NEW OCCURENCES OF ZEOLITE IN THE MÁTRA MOUNTAINS

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In the upper reaches of brook Madarász, region of Tar, western Mátra Mountains, the so called Lower Andesite Formation of Helvetian age over-lying the similarly Helvetian clayey-marly sandstones contain some heulandite associated with few natrolite. Heulandite is found partly in groups of clear crystals grown on the walls of cavities, partly in closely-packed fine-grained crystal aggregates forming rather thin veinlets. The country rock is andesite tuffite.

Clear heulandite also appears in the loose porous andesites of the depth interval 42,0—46,6 m of mapping borehole Hasznos Nr. 1 sunk on the south-ern slope of Mt. Hegyes, and it is encountered in the outcrop of the andesite, too, where it occurs grown on cavity fillings, accompanied by chlorite and natrolite.

Both occurrences can be regarded as lateral secretion products. The re-sults of their study are completed by chemical analyses, DTA curves and X-ray diffractometric patterns.

In the central Mátra Mountains occurrences of natrolite and chabasite were earlier discovered between the Helvetian sandstones and the Helvetian chloritic-andesite tuffs. Detailed geological mapping led later to the discovery of a new occurrence of zeolite in the western Mátra Mountains.

In the upper reaches of brook Madarász — named „Pena gödör" recently — E of village Tar a formation of interesting habit is exposed. About 100 m W of the junction of the two upper branches of „Pena gödör" greenish-grey clayey tuffites intercalating marly-clayey sandstones (schlier) are exposed which sometimes show yellowish-brown patches due to limonitic stain. At many instances, a gellike, dark-grey to grey colloidal substance filling fis-sures, cracks or cavities is encountered, on the surface of which there appear minute cracks due to loss of water. This formation of pelitic grain size repre-sents a clay stained by iron hydroxide. In this area cascades 5—6 m deep are sometimes found in the thin-bedded, lamellar sandstones and the tuffites.

The rock seems to be homogeneous by naked eye, but under microscope it consists of pelitic groundmass locally with chloritic embeddings. Some-times minute andesite lapillis and volcanic sand particles are recognized in it *(Fig. 1)*.
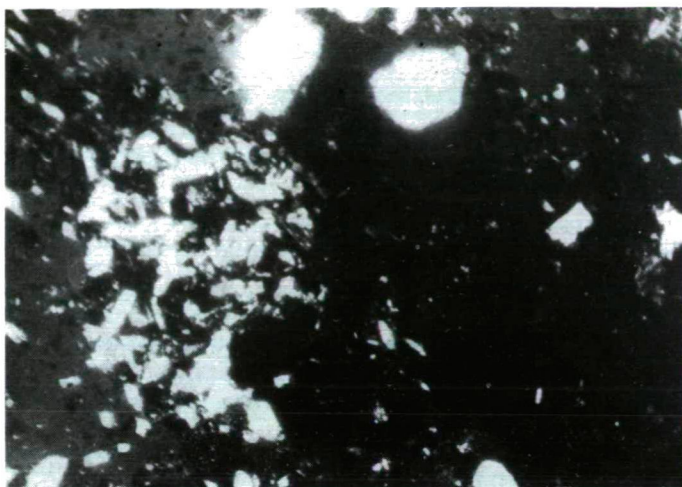
Fig. 1. Fine-grained lapillies in andesite tuffite. Crossed nicols, 40×

In the cement the grain size of the detritus of the rock-forming minerals does not exceed 0,2 mm. Most of these particles is represented by twinned plagioclase feldspar, the minor part by quartz grains which may derive from the underlying marly sandstones or may have been redeposited from a higher level still during diagenesis. No mafic minerals are recognizable in the cement. Chlorite was formed not during the weathering of mafic minerals, but probably during diagenesis. Sometimes, it impregnates the whole rock. It is always granular, radial-fibrous varieties cannot be observed.

The crystals in the detritus of the andesite lapillis hardly attain the size range of 0,1 to 0,2 mm. This detritus, as a rule, does not contain any mafic minerals, any minerals of porphyric segregation. The groundmass is hyalopilitic. It derives from an andesite devoid of mafic minerals or containing but scarce femic components.

