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Tuzlaite, $NaCa[B_5O_8(OH)_2]\cdot 3H_2O$, a new mineral with a pentaborate sheet structure from the Tuzla salt mine, Bosnia and Hercegovina

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ABSTRACT

Tuzlaite, $NaCa[B_5O_8(OH)_2]\cdot 3H_2O$, is a monoclinic sheet borate [$P2_1/c$, $a = 6.506(1)$, $b = 13.280(3)$, $c = 11.462(3)$ Å, $\beta = 92.97(2)°$, $V = 989(1)$ Å^3, $Z = 4$], occurring in nearly monomineralic veinlets formed in the course of dolomitic marl diagenesis at the Tuzla salt mine, located in the northeast part of Bosnia and Hercegovina. Intergrowths with halite have been observed where halite covers tuzlaite in later stages of diagenesis.

The crystal structure, including H positions, was solved and refined from X-ray single-crystal data to $R = 2.8$, $R_w = 3.3\%$. Tuzlaite possesses a new type of pentaborate sheet structure with fourfold- and threefold-coordinated B ($5{:}2\Delta + 3T$). Borate triangles and tetrahedra form ten-membered rings. The sheets are connected by Na and Ca, which are coordinated to additional H_2O.

The new mineral is colorless to white. It is biaxial positive, with the following refractive indices: $n_x = 1.532(2)$, $n_y = 1.544(2)$, and $n_z = 1.561(2)$. The optical orientation is $Y = b$, $Z{:}a = 14°$ (in acute angle β). Tuzlaite has one perfect cleavage, parallel to {001}, and hardness 2–3; $D_{meas} = 2.21$, $D_{calc} = 2.23$ g/cm^3. The chemical composition is CaO 14.64%, Na_2O 10.25%, SrO 0.21%, B_2O_3 52.19%, Al_2O_3 0.26%, and H_2O 21.66%. Tuzlaite is chemically related to the pentaborates probertite, $NaCaB_5O_7(OH)_4\cdot 3H_2O$, and ulexite, $NaCaB_5O_6(OH)_6\cdot 5H_2O$. The new mineral is named after the town Tuzla, where it was found.

OCCURRENCE

The Tuzla salt mine is located in northeastern Bosnia and Hercegovina and is the only major evaporite deposit in the Balkans. Several rare evaporite minerals have been found in the Tuzla mine paragenesis: northupite, searlesite, and bradleyite (Bermanec et al., 1987; Brajković et al., 1988). The new borate mineral described in this work (tuzlaite) was probably mistaken for probertite (Barić and Trubelja, 1984). The paragenesis and geochemical characteristics of the evaporites from the Tuzla area have been described by several investigators (Janjić and Jovanović, 1971; Kniewald et al., 1986). Between the salt layers there are gray to black dolomitic marls, approximately 50 m thick. The marls are occasionally cut by white veinlets (5–10 mm thick), composed mainly of the new borate mineral tuzlaite, named for the locality. Sometimes a coronitic halite phase can be observed around tuzlaite. The surrounding halite can be dissolved in H_2O, releasing clear, colorless to white crystals up to 0.5 mm in length. Most of these crystals appear to be intergrown, but some are suitable for X-ray single-crystal structure analysis.

This new mineral has been approved as tuzlaite by the International Commission on New Minerals and Mineral Names. The holotype of the investigated material is deposited in the mineralogical department of the Croatian Museum of Natural History in Zagreb, Croatia (catalogue no. HPM 8888) and in the Naturhistorisches Museum Bern, Switzerland (catalogue no. NMBE-B 8361). Morphology and optical data were determined on the crystals from the holotype deposited in the Department of Mineralogy, Royal Ontario Museum, Toronto, Canada (catalogue no. M45848a).

