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ZEOLITE MINERALS FROM INTERMEDIATE VOLCANIC ROCKS OF TOKAJ MTS., NE-HUNGARY

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ABSTRACT

In recent years zeolite minerals have been found in large number in the Tokaj Mts. The examinations show that the parageneses in the intermediate rocks differ from those known in the acid rocks or pyroclastites of the area. The dominating minerals are mordenite, heulandite and stellerite. As a rarity two species the hungarian occurence of which was unknown up to now were found in an outcrop near Regéc. In this paper the author gives the description of the parageneses, the species identified, discusses the formation of the assemblages and crystal morphology referring to instrumental examinations.

INTRODUCTION

There are very few data presented on zeolites occurring in the intermediate volcanic rocks of the Tokaj Mts. As first TOKODY (1959) described heulandite and chabasite crystals found in the cavities of andesite in a quarry near Füzérkomlós. In the sixties G. PANTÓ collected heulandite crystals occurring in andesite, near Ujhuta (KULCSÁR oral communication). The exact place of the locality is not known however. In the course of the recently commenced geochemical research of the old workings at Telkibánya white chabasite rhombohedras reaching half centimetre were found in the Teréz-adit (FEGYVÁRI oral communication). JÁNOSSY *et al.* (1987) referred to mesolite and stilbite from the Mt. Kopasz, near Tokaj, without further data. SZAKÁLL (1991) wrote up a locality with abundant zeolites at Óhuta and Regéc.

METHODS

The equipment used for the examinations: SIEMENS D 500 (Dept. of Mineralogy, ELTE, Budapest) and PHILIPS PW 1730/10 (Dept. of Mineralogy, University of Veszprém) X-ray diffractometers. EDAX 9900 energy dispersive spectrometer and AMRAY 1830 I scanning electron microscope (Dept. of Metallurgy, University of Miskolc).

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Localities and Minerals

Óhuta

The richest zeolite occurrence is in an outcrop on Mt. Kis-Zabarla by a dirt track along the right side tributary of the Hutavölgyi brook between Óhuta and Regéc. Here the andesite is strongly altered and cracked the fissures are filled with the mineral assemblage formed by the postvolcanic processes (*Fig. 1*).

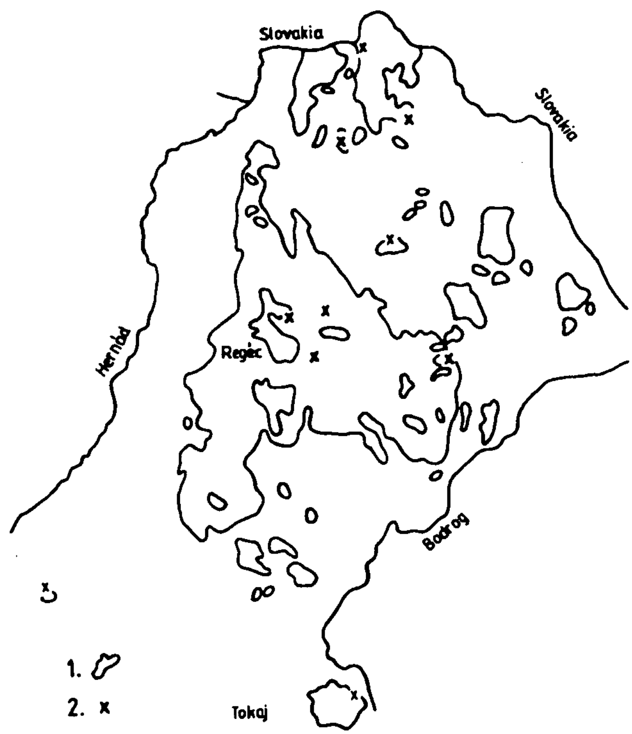


Fig. 1. Zeolite-occurrence in the intermediate volcanic rocks in the Tokaj Mts. (North-Hungary)
1. outcrops, 2. occurrences

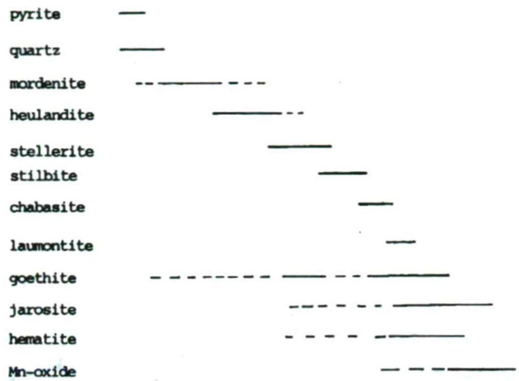
The minerals observed in order of crystallization (Table 1.): pyrite, quartz, mordenite, heulandite, stellerite, stilbite, laumontite, chabasite, hematite, goethite, jarosite.

