THERMOANALYTICAL INVESTIGATION OF CAVITY FILLING NATROLITE GROUP MINERALS IN BASALTS
Balaton Highland, Hungary

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Cavity filling natrolites in basalts from several localities of Balaton Highland were investigated by different methods. The measurements of different thermal parameters (corrected decomposition temperature and activation energy) were first applied for natrolite. Energy dispersive spectroscopy (EDS) was used for the observation of chemical composition. Few of the minerals are regular, ordered natrolite, the majority proved to be so called 'tetranatrolite'. According to our observations both natrolite and 'tetranatrolite' may appear in the same locality and chemical inhomogenity can be demonstrated within a single natrolite needle.

Introduction

Pécsi-Donáth in the 1960s carried out first of all thermoanalytical investigation of zeolites [1–3]. She indicated that cavity filling natrolites in basalt from Uzsa (Hungary) have anomalous thermal behaviour as compared to the natrolite minerals from other localities. According to the chemical analyses certain Hungarian zeolites contain more water and calcium and less silica than others. Later [4–5] explained the different features of the natrolite from Gulács (Hungary) with the partial disorder in the Si,Al distribution and called the disordered phase 'tetranatrolite'. A decade later [6] identified the same minerals as gonnardite, based on the Al/Si ratio. In natrolites from Uzsa studied by [7] different degrees of Si,Al disorder were found [5] showed that sample Na II from Uzsa investigated by [7] has the highest disorder of natrolite. According to computed cell parameter studies of [8] the natrolites from Balaton Highland are ordered while gonnardites are disordered.

In this study systematic comparative investigations were made on the cavity filling natrolite minerals in the basalt quarries Bazsi, Gulács, Haláp, Hermántó and Uzsa (Balaton Highland).

Experimental

Basic structural features of natrolite group minerals

The basic structural units of natrolite group zeolites are chains of $(Si,Al)O_4$ tetrahedra running parallel to the *c*-axis. In the framework three different tetrahedra occur. In fully ordered natrolite Si atoms occupy the tetrahedral sites T1 and T2. The Al atom occupies the third terahedral site, T3. Depending on the cross-linking of the T_5O_{10} tetrahedral chains, three different framework topologies exist leading to three subgroups: natrolite subgroup (NAT) (natrolite, mesolite, scolecite, paranatrolite, 'tetranatrolite', gonnardite); thomsonite subgroup (THO); subgroup of edingtonite and kalborsite (EDI). Morphologically, this mineral group often appears in needle-like and fibrous crystals extended parallel to the chains of tetrahedra [9].

Methods

The natrolite samples were selected from other minerals by binocular microscope.

X-ray diffraction analyses were made by a Philips PW 1710 diffractometer under the following conditions: Cu anti-cathode, 40 kV and 30 mA tube current, graphite monochromator, goniometer speed $2°\ 2\theta\ min^{-1}$, measurement range 2–66° 2θ.

Because XRD methods are not always sufficient for the correct identification of these minerals, the joint application of more methods was necessary.

The thermal analyses were completed by Derivatograph PC with simultaneous registration of TG, DTG, DTA curves, in a ceramic (corundum) crucible, with a heating rate of 10°C min^{-1} up to 1000°C and with Al_2O_3 as inert material.

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Table 1 X-ray diffraction data of the pure natrolite sample

