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Zeolite occurrence in the vein mineral paragenesis near Dunje, Macedonia

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In this paper we present results of our mineralogical investigations of zeolites from Dunje. We have found two zeolites: heulandite and stilbite.

U radu su izloženi rezultati mineraloških analiza istraživanja zeolita iz Dunja, gdje su određena dva zeolita: heulandit i stilbit.

There are many occurrences of pegmatitic and pegmatitic-hydrothermal veins on the peripheral parts of the granitic body of Selečka monutain, most often in gneisses (Tajder, 1952 and Štojanov, 1958). About 2.5 km SW from the village Dunje there is one vein south of Gornji Kamen hill above Slimevski Dol valley. In that vein crystals of albite, epidote, amphibole, sphene, quartz, pyrite, muscovite, apatite, microcline, chlorite and zeolites can be found. A short paper about these minerals was published by Barić (1958), while albite and epidote were investigated in more detail by Raffaelli (1961) and Zebec (1980 and 1984).

HEULANDITE

Crystals are up to 2 mm in size, milky white to colourless with a pearly luster. They crystalized in small groups over albite or as older crystals covered by stilbite. Heulandite is very rare here: we have found only about ten crystals during our investigations. Three crystals were measured by a two circle reflecting goniometer and the following forms were determined: {001}, {010}, {100}, {201} and {$\bar{1}$11} (indexes are related to the unit cell referred to in the part of the text on X-ray investigations). Figure 1. shows the most usual habit of heulandite crystals, which are sometimes elongated parallel to [010].

Ten thin sections oriented parallel to (010) were made. In all thin sections zonal growth and sectional extinction was significant. Optic axial angle was measured by an universal stage in convergent light. In the various crystals and in the various zones of the same crystal, different values were obtained. About 30 measurements showed $2V_x = 30—100^0$ and this is common for heulandite. Optic angle values increase

from the center towards the rim of the same crystal. Apart from these variations of optic angle values changes of orientation of the optic plane was found in zones of same crystal.

An X-ray powder pattern was obtained from part of the collected material. The diffractogram was indexed on the basis of calculated X-ray powder pattern for heulandite (Borg & Smith, 1969). Unit cell dimensions were calculated by computer programme POWDER

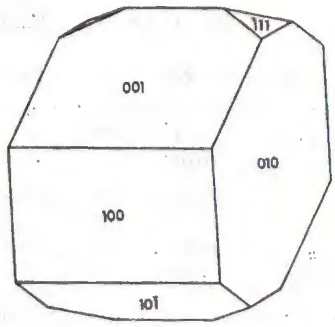

Fig. 1. Heulandite from Dunje
Sl. 1. Heulandit od Dunja

(Lindqvist & Wengelin, 1967). Observed and indexed reflections are listed in table 1. Calculations gave following unit cell dimensions:

$a = 17.711(16)$ Å
$b = 17.867(9)$ Å
$c = 7.427(6)$ Å
$\beta = 116.35(8)^0$

These values show that we have a typical heulandite i. e. mineral from the heulandite group with a high content of Al and divalent cations. Thermal stability examinations of heulandite from Dunje indicate that, too. After heating at 550 °C for 12 hours and cooling to room temperature, as proposed by Alietti (1972), the X-ray pattern showed lattice destruction. This procedure repeated at 400 °C gave the same result. The low temperature at which lattice destruction occurs, show that heulandite belongs to the first group after Boles (1972).

Because of small ammount of collected material it was impossible to perform chemical analyses which could confirm these conclusions.

STILBITE

Stilbite is more abundant than heulandite. It occurs in characteristic sheaflike curved agregates. Commonly they have crystal faces on the end. Crystals are usually milky white, sometimes yellowish-brown due to a thin limonite crust which covers them. Sometimes they are semitransparent to transparent. Crystals are up to 5 mm in size. With

Table — Tabela 1.

X-ray powder data for heulandite from Dunje

Podaci rendgenske analize heulandita iz Dunja

d	I	hkl	d	I	hkl
8.916	100 P	020	* 3.2387	5	—
7.928	3	200	3.1821	4	42$\bar{2}$
6.831	4	20$\bar{1}$	3.1232	7	44$\bar{1}$
6.647	2	001	3.0727	2	13$\bar{2}$
5.9060	1	220	2.9727	29	151.112
5.3211	2	021	2.8002	6	530.62$\bar{1}$
5.2584	3	31$\bar{1}$	2.7255	7	26$\bar{1}$
5.1198	4	111	* 2.5481	1	35$\bar{2}$
5.0733	3	310	2.5204	3	170.55$\bar{1}$
4.6513	12	13$\bar{1}$	* 2.4853	1	351
4.4703	3 P	040	2.2336	4 P	080
4.3702	1	40$\bar{1}$	2.02210	1	64$\bar{3}$
3.9689	19	131.400	* 1.97782	1	660
3.9001	10	240	1.95926	2	15$\bar{3}$
3.8436	1	221	* 1.91941	1	19$\bar{1}$
3.7200	3	24$\bar{1}$.202	1.78802	7 P	010.0
3.5645	1	31$\bar{2}$	1.76358	2	77$\bar{2}$
3.4822	3	51$\bar{1}$	* 1.72890	2	57$\bar{3}$
3.4321	4	22$\bar{2}$	* 1.72407	2	010.1
3.3143	3	002	* 1.59663	1	353
* 3.2927	2	—			