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TABLE 2. Angle table for tuzlaite from Tuzla mine

		Measured		Calculated	
	hkl	ϕ	ρ	ϕ	ρ
b	010	0°0′	90°0′	0°0′	90°0′
a	100	90°0′	90°0′	90°0′	90°0′
m	110	63°30′	90°0′	63°56′	90°0′
d	011	4°0′	40°30′	3°13′	40°48′
p	$\bar{1}11$	−62°30′	61°0′	−63°18′	62°28′

Note: $a = 6.503$, $b = 13.278$; $c = 11.445$ Å; $\beta = 92°55'$.

TABLE 3. Compositional data for tuzlaite (1 and 2), probertite (3), and ulexite (4)

	1	2	3	4
Na_2O	10.25	9.30	8.82	7.65
CaO	14.64	16.83	15.97	13.84
SrO	0.21			
B_2O_3	52.19	52.24	49.56	42.95
Al_2O_3	0.26			
H_2O	21.66*	21.63	25.65	35.56
Total	99.21	100.00	100.00	100.00
Na	1.10	1.00	1.00	1.00
Ca	0.87	1.00	1.00	1.00
Sr	0.01			
B	4.98	5.00	5.00	5.00
Al	0.02			
O	8	8	7	6
OH	2	2	4	6
H_2O	3	3	3	5
D	2.21(2)		2.13	1.96
n_{av}	1.545		1.53	1.51

Note: the tuzlaite formula is calculated on the basis of B + Al = 5; 1 = the average value of six ICP-AES, flame photometric, and spectrophotometric analyses of tuzlaite, 2 = the theoretical end-member of tuzlaite, 3 and 4 = the chemical compositions of probertite and ulexite, respectively.

* H_2O content determined in two thermogravimetric analyses.

EXPERIMENTAL PROCEDURES

Physical properties and chemical composition

The crystal habit was measured and the forms identified on an optical goniometer with limited precision only, since the measurements were performed on two or more parallel intergrown crystals, thus leading to a slight rotation of their crystallographic axes. The orientation of the crystallographic axes derived from goniometric measurements was substantiated by single-crystal X-ray precession photographs.

A polarizing microscope equipped with a spindle stage was used for the determination of optical properties. The positions of the principal vibration directions *X, Y,* and *Z* were measured by the spindle-stage method (Bloss, 1981) on crystals of previously determined orientation by the Buerger precession technique. The optic axial angle was determined on a crystal oriented with the principal vibration direction *Y* parallel to the spindle axis. Refractive indices were measured by the immersion method with white light. The birefringence was obtained from retardation measurements with a Berek compensator, and the thickness was measured with an eyepiece with a moving hairline.

The chemical composition was determined by ICP-AES, flame photometry (Ca, Na, Sr, Al), thermogravimetric analysis (H_2O), and X-ray single-crystal structure refinement (B and H_2O) (Hawthorne and Grice, 1990). In addition, a spectrophotometric analysis using the azomethine-H complex was carried out to analyze B_2O_3 in tuzlaite. A thermogravimetric analysis was made on a 15-mg sample in air up to 900 °C to determine the weight loss from ignition, which was assumed to be H_2O. An IR spectrum of tuzlaite was recorded using a 1:100 KBr disk with a Perkin-Elmer IR-398 spectrometer in the range 4000–300 cm^{-1}. Density measurements were performed pycnometrically.

Crystal structure and X-ray powder data

Single-crystal X-ray data of tuzlaite were measured on a CAD4 single-crystal diffractometer with graphite monochromatized Mo*Kα* radiation up to $\theta = 25°$ in the ω scan mode. Cell dimensions were refined from reflections with $20° > \theta > 10°$ in monoclinic symmetry, yielding $a = 6.503(4)$, $b = 13.278(2)$, $c = 11.445(2)$ Å, $\beta = 92.91(2)°$, $V = 987.0$ Å^3. Data reduction, including background and Lorentz-polarization corrections, was carried out using the SDP program library (Enraf Nonius, 1983). The structure was solved by direct methods with the program SHELXS-86 (Sheldrick, 1986) in the space group $P2_1/c$. Of the 1915 reflections corrected for absorption by ψ scans, 1150 observed unique reflections [$I > 3\sigma(I)$] were submitted to the program SHELX76 (Sheldrick, 1976) for structure refinement (weighted $1/\sigma^2$) and to locate H atoms on difference-Fourier maps. Neutral-atom scattering factors and real, as well as imaginary, dispersion corrections were used. The refinement converged to $R = 2.8$, $R_w = 3.3\%$, with 205 parameters including anisotropic displacement parameters for all atoms except H. The largest residual peaks in the difference-Fourier maps were ± 0.25 e/Å^3. Observed and calculated structure factors are given in Table 1.[1]