U 142			Natrolite JCPDS 20-0759		
2°theta/deg	d(hkl)/Å	I(rel)/%	d(hkl)/Å	I(rel)/%	hkl
13.58	6.519	45	6.550	60	220
15.05	5.887	47	5.890	85	111
19.10	4.647	22	4.660	25	040
19.37	4.582	22	4.580	16	400
20.30	4.374	55	4.350	70	311
21.45	4.142	33	4.150	35	240
21.64	4.107	26	4.100	6	420
24.55	3.627	5	3.630	2	331
27.33	3.264	10	3.270	4	440
27.98	3.189	46	3.190	45	151
28.27	3.157	51	3.160	50	511
28.75	3.105	31	3.110	25	022
30.38	2.943	39	2.940	35	222
			2.870	80	351
31.30	2.858	100	2.850	100	531
34.83	2.576	21	2.570	20	422
36.80	2.443	25	2.440	16	171
37.27	2.413	23	2.410	16	711
38.79	2.322	14	2.320	2	080
39.37	2.289	8	2.290	4	800
39.92	2.259	10	2.260	6	062
40.24	2.241	7	2.230	4	820
41.17	2.193	19	2.200	20	262
41.46	2.178	24	2.180	16	622
44.02	2.057	8	2.060	6	313
46.25	1.963	6	1.962	4	191
46.95	1.935	2	1.932	2	911
48.49	1.878	10	1.876	8	513
50.00	1.824	9	1.825	4	2100
50.58	1.805	21	1.798	20	771
52.11	1.755	8	1.753	6	482
52.52	1.742	7	1.739	6	591
53.14	1.724	16	1.723	10	4100
53.76	1.705	13	1.703	8	1040
54.54	1.683	6	1.680	4	553
55.74	1.649	8	1.646	6	
56.39	1.632	13	1.632	10	1111
56.77	1.622	11	1.622	10	102
57.24	1.609	11	1.601	8	224

Table 2 X-ray diffraction data of the sample containing dominantly 'tetranatrolite' with some paranatrolite

H 158/1			'Tetranatrolite' JCPDS 33-1205			Paranatrolite 42-1386		
2°theta/deg	d(hkl)/Å	I(rel)/%	d(hkl)/Å	I(rel)/%	hkl	d(hkl)/Å	I(rel)/%	hkl
13.13	6.744	32				6.750	100	220
13.49	6.566	59	6.549	50	200			
						5.960	20	11
14.95	5.927	64	5.912	40	101	5.900	15	
						4.790	30	040
18.59	4.773	29				4.740	30	400
19.09	4.648	41	4.635	40	220			
						4.490	20	131
20.24	4.388	65	4.387	50	211	4.440	15	311
20.84	4.263	7				4.270	10	240
21.43	4.147	47	4.143	40	310			
23.92	3.720	3				3.750	2	331
26.46	3.369	2				3.370	1	440
27.29	3.268	20				3.270	20	151
27.97	3.190	62	3.189	50	321	3.200	8	060
						3.140	3	600
28.63	3.118	21	3.120	10	112			
29.65	3.013	6				3.000	10	620
30.35	2.945	62	2.960	20	202	2.950	70	22
30.66	2.916	37	2.926	10	420	2.920	40	531
31.22	2.865	100	2.867	100	411	2.900	50	
33.91	2.644	13				2.640	30	640
34.71	2.585	15	2.588	10	312	2.591	1	422
35.87	2.503	11				2.510	25	171
36.29	2.476	5				2.462	2	711
36.81	2.442	23	2.438	40	431			
37.75	2.383	4				2.394	3	080
38.73	2.325	11	2.319	10	402			
39.38	2.288	7	2.312	5	440			
39.88	2.261	9	2.256	10	332	2.246	20	660
41.31	2.186	24	2.195	30	422			
			2.183	10	600			
43.82	2.066	4	2.070	10	213	2.079	2	462
44.50	2.036	13				2.013	1	191
46.04	1.971	3	1.973	5	303			
46.29	1.961	4	1.954	5	541	1.956	1	082
48.30	1.885	6	1.887	10	323	1.878	5	2100
48.77	1.867	6				1.861	7	1020
50.21	1.817	15	1.816	40	640			
50.47	1.808	16	1.800	10	701	1.802	3	482
51.60	1.771	7				1.776	10	951
52.01	1.758	7	1.757	10	622	1.764	10	1040
52.78	1.735	4	1.737	10	721			
53.15	1.723	12	1.721	40	730			

Table 3 X-ray diffraction data of the sample containing dominantly gonnardite and some 'tetranatrolite'