P — intensities of these reflections are higher because prefered orientation was present

* — these reflections were not used for calculations of unit cell dimensions

the two circle reflecting goniometer the following forms were found: {001}, {010}, {10$\bar{1}$}, {110} and {230} (indexes are related to the monoclinic C-cell). Untwinned crystals are absent; pseudo-orthorhombic penetration twins are present (figs. 2, 3 and 4).

Stilbite occurs as overgrowts on all other minerals, more often heulandite and apatite than others.

Classical gravimetric chemical analysis were done on part of the collected material. Results of the chemical analysis are shown in table 2 together with coefficients of the chemical formulas on the basis of 72 oxygen atoms. The formula of stilbite is:

$$Na_{0.98}\ K_{0.34}\ Ca_{4.48}\ Mg_{0.09}\ Fe_{0.12}\ Al_{9.61}\ Si_{26.09}\ O_{72}\ 31.18\ H_2O$$

An X-ray powder diffractogram was taken and it was indexed on the basis of a calculated X-ray pattern which was made by computer programme LAZY PULVERIX (Yvon & al., 1977) using data on the structure of stilbite (Galli, 1971). The indexed reflections, which were used for calculations of unit cell dimensions by computer pro-

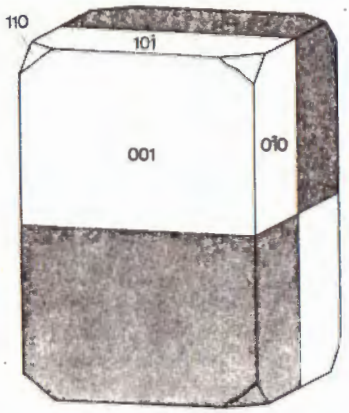

Fig. 2. Stilbite from Dunje
Sl. 2. Stilbit od Dunja

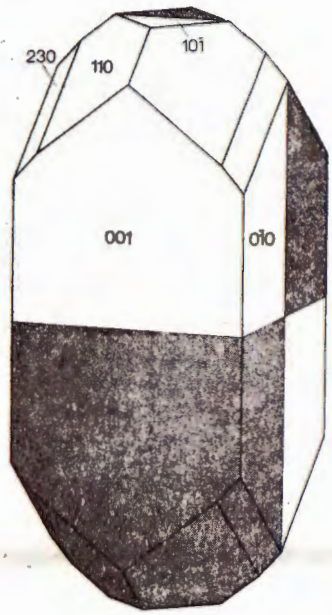

Fig. 3. Stilbite from Dunje
Sl. 3. Stilbit od Dunja

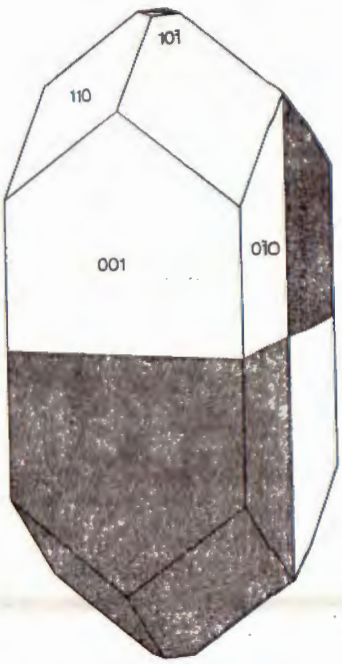

Fig. 4. Stilbite from Dunje
Sl. 4. Stilbit od Dunja

Table — Tabela 2.

Chemical analysis of stilbite from Dunje

Kemijska analiza stilbita iz Dunje

	%	f.
SiO_2	53.52	26.09
TiO_2	tr.	
Al_2O_3	16.72	9.61
Fe_2O_3	0.32	0.12
MgO	0.13	0.09
CaO	8.58	4.48
Na_2O	1.04	0.98
K_2O	0.55	0.34
H_2O	4.50	31.18
H_2O+	14.68	
Summ	100.04	

gramme POWDER (Lindqvist & Wengelin, 1967), are listed in table 3. C and F unit cells were calculated because we can find both of these in recent papers:

	C-cell	F-cell
a	13.637(8)	13.624(6)
b	18.249(6)	18.245(6)
c	11.265(8)	17.811(8)
β	127.94(3)	90.67(4)

$\varrho_{cal} = 2.20\ g/cm^3$

On the basis of the shape and splitting of the reflections 204 and $20\bar{4}$ (F-cell) it is possible to determine angle β and homogenity of the sample (Passaglia & al., 1978). For these determinations different conditions of X-ray recording must be used (scanning speed 1/4° 2 Θ/min, chart speed 0.5 cm/min and time constant 8 sec). Under these conditions two separate reflections were obtained and that corresponds to stilbite with $\beta \approx 90.80°$. $\beta = 90.72$ was obtained using the equation for calculation of angle β from splitting $20\bar{4}$ i 204 reflections (Passaglia & al., 1978).