Quartz occurs as small, short crystals or in the form of some millimetres thick chalcedony crusts. The first crystallized zeolite is mordenite which is the dominating phase of the assemblage. (To identify the zeolite phases, X-ray powder diffractometry and electron microprobe analysis were applied in each occasion.)

Modernite forms acicular crystals or found in fibrous masses. According to SEM images the individual crystals are hexagonal in cross-section and their surface is often eroded due to weathering (*Fig. 2.*).

TABLE 1.

Order of crystallization in thr zeolite-assemblage at Óhuta (Mt. Kis-Zabarla)



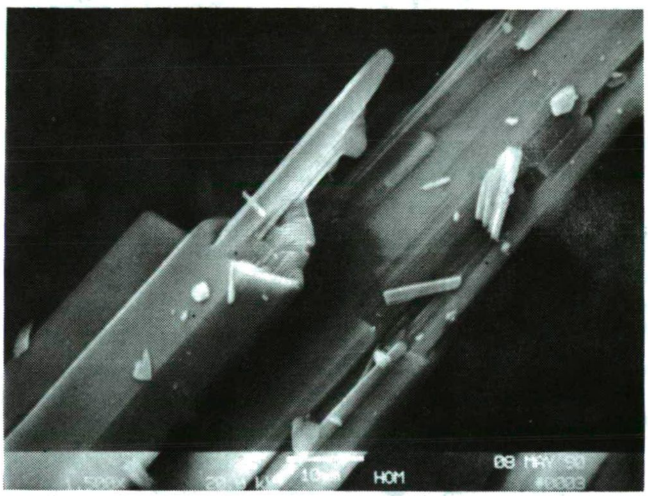


Fig. 2. Mordenite crystals, hexagonal in cross-section. Mt. Kis-Zabarla, Óhuta, SEM micrograph

Heulandite is sometimes found alone but most frequently it is associated with fibrous mordenite. It is well-developed crystals penetrated by modernite are really amazing. It is often found in clear, colourless tabular crystals reaching 1 centimetre. (100), (010), (101) forms can be observed on them.

Stellerite has coloumnar or thick tabular colourless crystals, reaching 0.5 centimetres in length, with faces of the (010), (110), (111) forms. Sometimes it is also found in flabelliform aggregates made up by 6-7 individual crystals. Stilbite is found in 2-3 centimetres large colourless or white tabular crystals with the forms (010), (110), (001).

Chabasite occurs rarely, forming colourless or white rhombohedras reaching 1 centimetre.

The latest crystallized zeolite is laumontite which has been observed twice forming milky white half centimetre large columnar crystals with the forms (110) and (201) (*Fig. 3.*).

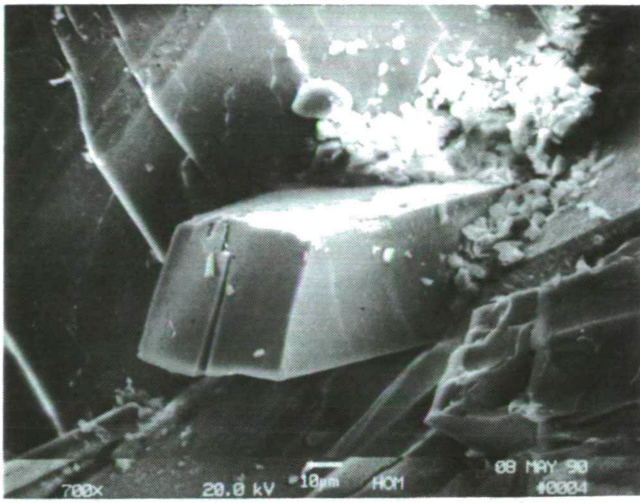


Fig. 3. SEM micrograph of a short, columnar laumontite crystal. Mt. Kis-Zabarla, Óhuta.