16			Gonnardite JCPDS 42-1380			'Tetranatrolite' JCPDS 33-1205		
2°theta/deg	d(hkl)/Å	*I*(rel)/%	d(hkl)/Å	*I*(rel)/%	hkl	d(hkl)/Å	*I*(rel)/%	hkl
13.30	6.657	37	6.642	80	200			
13.53	6.546	47				6.549	50	200
14.97	5.918	61	5.898	90	101	5.912	40	101
18.73	4.737	41	4.698	80	220			
19.07	4.654	31				4.635	40	220
20.11	4.416	52	4.409	90	211	4.387	50	211
21.01	4.229	15	4.199	20	310			
21.42	4.149	37				4.143	40	310
24.49	3.635	5	3.678	10	301			
25.38	3.509	3	3.324	10	400			
27.64	3.228	31	3.219	70	321			
27.93	3.195	38				3.189	50	321
28.67	3.114	24	3.110	40	112	3.120	10	112
30.27	2.952	48				2.960	20	202
30.72	2.910	100	2.897	100	411	2.926	10	420
31.23	2.864	84				2.867	100	411
34.08	2.631	15	2.599	40	510			
34.69	2.856	14				2.588	10	312
36.23	2.480	18	2.466	50	431			
36.77	2.444	19				2.438	40	431
37.98	2.369	8	2.350	5	440			
38.72	2.325	14	2.311	5	521	2.329	10	402
39.39	2.288	8	2.271	20	530	2.312	5	440
39.92	2.258	8				2.256	10	332
40.65	2.219	13	2.212	50	600			
41.10	2.196	14				2.195	30	422
41.42	2.180	12				2.183	10	600
43.96	2.060	6	2.063	20	611	2.070	10	213
44.72	2.026	14	1.972	10	541			
46.15	1.967	4				1.973	5	303
48.24	1.886	7	1.884	20	631	1.887	10	323
49.00	1.859	8	1.845	10	640			
50.01	1.824	13	1.817	30	701	1.816	40	640
50.67	1.802	12				1.800	10	701
51.95	1.760	11	1.771	10	622	1.757	10	622
52.54	1.742	6	1.749	20	721	1.737	10	721
53.67	1.708	6	1.694	10	503			
55.84	1.647	9	1.648	30	800			
56.45	1.630	11	1.634	20	712			
57.18	1.611	10	1.604	20	820			

In sample 16 beside gonnardite some 'tetranatrolite' was identified (Table 3)

The scanning electron microscopy and EDS investigations were made by energy dispersive AMRAY 1830i instrument at 25 kV beam current.

The infrared spectroscopy analyses were carried out using FTIR 'Perkin Elmer-1600' spectrometer in the interval 400–4000 cm^{-1}, using KBr psastille.

Results and discussion

X-ray powder diffraction

In the natrolite samples of the basalts from the Balaton Highland the following minerals were identified by X-ray diffraction methods, based on JCPDS card data [10]: natrolite (20-0759), 'tetranatrolite' (33-1205), 'tetranatrolite'–Ca (42-1381), paranatrolite (42-1386) and gonnardite (42-1380) [11]. The 'tetranatrolite' card data are already not valid, because of the discreditation of this mineral. The minerals identifed as 'tetranatrolite' based on our X-ray diffraction patterns are probably identical with gonnardite–Na. Accompanying minerals are phillipsite, thomsonite, analcime and calcite.

Natrolite without accompanying minerals occurred in only two from the 26 samples studied. In other samples some gonnardite or thomsonite, and in traces paranatrolite, phillipsite and analcime appeared beside more natrolite. Due to the disordered structure, the diffraction pattern of 'tetranatrolite' has less reflections than natrolite.

Among the investigated samples 18 were identified as 'tetranatrolite'. In addition all such samples contain little natrolite, paranatrolite, gonnardite or in traces analcime, phillipsite and calcite. In one sample (H 158/1) high quantity of paranatrolite was identified. The diffractograms of paranatrolite and 'tetranatrolite' may be reliably separated.