Density measurements were done with a pycnometer. The value obtained (2.17 g/cm³) agrees with the calculated one.

Zeolites in the vein occurrence near Dunje are of hydrothermal origin and have crystalized as the last minerals in that paragenesis. As mentioned earlier heulandite crystals are covered by stilbite crystals. So it is clear that heulandite has crystalized earlier at higher temperatures. This is normal because heulandite contains less water.

Table — Tabela 3.

X-ray powder data for stilbite from Dunje

Podaci rendgenske analize stilbita iz Dunje

	d	I	hkl C-cell	hkl F-cell
	9.137	100 P	020	020
	6.820	2	20$\bar{1}$	200
*	6.408	2	021	022
	5.4578	3	20$\bar{2}$.22$\bar{1}$	20$\bar{2}$.220
	5.3084	8	13$\bar{1}$.130	13$\bar{1}$.131
	4.6707	18	22$\bar{2}$	22$\bar{2}$
	4.6321	18	220	222
	4.5613	3 P	040	040
	4.4482	4	002	004
	4.2785	15	31$\bar{2}$.31$\bar{1}$	31$\bar{1}$.311
	4.0620	87	13$\bar{2}$.041	13$\bar{3}$.042
	3.7478	8	20$\bar{3}$	20$\bar{4}$
	3.7047	7	201	204
	3.4796	5	240	242
	3.4038	19	40$\bar{2}$	400
	3.1955	23	40$\bar{3}$.42$\bar{2}$	40$\bar{2}$.420
	3.1168	6	33$\bar{3}$	33$\bar{3}$
	3.0339	46	15$\bar{2}$.151	15$\bar{3}$.153
	2.8874	4	061	062
	2.8191	2	023	026
	2.7782	17	26$\bar{1}$	260
	2.7223	7	40$\bar{4}$	40$\bar{4}$
	2.5938	3	222	226
	2.5707	5	35$\bar{3}$	35$\bar{3}$
	2.5594	6	350.33$\bar{4}$	353.335
	2.5081	4	062	064
	2.4840	3	043	046
	2.4629	3	113.51$\bar{4}$	117.51$\bar{3}$
	2.4435	2	51$\bar{1}$	513
	2.3500	5	17$\bar{2}$.261	17$\bar{3}$.264
*	2.3105	1	440	444
*	2.2692	2	60$\bar{3}$	600
*	2.2136	3	31$\bar{3}$.351	317.355
	2.1649	2	55$\bar{2}$	551
*	2.1260	3	063	066
	2.1043	2	28$\bar{2}$	28$\bar{2}$
*	2.0579	4 P	53$\bar{3}$	53$\bar{3}$
	2.02984	5	530	535
*	1.90202	2	191.48$\bar{2}$	193.480
*	1.87041	2	57$\bar{3}$	57$\bar{1}$
	1.82408	10 P	010.0	010.0
*	1.80920	3	083	—
*	1.78077	4	66$\bar{2}$	—
*	1.73011	2	210.$\bar{2}$	—
*	1.67231	2	82$\bar{4}$	—
*	1.64150	1	82$\bar{3}$	—
*	1.59612	5	466.084	—
*	1.58163	2	111.1.68$\bar{2}$	—
*	1.55544	5	010.3	—

P — intensities of these reflections are higher because preferred orientation was present

* — these reflections were not used for calculations of unit cell dimensions

Measured crystals are housed in Mineralogical-petrological museum in Zagreb (heulandite has invetory number 3368 and stilbites have inventory numbers 3370—3372).

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Pojave zeolita u žilnoj mineralnoj paragenezi nedaleko Dunja, Makedonija

D. Tibljaš, V. Zebec i V. Bermanec

U hidrotermalnoj pegmatitskoj žili oko 2,5 km JZ od sela Dunje uz kristale albita, epidota, amfibola, titanita, kremena, pirita, muskovita, apatita, mikroklina i klorita sada su određena i dva zeolita: heulandit i stilbit. Goniometrijski su izmjereni kristali, snimljeni su rendgenogrami praha i izračunate su dimenzije jediničnih ćelija, a kod stilbita je načinjena i kemijska analiza.

Izgled kristala heulandita je prikazan na slici 1, a stilbita na slikama 2, 3 i 4.

Kemijska analiza stilbita je prikazana u tabeli 2.

Rendgenografski podaci za heulandit su u tabeli 1, a za stilbit u tabeli 3.