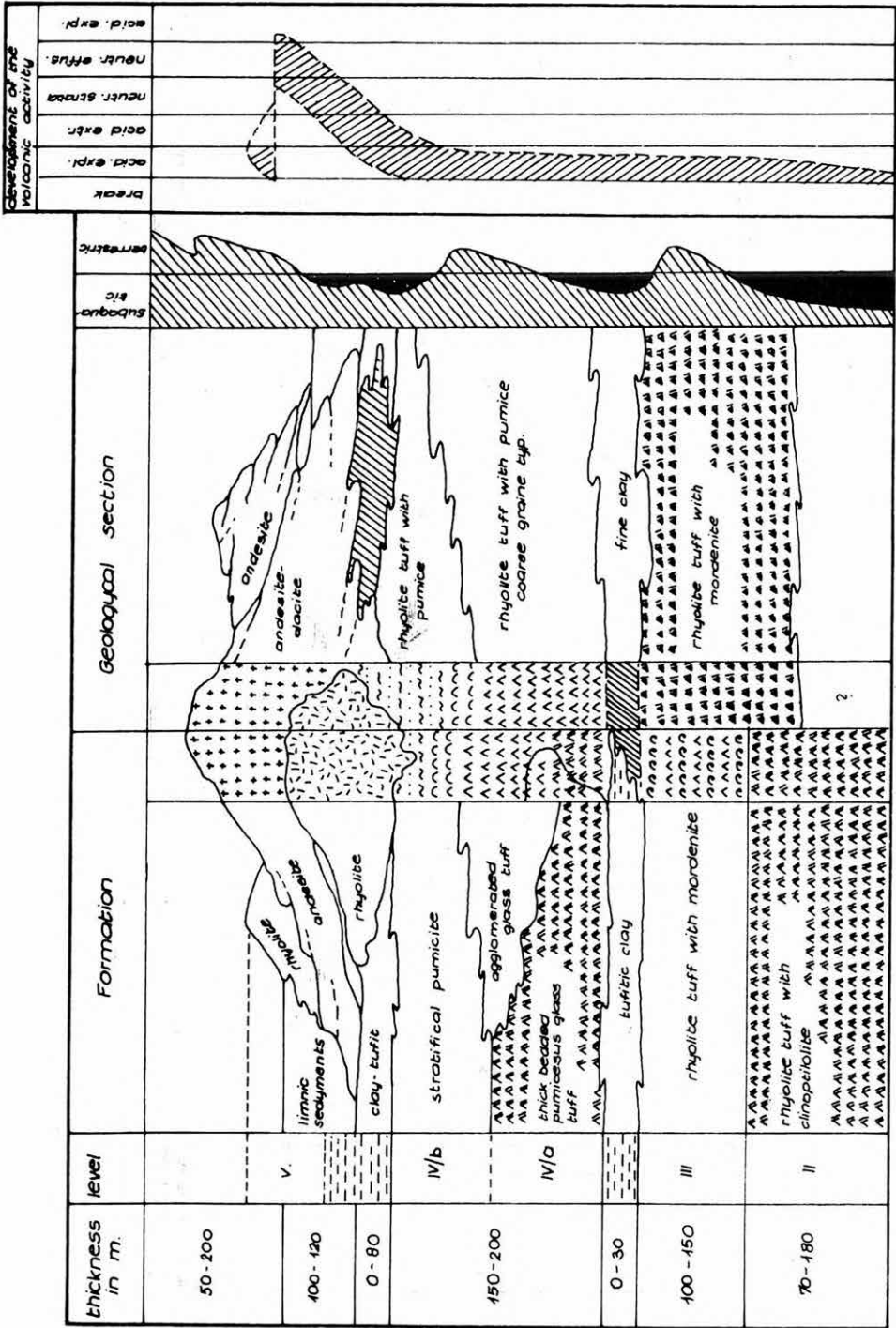


Fig. 6. Local geological development of formation

The mordenite content varies between 25 to 70 and 75%. The pyroclastic material with a mordenite content of 60 to 70% is found in separate, 1 to 2 m thick lenses within the tuff complex. *These deposits of pyroclastic rocks have the highest mordenite content in Hungary.*