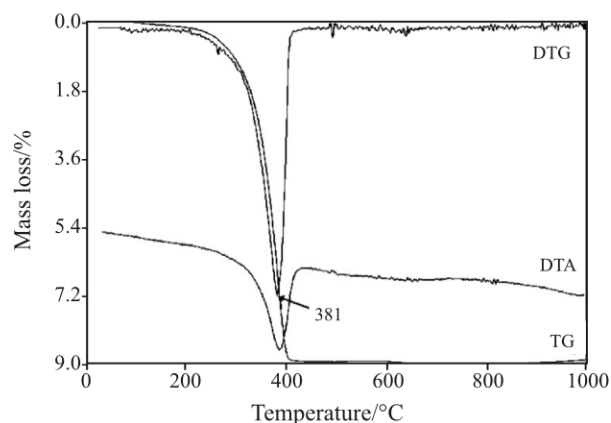In one of the samples (sample 16) gonnardite and some 'tetranatrolite' was identified.

Fig. 1 Thermoanalytical curves of sample Gulács 2581 containing natrolite

Table 4 Dehydration temperatures of natrolite according to the literature*

References	Dehydration temperatures of natrolite/°C		
	200–300	300–400	400–500
[12]	210	300–400	405*
[13]			455*
[1, 2]			400*
[14]		300–350	400–425*
[15]			440–450*
[16]			
[17]		350*	
[18]		350*	
[19]		350–370*	
[20]		300–420*	
[21]		388*	
[22]	255	330* 380	425–480*
[23]		360*	
[23]) Quantity of dehydration		300-310	405-410, 455-460, 470
		2%	6.8%+1%

*Main dehydration peaks

Thermal analysis

The dehydration of natrolite generally takes place in one sharp, well defined step at 350–450°C: release of crystalline water (Fig. 1).

The product of the reaction is metanatrolite.

$$Na_2Al_2Si_3O_{10} \cdot 2H_2O \rightarrow Na_2Al_2Si_3O_{10} + 2H_2O$$
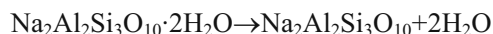
Data of the thermal reactions of natrolite found in different publications show relatively high variation (Table 4).

Many authors e.g. [1–3, 16, 18, 23] observed the temperature deviation. Many publications also not, that there are weak endothermic peaks on the low temperature side or on both sides of the mean peak.

In connection with the data given in the literature no (logarithmic) relationship between the decomposition temperature and the quantity of the mineral could be observed so far. In order to obtain comparable data of minerals investigated in different quantities we used the method of the corrected (or interpolated) decomposition temperature [24]. In this case the measured temperature data were recalculated to the same quantity (18 mg) of the product of decomposition. For this method a calibration curve was made based on the data of different masses of Gulács 2580 sample (Fig. 2). It may be seen from the calibration curve that instead of the measured 320°C

Table 5 Measured dehydration temperatures of natrolite from the literature and the calculated corrected decomposition temperatures

Reference	Localities	Measured temperature	Corrected decomposition temperature
[18]	unkown	350	361.8
[18]	Kirchberg, Germany	370	396.9
[22]	Hammerunterwiesenthal, Germany	425	386.3
[22]	Sontra, Germany	460	421.3
[22]	Puy de Marmant , France	480	441.3
[22]	Fassa Valley, Italy	450	411.3
[23]	Hammerunterwiesenthal, Germany	360	356.6
[23]	Malad, India	405	401.6
[23]	Malad, India	410	391.4
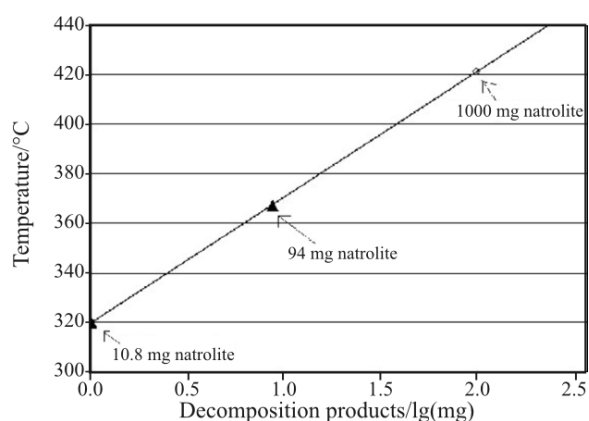
Fig. 2 Quantity-dehydration temperature calibration curve of natrolite (Gulács 2580). In the diagram the quantities of the total sample are indicated.