The zeolites are associated with disseminated pyrite, goethite, hematite, jarosite and a Manganese-oxide not identified yet.

There is also another locality near Óhuta where zeolites have been found. This is a small outcrop of a dirt track along side the Cserkő brook. Zeolites are found here in the cavities of andesite associated with celadonite and chalcedony. The most frequent species is mordenite which forms fibrous aggregates and is often found without any associating phase. There is also stellerite, occurring with mordenite (*Fig. 4.*) and sparsely chabasite is found as crystals smaller than one millimetre.

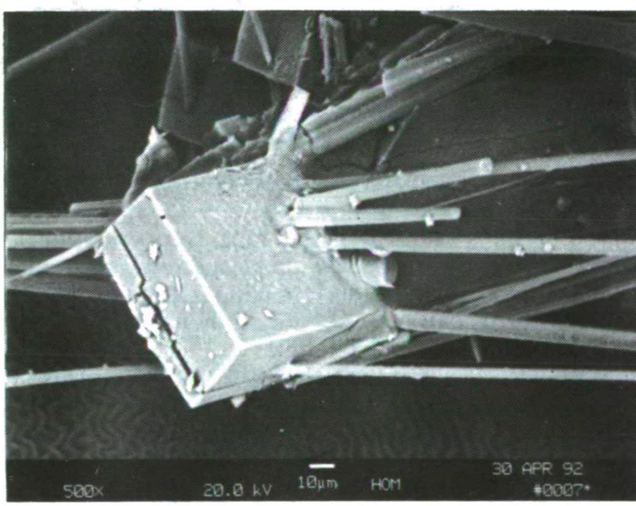


Fig. 4. Fibrous mordenite with stellerit. Cserkő-brook, Óhuta, SEM micrograph.

Regéc

Rare mineral assemblage was found in a small quarry near Mt. Torintás, north of the village. In the small cavities of andesite ferrierite and dachiardite was formed associated with pyrite hexahedras, smaller than 1 millimetre, epigene goethite, jarosite, gypsum and chalcedony.

Ferrierite is white, sometimes yellowish due to goethite and forms spherical aggregates built up by acicular crystals (*Fig. 5-6.*). This morphology is similar to that of described from Weitendorf, Austria (ZIRKL 1973). The microprobe analysis of the ferrierite from Regéc (Table 2.) suggests that it contains a lot of Mg and poor alkalies. Having regard to it is chemical composition, it is resembling to ferrierites from Monte Lake, Canada (WISE-TSCHERNICH 1976) and Philip Island, Australia (BIRCH 1989) (Table 3.). The difference between it is X-ray diffraction

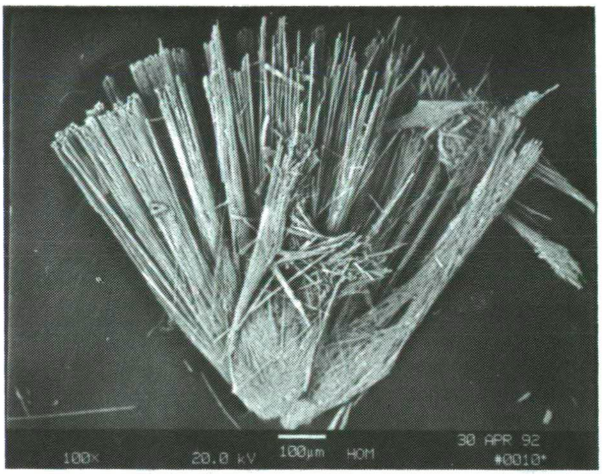


Fig. 5. Radiating aggregate of ferrierite crystals. Mt. Torintás, Regéc. SEM micrograph

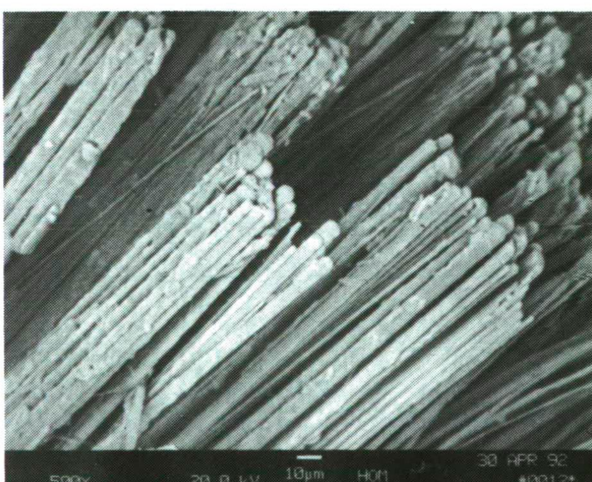


Fig. 6. Elongated ferrierite crystals. Mt. Torintás, Regéc. SEM micrograph

data on those of the right JCPDS card can possibly be caused by the difference in chemical composition (Table 4.).