This new occurrence is conspicuous for the appearance of zeolite in fissures and sometimes in minor cavities. One type occurs in the cavities of the andesite tuffite *(Fig. 2)*. Clear zeolite crystals of 4—5 mm in size are grown on the walls of cavities. The crystals identified with heulandite are of tabular, lamellar habit *(Fig. 3)*. Their size varies from 1 to 3 mm. On tabular, lamellar crystals the following forms were observed:

$$001 \qquad 110 \qquad 101 \qquad 101$$

The perfect cleavage along (010) is always distinct. On cleavage face the crystal is commonly of pearly luster. The specific gravity of the clear crystals is 2,17. $n_\beta \sphericalangle c = 23°$. Refraction as determined by immersion method was found to be 1,49, the birefringence as determined by Ehringhaus compensator 0,0056.

The above determinations were confirmed by X-ray diffraction measurements. The results are shown in Table I. These values coincide well with those known from literature. (The X-ray diffraction measurements and their
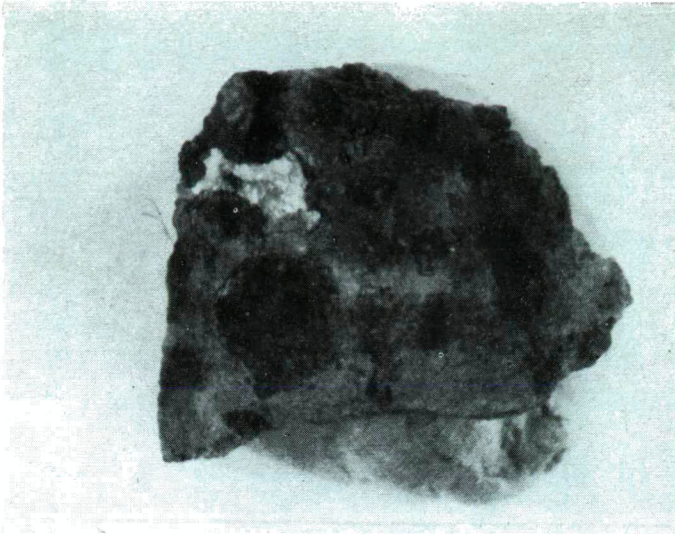
Fig. 2. Heulandite as cavity-filling in andesite tuff. 2× of natural size

interpretation were performed by G. Rischák, research worker of the Hungarian State Geological Institute, whose work is highly appreciated by the author.)
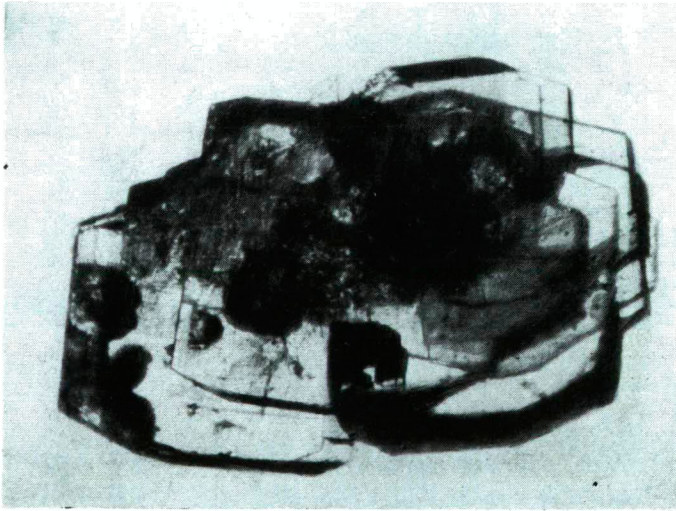

Fig. 3. Crystal of heulandite. 20× of natural size

The other type of zeolite occurs in the fissures of the rock. It fills up thin veinlets within the grey clayey-marly tuffite. *(Fig. 4—5).* These white veinlets form an irregular network throughout the rock mass. Heulandite is represented here by a fine-grained crystalline mass of vitreous or possibly

Fig. 4. Crystalline heulandite as fissure-filling. $3\times$ of natural size

Fig. 5. Fissures filled with heulandite in andesite tuffite. Crossed nicols, $40\times$

pearly luster. Sometimes calcite accompanied may be observed. The heulandite grains are always smaller than 0,5 mm in size. The microscopic picture of the rock completely corresponds with that of the former type. Zeolite is always of white colour, calcite of yellowish-white. It is peculiar that heulandite sometimes carries very fine needle aggregates, small „brushes" of natrolite. This variety of zeolite is, however, unusually scarce here.