Fig. 3 Corrected decomposition temperature *vs.* activation energy of the investigated samples. In the legend the dominant minerals are given according to the X-ray diffraction analysis
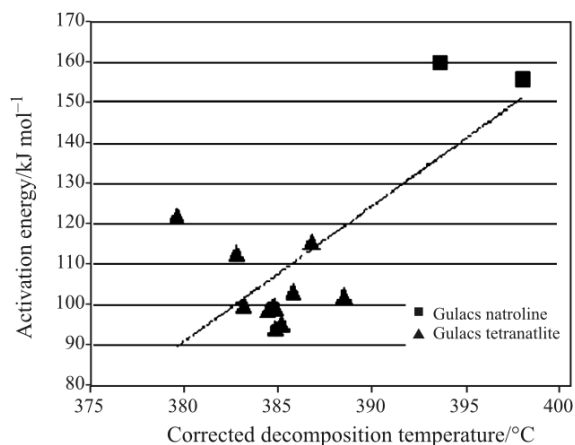
Fig. 4 Corrected decomposition temperature *vs.* activation energy of the samples from Gulács

(10.8 mg) and 367°C (94 mg) peak temperature, the temperature would be 421°C in the case of 1000 mg of the same natrolite.

Most of the references do not indicate the quantity of the investigated natrolite. For the data of publications which contain the quantity of the investigated sample the corrected decomposition temperatures were calculated. The data are summarised in Table 5. The variation of the corrected temperature data is much lower than that of the simple measured data.

The same method was used for all the investigated minerals in this paper, i.e. the corrected decomposition temperature was taken into account instead of the measured dehydration temperature.

For characterisation of the minerals the activation energy of the dehydration reaction was also used. The calculation of activation energy was carried out according to [25].

Figure 3 shows the data of corrected decomposition temperature *vs.* activation energy of the investigated samples. For true natrolites both decomposition temperature and activation energy are high indicating the ordered structure. Thermal parameters of the samples identified by X-ray diffraction as 'tetranatrolite' or gonnardite occupy the low interval (2620, 2627 and 2588/1). Also data of a few samples which contain 'tetranatrolite', paranatrolite or gonnardite beside the predominant natrolite are found in the low range. The numbered samples in the figure were studied also
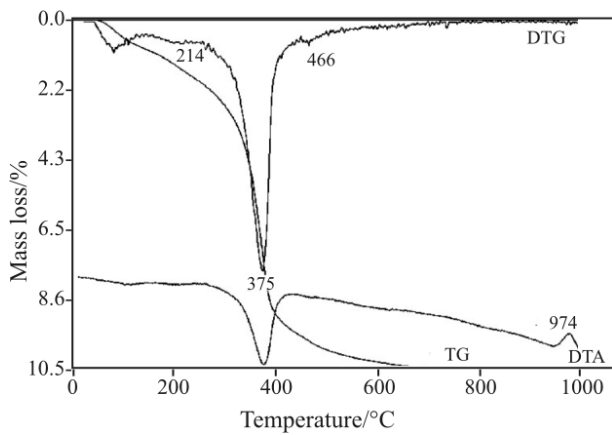
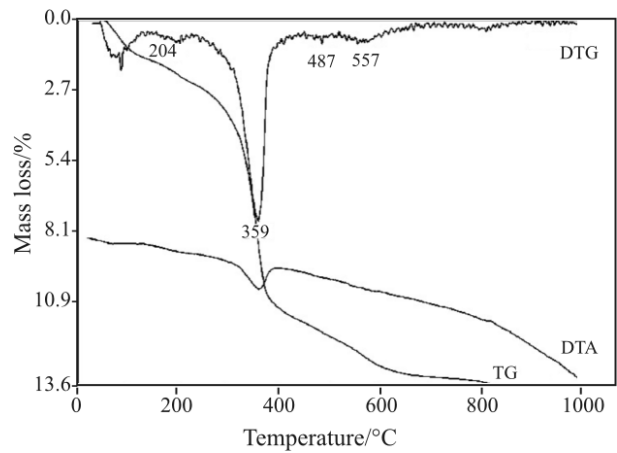**Fig. 5** Thermoanalytical curves of sample lszn-1 containing dominantly 'tetranatrolite'

Fig. 6 Thermoanalytical curves of sample 16 containing dominantly gonnardite

by IR spectroscopy and the Na/Ca ratios were calculated from data measured by EDS.