TABLE 2.

Quantitave microprobe analysis of ferrierite from Regéc

mass %	1	2	3	mean
SiO_2	66.88	63.96	67.20	66.01
Al_2O_3	12.11	11.84	12.13	12.03
Fe_2O_3	0.10	0.12	0.05	0.09
MgO	3.20	3.15	3.20	3.19
CaO	1.45	1.41	1.43	1.43
Na_2O	0.12	0.12	0.12	0.12
K_2O	0.63	0.58	0.63	0.61
BaO	0.34	0.35	0.18	0.29
SrO	0.10	0.15	0.06	0.10
H_2O	n.d.	n.d.	n.d.	n.d.
Sum.	84.93	81.68	85.00	83.87
cation numbers on the basis of 72 oxygen				
Si	29.67	29.54	29.70	
Al	6.33	6.46	6.32	
Fe	0.03	0.04	0.02	
Mg	2.12	2.16	2.12	
Ca	0.69	0.70	0.68	
Na	0.10	0.11	0.10	
K	0.36	0.34	0.36	
Ba	0.06	0.04	0.03	
Sr	0.02	0.04	0.02	
Si/Al	4.7	4.6	4.7	

Anal. B. Birch (Victoria Museum, Melbourne)

TABLE 3.

X-ray powder diffraction data of ferrierite from Regéc

Ferrierit Regéc		Ferrierit JCPDS 11-429	
d(Å) obs.	int.	d(Å)	int.
9.57	49	9.61	100
7.03	12	7.00	30
6.63	9	6.61	20
5.82	16	5.84	50
4.97	7	4.96	10
4.79	2	4.80	10
4.57	3	4.58	10
4.01	55	3.99	90

TABLE 3.
(continuation)

Ferrierit Regéc		Ferrierit JCPDS 11-429	
d(Å) obs.	int.	d(Å)	int.
3.88	19	3.88	10
3.79	43	3.79	20
3.70	21	3.69	50
3.53	100	3.54	80
3.49	52	3.49	80
3.41	10	3.42	20
3.30	20	3.31	20
		3.20	10
3.15	24	3.15	30
3.07	18	3.07	30
2.97	23	2.97	30
2.90	10	2.90	20
2.72	7	2.72	20
2.58	8	2.58	30
2.48	5	2.49	30
2.42	3	2.43	20
2.36	11	2.37	40

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TABLE 4.

Chemical analyses of some ferrierites

	1	2	3	4
SiO_2	56.80	66.33	62.62	63.69
Al_2O_3	12.71	13.18	9.94	12.19
Fe_2O_3	3.29	0.27	0.58	0.04
MgO	4.12	3.41	2.61	3.16
CaO	5.52	1.39	5.78	0.53
SrO		0.34	0.18	
BaO		0.41		
Na_2O	0.27	0.50	0.13	0.58
K_2O	0.82	1.17	1.13	1.41
H_2O	14.32	13.00	13.22	
Sum.	100.79	100.00	100.16	81.80
Cat. numb. on the basis of 72 ox.				
Si	27.50	29.05	30.22	28.94
Al	7.25	6.80	5.65	6.64
Fe	1.20	0.09	0.21	0.02
Mg	2.98	2.23	1.87	2.18
Ca	0.99	0.65	0.41	0.26

TABLE 4.
(continuation)

	1	2	3	4
Sr	0.09	0.05		
Ba		0.07		
Na	0.25	0.43	0.12	0.52
K	0.51	0.65	0.70	0.83

1. Vicenza, Italy
2. Monte Lake, British Columbia, Canada
3. Weitendorf, Steiermark, (GOTTARDI-GALLI 1985)
4. Phillip Island, Victoria, Australia (BIRCH 1989)

The appearance of dachiardite is quite special (X-ray diffraction data of the dachiardite can be seen on Table 5). According to the technical literature, dachiardite is usually of acicular or radiation appearance with rare exceptions. In this locality it was observed in 2-3 millimetres large tabular crystals. SEM-images show that the crystals are commonly parallel twins, the composition surface is (001) (*Fig. 7.*) The crystals are often flattened on (001), and bushlike groups also. (001), (100), (1$\bar{0}$0) forms can be observed on them.