Stratigraphically, the zeolite-bearing pyroclastic rocks are in the lower part of the Sarmatian volcanosedimentary complex and crop out of the tectonically tilted "erosion windows" in the mountain margin area, providing a possibility for open-pit mining. The valley of the *Szerencs* creek in the Rátka area is such a region of morphological inversion and weathering. The largest mordenite-bearing rhyolite tuff deposit in the Tokaj Mts is 5 km long, having been uplifted and thrust over the mountain margin between Bodrogkeresztúr and Mezőzombor. Therefore the exploration of natural zeolites is concentrated in this part of the mountains. As to the dressing of the zeolites it is favourable that the extraction of other non-metallic minerals is also concentrated in the Mád area. Therefore the special infrastructure of the mining and dressing industry has been available (Fig. 6).

Favourable parameters of the natural zeolites from the Tokaj Mountains

One of the good qualities of the zeolite cemented rhyolite tuffs, their relatively high porosity and insulation characteristics, was known to man in the Middle Ages already. Other qualities have been discovered in the last 10 to 15 years. As to the practical use the most important parameters are as follows (Fig. 7):

- 1 Biogenic gas adsorption.
- 2 Ionic exchange capability.
- 3 Trace and rare element content.
- 4 Antiparasitic effect.
- 5 Coherence with organisms of higher order.
- 6 Heavy-metal-trapping effect.

The discovery of the good qualities of zeolites and the emergence of social demand led to the launching of a programme for the utilization of natural zeolites in Hungary. Immediately at the beginning it became evident that the rocks from the deposits with zeolite content are not suitable for odour control, feeding, improvement of soil quality and environment protection without dressing, modification, regardless of their outstanding qualities.

Suitably prepared zeolitic rocks as well as rocks with associated minerals mixed with other non-metallic materials such as siliceous earth, kaoline, bentonite, illite, perlite, etc and dressed will represent products of natural zeolite content, suitable for the elimination of the above-mentioned problems.

It is especially advantageous in the Tokaj Mts that these minerals are mined in zeolite areas (Fig. 3).

These composite mineral products bear the advantageous qualities of both the natural zeolitic minerals and other non-metallic minerals.

1 A special composite-mineral product, displaying ionic exchange and gas absorption qualities with an appropriate trace rare element composition, was developed so as to be used for enhancing the growth of the crops and improvement of soil quality.

2 When used for feeding and making up for trace- and rare element deficiency, products of different grain size, consistency and mineralogical and chemical composition are required for different animals. Considering these requirements a special