The differences appearing on the Fig. 3 are not connected to a specific locality. Usually both natrolite and 'tetranatrolite' may occur in the same locality (Fig. 4).

Similar results were obtained by the investigation of long-range order coefficient for natrolite from Uzsa [6].

On the thermoanalytical curves of the samples which dominantly contain 'tetranatrolite' commonly the weak endothermic reactions appear with mass loss before and after the mean peak (Fig. 5). Another difference of the DTA curves is that in the case of 'tetranatrolite' the transition to nepheline may be seen as an exothermic peak between 900–1000°C, but at natrolite this reaction occurs probably higher than 1000°C (Figs 1 and 5).

One of the investigated samples contains dominantly gonnardite. The peaks before and after the main peak are more pronounced (Fig. 6). The data of literature for gonnardite also indicate several steps of dehydration (Table 6).

Table 6 Dehydration temperatures of gonnardite according to the literature

References	Dehydration temperatures of gonnardite/°C			
[26]		140	250	380*
[16]	75		220	420*, 450*
[19]			200–300	320–450	500–600

*Main dehydration peaks

Infrared spectroscopy

Infrared spectra of natrolite and 'tetranatrolite' published in the literature show well the difference of two minerals [3, 5, 26–29]. In the case of natrolite the range of OH stretching vibration of water (3600–3200 cm^{-1}) and

also Si,Al–O stretching vibration (1100–900 cm^{-1}) of the framework are well resolved. On the spectra of 'tetranatrolite' these bands in the ranges above mentioned are poorly defined. Similar differences are at the bending vibration T–O, and at the libration of H$_2$O, respectively, in the low wavenumber range (400–700 cm^{-1}).

The samples for infrared spectroscopic investigation were selected in accordance with the thermoanalytical parameters. According to the data of Fig. 3 two spectra belong to the highly ordered (U 142 and 2581) and three to the weakly ordered (2620, 2627 and 2588/1) of samples. Figure 7 and the bands in Table 7 containing the IR data of the five samples clearly show the difference between natrolite and 'tetranatrolite'. According to the IR data the sample 2588/1 from Gulács
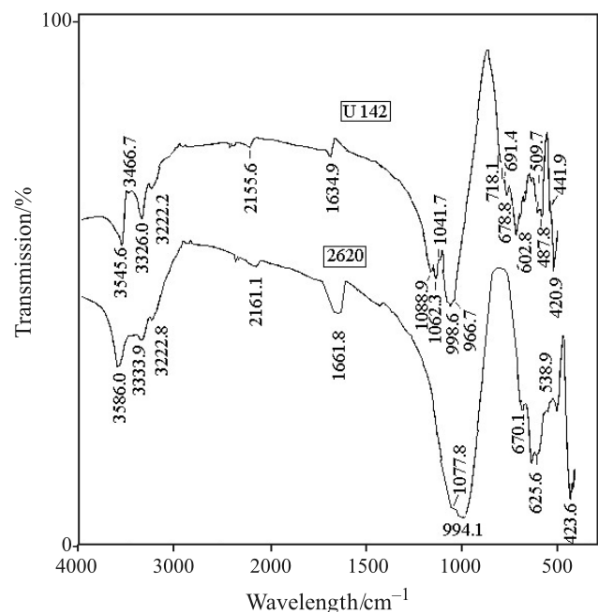

Fig. 7 Infrared spectra of samples U 142 (highly ordered natrolite) and 2620 (weakly ordered 'tetranatrolite')