DTA yielded the following results *(Fig. 6.)* After the appearance of a large endothermic peak at about 100 C°, two typical endothermic effects indicative of structural water loss were found at 280 C° and 370 C°, respectively. KOIZUMI and É. PÉCSI—DONÁTH who studied the behaviour of zeolites including heulandite in dependance on changes in temperature obtained simi-

lar results. The only difference with respect to my results is that I found a small endothermic bend at 280 C° and that I did not find any double peak at 340—360 °C, whereas above 450 °C an endothermic broadening appeared in my experiment, too, just as was the case with that of É. PÉCSI—DONÁTH. It should be noted, however, that quite distinct as they were at about 590°—600° C in É. PÉCSI—DONÁTH's experiment, the effects of endothermic decomposition scarcely discernible in my experiment. The endothermic peaks observed at higher temperatures (670°—910°C) were due to montmorillonitic impurities, for the sample material subjected to DTA was not altogether pure. CAJKOVÁ and HARAMIOVÁ observed an endothermic peak between 160°C and 180°C, an exothermic one at 330°C, and again an endothermic peak at 400°C. The curve obtained by KOSTOV shows endothermic peaks at 170°C and 390°C, and an exothermic one at 330°C.
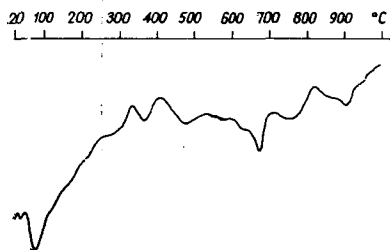

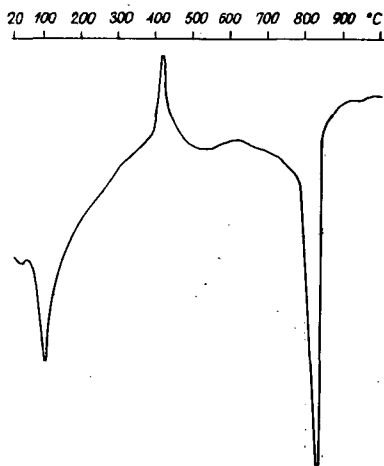*Fig. 6.* DTA curve of heulandite   *Fig. 7.* DTA curve of marly andesite tuffite

Consequently, at low temperatures double peak may appear everywhere, only the temperature values show some shifting following the cases, a fact that may possibly be due to different technologies of sample preparation.

The DTA curve of the grey tuffitic rock in which calcite portions are in most cases visible even to the naked eye has apparently shown the presence of calcite. Beside the endothermic peak due to initial water loss, the DTA curve yielded a large, typical endothermic peak only at 850°C, corresponding to dissociation of $CaCO_3$ *(Fig. 7).* The exothermic peak at 430°—440°C is due to the presence of finely dispersed marcasite which appears to be responsible for the grey colour, too. The occurrence of marcasite also suggests a reductive environment rather than an oxidative one, since otherwise the appearance of marcasite, i. e. the presence of ferrous iron could not be accounted for.

The habit shown by the heulandite found in borehole Hasznos Nr. 1 sunk on the southern slope of Mt. Hegyes (529,2 m) was similar to that of the crystallized heulandite. The boring started from the Helvetian dacite tuff near to the rim of the Tortonian andesite of the Mount Hegyes. At 39 m depth

the dacite tuff showed a sharp delimitation from the Helvetian andesites belonging to the Lower Andesite Formation. This rock is brownish grey, slinghtly altered, porous, extending to 46,6 m depth, from where downwards we find agglomeratic andesite tuffs to 51 m depth, where the former rock is underlain by fresh, dark-grey andesites 2 m thick which may represent a small apophyse of the Tortonian andesites of Mt. Hegyes. The andesites within the range of 39,0—46,6 m are rather homogeneous, loosely crumbling, with cavities in which ferric hydroxide segregations can often be recognized. The feldspar particles 2,5 to 3 mm in size are well differenciated from the ground mass. No dark rock-forming constituents are visible to the naked eye; even when viewed with a microscope, the rock exhibits only traces of femic components which must have been rather scant at the very beginning.