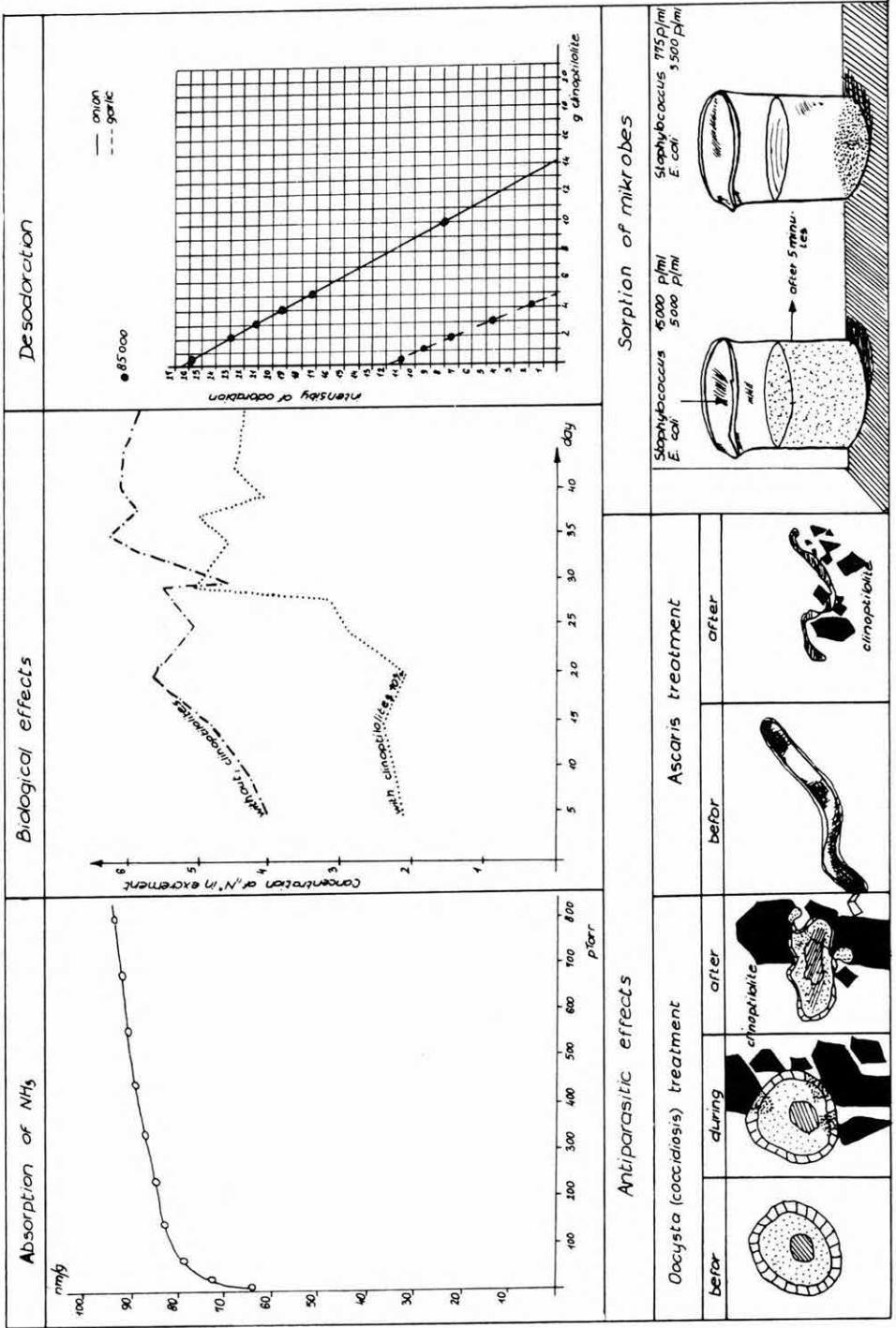


Fig. 7.

product was developed under the name **ZEOVIT—RCL—O**. Given its trace element content with qualities improving the climate of poultry-houses controlling odours and serving as a natural sorbent, it is readily utilized in poultry farming.

3 As to environment protection, **ZEOIRIX—8—M**, a multi-purpose animal litter is designed to solve the problems concerning animals, kept in blocks of flats (odour control, desinfection, feeding). This product has all the advantageous qualities of the natural zeolites and besides, it has an increased moisture capacity.

ZEOIRIX—8—O is a similar product with a moisture capacity of 40 to 50%, suitable for the absorption of hydrocarbons, quick elimination of oil puddles and other contaminations from workshops.

4 **AKVAROSORB** is another zeolitic product deserving attention. This product has a good effect on the environment of large-scale fish ponds by filtering out ammonia and ammonium ions and absorbing the toxic materials discharged by the fish.

5 Bacterio-sorbency, desinfection and antiparasitic effect are important with products used for the desinfection of playgrounds, parks and sand-boxes. These products are harmless for higher organisms (children).