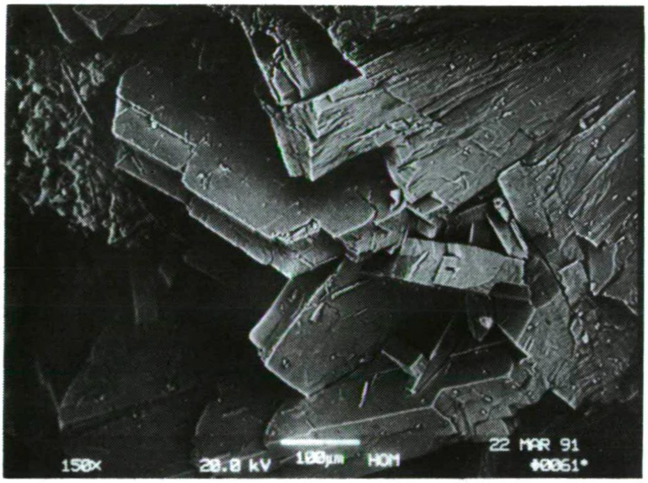

Fig. 7. Tabular twin crystals of dachiardite, Mt. Torintás, Regéc. SEM micrograph

The microprobe analyses of the samples show that they have the highest content of Ca and the lowest of Na (Table 6). High Ca and low Na content is characteristic the dachiardite variety called svetlozarite described from Bulgaria (MALEEV, 1976). Comparing the two varieties, svetlozarite contains 3.91% CaO, 0.85% NaO, dachiardite Regéc contains 5.55% CaO and 0.08% NaO. The svetlozarite is found in the Rodope Mts. in andesite-brescia in chalcedony veins. The X-ray data of dachiardite however show the best correspondence with the JCPDS card N. 30-1149 (Na-dachiardite) (Table 7.), so it needs further investigation. The associated occurrence of ferrierite and dachiardite is a rarity up to now it is described from only one assemblage formed in basalt in the USA (WISE-TSCHERNICH 1978).

TABLE 5.

X-ray powder diffraction data of the dachiardite from Regéc

Dachiardit Regéc		Dachiardit-Na JCPDS 30-1148	
d(Å)	int	d(Å)	int
9.73	6	9.77	18
8.80	100	8.86	75
6.89	6	6.92	8
5.97	4	5.96	3
4.98	34	5.00	16
4.87	8	4.88	90
		4.62	8
4.416	8	4.429	5
3.943	55	3.959	25
3.800	9	3.793	40
3.747	13	3.755	13
3.624	27	3.625	17
3.454	99	3.453	100
3.411	39	3.397	10
3.324	21	3.330	10
3.254	21	3.253	12
3.196	31	3.202	12
3.130	13	3.143	9
3.077	7	3.099	8
2.964	58	2.973	30
2.862	45	2.861	25
2.720	13	2.725	10
2.670	16	2.668	12
2.570	20	2.573	5
2.495	10	2.459	5

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TABLE 6.

Quantitative microprobe analysis of dachiardite from Regéc

mass %	1	2	mean
SiO_2	69.71	71.44	70.58
Al_2O_3	12.25	12.12	12.19
Fe_2O_3	0.07	0.10	0.09
MgO	—	—	—
CaO	5.62	5.48	5.55
Na_2O	0.12	0.05	0.08
K_2O	1.53	1.56	1.55
BaO	0.10	0.10	0.10
SrO	—	—	—

TABLE 6.
(continuation)

mass %.	1	2	mean
H_2O	n.d.	n.d.	n.d.
Sum.	89.40	90.74	90.14
Cation numbers on the basis of 48 oxygen			
Si	19.88	20.01	
Al	4.12	4.00	
Fe	0.01	0.01	
Mg	—	—	
Ca	1.72	1.65	
Na	0.07	0.03	
K	0.56	0.56	
Ba	0.01	0.01	
Sr	—	—	
Si/Al	4.8	5.0	

Anal. B. Birch (Victoria Museum, Melbourne)

TABLE 7.