Table 7 Infrared spectroscopic data (cm^{-1}) of the investigated samples

Samples					Assignment of bands	Minerals
Gulács 2581	Uzsa U-142	Gulács 2588/1	Haláp 2627	Haláp 2620		
			3586.7	3586.0	stretching vibration OH of water	'tetranatrolite'
		3567.2			stretching vibration OH of water	transition
3541.2	3545.6				stretching vibration OH of water	natrolite
	3466.7*				stretching vibration OH of water	
3452.3*					stretching vibration OH of water	
		3433.3*			stretching vibration OH of water	
			3330.5	3333.9	overtone stretching OH of water vibration	'tetranatrolite'
3325.6	3326.0	**3327.8**			overtone stretching OH of water vibration	natrolite+transition
3219.7	3222.2	3222.2	3222.2	3222.8	overtone stretching OH of water vibration	
			2172.2		overtone libration and bending H$_2$O	
		2166.7			overtone libration and bending H$_2$O	
				2161.1	overtone libration and bending H$_2$O	
	2155.6				overtone libration and bending H$_2$O	
2149.9					overtone libration and bending H$_2$O	
			1661.9	1661.8	bending vibration water	'tetranatrolite'
1634.4	1634.9	**1635.4**			bending vibration water	natrolite+transition
		1416.7	1417.5		bending vibration C–O	calcite
1088.2	1088.9				stretching vibration Si,Al–O (external)	natrolite
		1080.6	1077.8	1077.8	stretching vibration Si,Al–O (external)	'tetranatrolite'
1063.2	1062.3				stretching vibration Si,Al–O (v_3)	natrolite
		1055.6	1054.2	1058.3	stretching vibration Si,Al–O (v_3)	'tetranatrolite'
1040.9	1041.7				stretching vibration Si,Al–O (v_3)	natrolite
					stretching vibration Si,Al–O (v_3)	
997.2	998.6				stretching vibration Si,Al–O (v_3)	natrolite
			989.2	994.1	stretching vibration Si,Al–O (v_3)	'tetranatrolite'
981.9	982.5	982.3			stretching vibration Si,Al–O (v_3)	natrolite+transition
966.6	966.7				stretching vibration Si,Al–O (v_3)	natrolite
719.4	718.1				stretching vibration Si,Al–O (v_4)	natrolite
694.4*	694.4*					
		684.7*				
679.0	678.8	978.5*				
			675.1		bending vibration C–O	
		668.3		670.1	libration H$_2$O and stretching vibration Si,Al–O	
625.9	925.7	623.9	625.1	625.6	libration H$_2$O and stretching vibration Si,Al–O	
604.2	602.8				libration H$_2$O and stretching vibration Si,Al–O	natrolite
		595.8	597.2*	600*	libration H$_2$O and stretching vibration Si,Al–O	'tetranatrolite'
579.2	580.0				libration H$_2$O and stretching vibration Si,Al–O	natrolite

Table 7 Continued

Samples					Assignment of bands	Minerals
Gulács 2581	Uzsa U-142	Gulács 2588/1	Haláp 2627	Haláp 2620		
		544.4*			libration H_2O and bending vibration Si,Al–O	
541.7	541.1				libration H_2O and bending vibration Si,Al–O	
			538.9*		libration H_2O and bending vibration Si,Al–O	
509.7	509.7				libration H_2O and bending vibration Si,Al–O	
					libration H_2O and bending vibration Si,Al–O	
			499.1	495.9	libration H_2O and bending vibration Si,Al–O	'tetranatrolite'
		409.6			libration H_2O and bending vibration Si,Al–O	transition
487.8	487.8				libration H_2O and bending vibration Si,Al–O	natrolite
442.4	441.9					natrolite
421.2	420.9			423.6	bending vibration Si,Al–O	
		417.2	418.1		bending vibration Si,Al–O	

Font types: natrolite; **transition**; 'tetranatrolite'; *shoulder
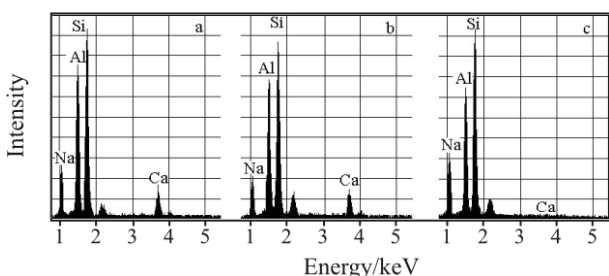
Fig. 8 EDS spectra of sample lszn-1, a) lower part of needle, b) middle part of needle and c) upper part of needle