6 We have developed special filter-lining for the treatment of liquid manure. These filters will trap the harmful components so effectively that it will be possible to canal the filtered material right into live waters. Other zeolite-based products help solving minor household problems like odour-control of refrigerators and ash-trays. Other products, such as *Zeolin* paste, *Surolit-ZHS* scrubber are useful in household scrubbing and cleaning. These products are harmless for the environment and facilitate sewage cleaning.

The utilization of special-quality products made from zeolites is advantageous not only for their immediate effect in the phase of application but their secondary effect as well.

With the approximately 20 varieties of natural zeolite-based special-quality products developed so far do not deplete our possibilities are not exhausted. Zeolites may play an important role in the future resolution of practical industrial problems owing to their good qualities. Specialists are experimenting with mordenite-rich rocks to produce filters for cleaning gases discharged from nitrosamine factories. Natural zeolite-based products will find application in cleaning industrial gases and sewage slurry from electroplating factories.

Production of natural zeolite-based products in Hungary

The development project for the utilization of natural zeolites was launched in 1979 when resources and mineral qualities were studied. Since laboratory and semi-industrial experiments had given positive results, a pilot plant was put in operation. The rapid increase in the rate of production volume is seen in Fig. 8. Sales figures of natural zeolite-based products for the past production period (Table 1):

Table 1

Period of production	Sold product in tons	Equivalents in hundred HUF
1978	40	120
1979	491	1,532
1980	601	4,425
1981	5,779	19,516
1982	8,828	32,743
1983	8,902	32,168
1984	15,000	48,100

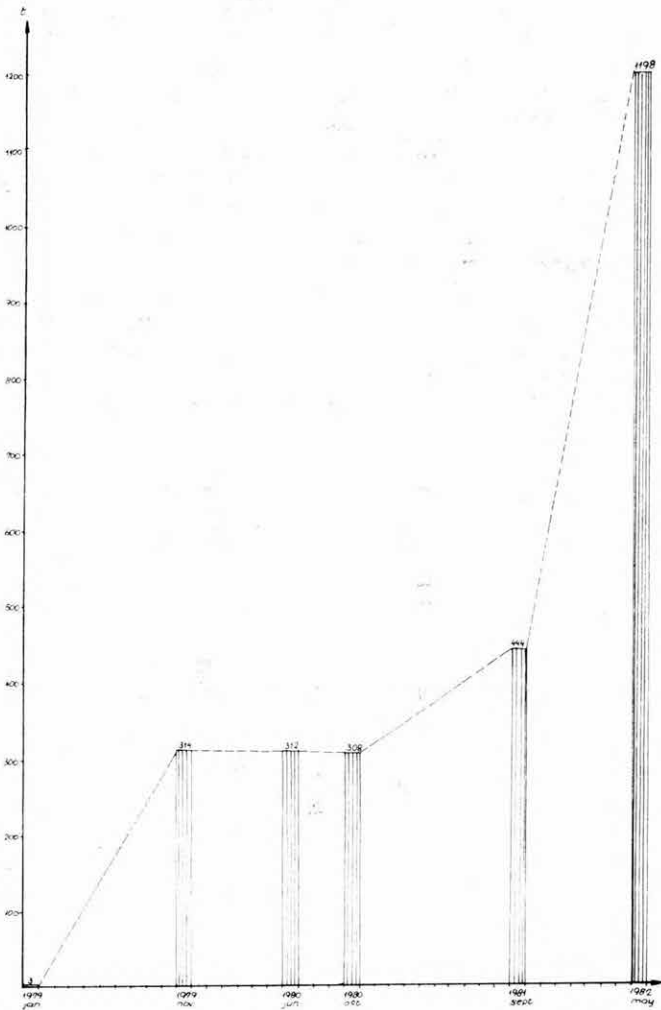


Fig. 8. Development of the utilisation of natural zeolites for animal feeding in Hungary

The special quality of the zeolite reserves and natural zeolites of the Tokaj Mts in Hungary provides a guarantee for their playing an important role in the solution of problems concerning the improvement of soil quality, animal feed production and environment protection both in Hungary, elsewhere in Europe.

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