In depth interval from 42,40 to 46,60 m the rock mass is traversed by yellowish-white calcite veinlets 1—3 cm thick. Sometimes bluish-grey veinlets of chalcedony a few mm thick are observed. This occurrence is conspicous for the fact that groups of clear heulandite crystalgroups 2—4 mm across appear in the cavities of the rock *(Fig. 8)*. The core is ochre having the appearance


Fig. 8. Crystal group of heulandite in porous pyroxene-andesite. Crossed nicols, 40×

as if it were impregnated by zeolite. The crystals exhibit the same physical properties as do the crystallized specimens found in „Pena gödör". The X-ray diffraction data also correspond to those obtained for the crystallized material of „Pena gödör". The values are given in Table I.

An outcrop of this brownish-grey, porous rock appears to be the andesite mass at the northern side of the road Pásztó—Mátrakeresztes extending on the southern slope of Mt. Hegyes. This rock is also porous, sometimes containing oxidized portions distributed irregularly. The upper part is represented by lava agglomerates, the lower one has a tuffaceous habit. In the lava rock the porphyric segregates are also well differentiated from the ground mass. The columnar feldspars 1—4 mm across belong to the labradorite series. Of the rather poor pyroxenes, augite is most abundant, hypersthene being scarcer. Consequently, the rock under consideration is a pyroxenic andesite.

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Here also, we can find heulandite in the cavities of the rock *(Fig. 9)*. It is represented, here too, by groups of clear cristals of vitreous luster. In some cavities heulandite is found overgrown by natrolite. The genetic succession of the minerals is as follows. Earliest of all appears chlorite on the wall of the cavities. It is overgrown by heulandite on which natrolite, the youngest mineral, is accumulated.
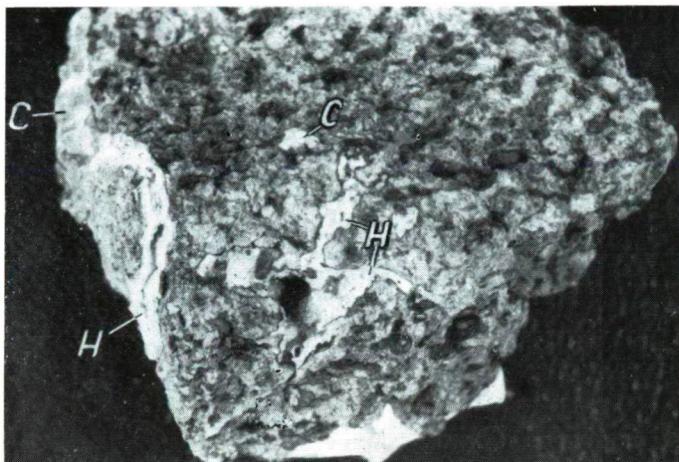
Fig. 9. Heulandite in the cavity of porous pyroxene-andesite. $^1/_2$ natural size
C=calcite, H=heulandite

The X-ray diffractometric measurements were performed by using a Mueller Mikro 111 diffractometer. CuKα served as source of radiation. Heulandite is not too frequent in the geological formations of Hungary. The best occurrence is at Nadap (Velence Mountains). Over there it was discovered in a few cm thickness at the granite-andesite contact. It can be regarded as a remobilized mineral produced by lateral secretion (KOCH). The heulandite of Füzérkomlós occurs in the cavities, fissures of pseudoagglomerated hypersthene-augitic andesites being represented by 0,5 cm crystals in assemblage of chalcedony, tridymite, opal, calcite, aragonite, chabasite and barite.

The heulandite crystals up to 2 cm across occurring at Sátoros are associated with chabasite, desmine, and laumontite.

In addition, heulandite has been recorded from the hill „Sulyom tető" in the valley of river Zagyva.

When considering the new occurrence in the Mátra Mountains including that of „Sulyom tető" at Nagybátony, we can realize that these are all within the Lower Andesite Formation overlying the Helvetian clayey-marly sandstones. So their distribution and changes in dependence of the height above sea level must be ascribed to later crustal movements.