Fig. 9 The average values of Na/Ca ratio determined by EDS *vs*. corrected decomposition temperature of the investigated samples. (The numbers indicate the samples investigated by all methods)

Fig. 10 The average values of Na/Ca ratio determined by EDS *vs*. activation energy of the investigated samples. (The numbers indicate the samples investigated by all methods)

is intermediate between the two groups, somewhat closer to 'tetranatrolite'.

Scanning electron microscopy

The samples for scanning electron microscopic investigation were selected on the basis of results of X-ray diffraction. The composition of natrolite needles was measured at three points: in the lower, middle and upper part of the needle.

Samples proved to be true natrolite by all other investigations (XRD, TA, IR) are characterised by high Na and low Ca contents. Such chemical homogeneity is very rare among the natrolite needles from Balaton Highland.

In the inhomogeneous samples which contain dominantly 'tetranatrolite' there may be remarkable differences in the Ca content in the same natrolite needle (Fig. 8).

Based on EDS investigation the samples U 142, 2578, 2588/1, 2620 and 2627 average values of measured Na/Ca ratio were compared with
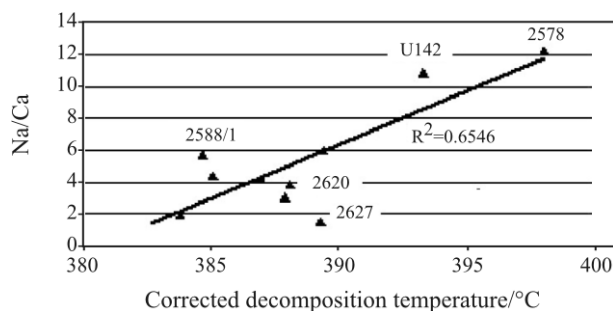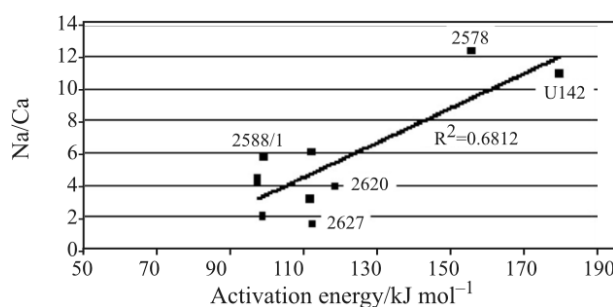
thermoanalytical parameters (Fig. 3). The corrected decomposition temperature and activation energy show correlation with the degree of Ca substitution in the framework (Figs 9 and 10).

Similar results were obtained for the decrease of temperature of Ca^{2+} and K^+ exchanged forms of

natrolite [29]. The decrease of the activation energy from 126.83 to 74.01 kJ mol^{-1} after the K exchange was measured by [30] and similar tendency can be found at [31].

Conclusions

It is well known for several decades in the Hungarian and international literatures, that natrolites occurring in the cavities of the basalts in Balaton Highland are unusual [2, 4]. This is well documented also by our investigations in which only one fourth of the samples were dominantly natrolite and only three samples proved to the pure natrolite. Most samples are dominantly 'tetranatrolite' in a mixture with small quantities of natrolite and gonnardite.

According to the author's XRD and EDS investigations the true natrolite samples are Ca-rich. Their thermal stability and activation energy are lower than those of disordered 'tetranatrolite'. It is the thermoanalytical indication of disorder of structure and/or of Ca substitution (Fig. 3).

According to the EDS measurements the mentioned compositional variation may appear in the same natrolite needle.

The presence of natrolite/'tetranatrolite' is independent of the locality. In most occurrences both variety can be found. It is the case in the localities Gulács and Uzsa where natrolites of disordered type were indicated by the literature.

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