Chemical analyses of some dachiardite

	1	2	3	4
SiO_2	66.15	69.58	67.38	72.41
Al_2O_3	12.91	10.26	12.65	10.15
Fe_2O_3		0.67	0.27	0.08
MgO		0.30	0.03	
CaO	3.88	3.91	0.51	1.78
Na_2O	2.57	0.85	5.15	3.04
K_2O	0.95	3.00	0.97	1.30
H_2O	14.42	10.94	12.91	
Sum.	99.88	99.51	100.00	
Cation numbers on the basis of 80 oxygen				
Si	19.50	20.19	19.76	20.62
Al	4.55	3.51	4.37	3.40
Fe		0.15	0.06	0.02
Mg		0.13	0.01	
Ca	1.24	1.22	0.16	0.55
Sr	0.02			
Ba			0.02	
Na	1.49	0.48	2.93	1.67
K	0.36	1.11	0.36	0.47
Cs	0.12			
H_2O	14.39	10.59	12.63	

1, Elba, Italy
2, "svetlozarit", Rodope, Bulgaria
3, Tsugawa, Japán
4, Altoona, Washington, USA (GOTTARDI-GALLI 1985).

Other occurrences

Stellerite and heulandite crystals associated with chalcite and pyrite in small cavities of rock were found in a quarry outcrop pyroxene-dacite in rhyolitic area near Rostalló, Kishuta. Stellerite crystals making up bunches are also common (*Fig. 8.*).

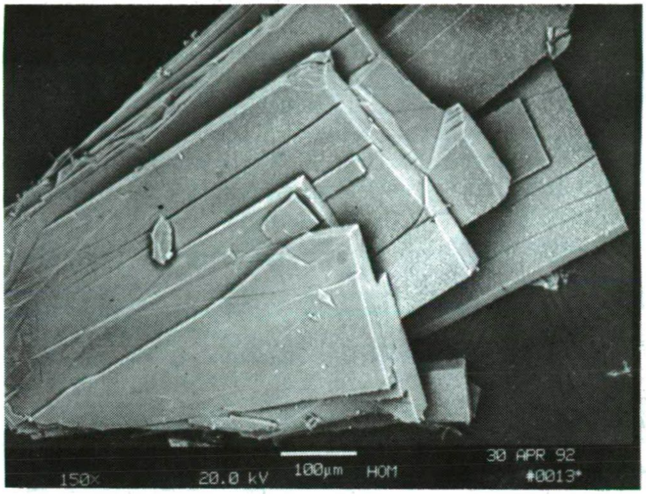

Fig. 8. Tabular stellerite forming tufted bunches. Rostalló, Kishuta. SEM micrograph

Stellerite, dachiardite and heulandite crystals can be found with pyrite, quartz, goethite, jarosite and gypsum in small cavities in an outcropt Mt. Kis-Sertés near Regéc.

Heulandite was found on Mt. Magos Hollóháza, Patkóbánya, near Tokaj and at Picpangos-spring, near Makkoshotyka. All these outcrops produced heulandite in aggregates of thick, tabular crystals without accesory minerals.

CONCLUSIONS

The zeolite assemblages in the intermadiate rocks of the Tokaj Mts. were formed due to in the course of postvolcanic processes by comparison with analogies from the technical literature (GOTTARDI-GALLI 1985). Two types of assemblages can be observed. One of them is caracterized by quartz (and chalcedony) as a first crystallized phase. They were followed by mordenite and later formed other zeolites in smaller quantities. This kind of assemblages are found particularly in the central areas to decompose due to weathering processes. JÁNOSSY *et al.* (1987) described a similar paragenesis and formation.

The other type is a poor in species. The formation of minerals follows the scheme that begins with the crystallization of quartz and chalcedony later precipitating one or two species of zeolites, most commonly heulandite, sometimes stellerite. The ferrierite-dachiardite bearing paragenesis at Regéc belongs to this better type, though due to the difference in the composition of the hydrothermal solutions not the ordinary zeolites were formed.

To summarize the results, we can accept that the presence of zeolite assemblages in the intermediate rocks of the area in question is familiar and is part of the postvolcanic processes.

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