Since in these places we can hardly encounter effects of hydrothermal solutions, it is merely the agents expounded by E. SZÁDECZKY-KARDOSS that may have been involved in the formation of zeolites.

Accordingly, one of the prerequisites of zeolite formation is the abundance of volatiles in the source material. Typical representatives of this facies may

presumably develop only at relatively high pH in an alkaline environment, chiefly in volcanic areas or in their neighbourhood, due to magmatic mobilization. If a high-temperature lava or pyroclastic material superimposes a volatile-rich sedimentary rock — clayey-marly sandstone, in the given case — or eventually is introduced into a shallow sea, then water vapour will develop penetrating the lava or eventually tuffite whose abundance in volatiles will thus increase. Here it is not the temperature gradient, but the pressure gradient that is of decisive importance. Any mobilized element migrates from an environment of higher pressure to another of lower pressure, regardless of whether this is opposed to the temperature gradient or not. Like in the case of the zeolites along the northern shore of Lake Balaton, the zeolites of the Mátra Mountains were not produced by any ascendent hydrothermal solution, but came about under the effect of water vapour released by glowing pyroclastics ejected during volcanic activity, due to the mobilization of elements provoked thereby. Zeolites of such genesis formed first of all at the contact between the clayey-marly sandstones and the Lower Andesite Formation. This is the reason why in the Mátra Mountains and surroundings zeolite is known to occur only in places like this. In the genesis of the zeolites occurring in the mine of Gyöngyösoroszi the hydrothermal solutions may also have been largely involved.

As well-known, the formation of zeolites commonly requires a high pH. The presence of this latter is substantiated by the fact that calcite as an associated mineral is always present, whether the occurrence in „Pena gödör" or the stratigraphic column of mapping borehole Hasznos Nr. 1 on Mt. Hegyes is considered.

Here and there heulandite is encountered in a chloritic environment. In such places a definite order of segregation can be observed. The oldest mineral in the cavities is chlorite which is followed by heulandite, the youngest segregate being natrolite. If we consider the formation temperature of these minerals, we shall realize that it also is roughly in line with the aforementioned order, since chlorites can be formed between 100° and 300°C, zeolites between 70°—90°, and calcite above 100°C. It thus stands to reason that these minerals follow each other in the order determined by the temperature.

Earlier it was pointed out by E. SZÁDECZKY-KARDOSS that the genetic succession of the minerals is partly controlled, or at least largely influenced, by geoenergetic factors dependent on lattice, characteristics (ionic potential, compound potential). Accordingly, first the cubic, then the foliaceous and finally the fibrous zeolites are formed. Considering the values of the ionic potential, the following data were obtained for the minerals occuring here:

compound potential of pennine $(Mg,Al)_3(OH)_2AlSi_3O_{10} = 2{,}02$
compound potential of heulandite $CaAl_2Si_7O_{18} \cdot 6\ H_2O = 0{,}88$
compound potential of natrolite $Na_2(Al_2Si_3O_{10}) \cdot 2\ H_2O = 0{,}83$

In the case of zeolites the number of the water molecules is not taken into consideration.

In conclusion, these zeolites can also be taken for lateral secretion products in the formation of which the volatiles were largely involved.

TABLE I

2Θ values of diffraction patterns of heulandite crystals from „Pena gödör" and Hasznos boring N⁰. 1. comparing to those of the heulandite from locality Zakyl. Radiation CuKα.

„Pena gödör" crystalline	„Pena gödör" grained	Hasznos boring N⁰. 1.	Zakyl
2Θ	2Θ	2Θ	2Θ
10,00	9,98	10,00	10,10
		11,40	11,18
			11,91
			13,30
			15.42
			16,64
17,50			17,77
			8,85
			19,39
			20,75
			21,74
22,50	22,50	22,45	22,55
	22,85	22,80	
			25,62
		26,05	
26,49			26,43
			27,38
27,98	27,90		
28,20	28,20	28,25	
28,70	28,60	28,60	28,86
30,20	30,00	30,05	
			30,67
			31,34
32,20	32,02		32,20
32,98	32,90	32,90	
			33,15
35,80	35,55	35,60	
37,02		37,01	
		46,40	
51,02	51,00	50,90	

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