X-ray powder data were collected on a Philips vertical X-ray goniometer, using graphite-monochromatized Cu*Kα* radiation. Reflection intensities were estimated from the peak height. The atomic positions and displacement parameters from the structure refinement were used to calculate an X-ray diffraction pattern using the Lazy Pulverix software (Yvon et al., 1977). These calculated diffraction data were used for indexing the observed pattern. Unit-cell dimensions were calculated with the program Gitter (Hummel, personal communication).

RESULTS

Morphology

Tuzlaite crystals are prismatic and elongate parallel to **a**. The larger crystals are about 0.5 × 0.1 × 0.1 mm. Forms given in Table 2 were determined on three crys-

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[1] A copy of Tables 1 and 5 may be obtained by ordering document AM-94-550 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 4. Atomic coordinates and B_{eq} (Å^2) values for tuzlaite

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Ca	0.2098(1)	0.89462(5)	0.08216(6)	0.93(1)
Na	0.3365(2)	0.9842(1)	0.3555(1)	1.88(3)
O1	0.1026(3)	0.0914(2)	0.0545(2)	0.78(4)
O2	−0.1367(3)	0.8327(2)	0.2282(2)	1.17(4)
O3	0.4159(3)	0.0519(2)	0.1541(2)	0.96(4)
O4	0.3098(3)	0.2278(2)	0.1374(2)	1.10(4)
O5	−0.2355(3)	0.0885(2)	0.1190(2)	0.96(4)
O6	0.6756(3)	0.9823(2)	0.2754(2)	1.11(4)
O7w	0.3315(4)	0.8150(2)	0.2692(2)	1.53(5)
O8hy	0.5789(3)	0.8617(2)	0.0321(2)	1.12(4)
O9	0.0286(3)	0.9889(2)	0.2199(2)	0.98(4)
O10w	0.1533(4)	0.7126(2)	0.0571(2)	1.62(5)
O11hy	0.0475(4)	0.0776(2)	0.5934(2)	1.47(5)
O12	−0.0220(3)	0.8302(2)	−0.2380(2)	1.16(4)
O13w	0.5450(5)	0.8800(2)	0.5267(3)	2.64(6)
B1	0.6216(6)	0.0410(3)	0.1812(3)	0.81(6)
B2	0.3128(6)	0.1275(3)	0.0750(3)	0.83(6)
B3	−0.1597(5)	0.7440(3)	0.2859(3)	0.88(6)
B4	−0.1221(6)	0.9343(3)	0.2827(3)	0.95(6)
B5	−0.0160(6)	0.0828(3)	0.1597(3)	0.79(6)
H7a	0.250(6)	0.772(3)	0.283(4)	2.37*
H7b	0.445(6)	0.789(3)	0.293(4)	2.37*
H8	0.665(6)	0.852(3)	0.084(4)	2.37*
H10a	0.090(6)	0.691(3)	0.121(4)	2.37*
H10b	0.082(6)	0.685(3)	−0.001(4)	2.37*
H11	0.907(7)	0.955(3)	0.444(4)	2.37*
H13a	0.443(7)	0.850(3)	0.546(4)	2.37*
H13b	0.610(6)	0.829(3)	0.495(4)	2.37*

* Fixed parameters. $B_{eq} = \frac{8}{3}\pi^2\Sigma_i(\Sigma_j[U_{ij}a_i^*a_j^*a_ia_j])$.

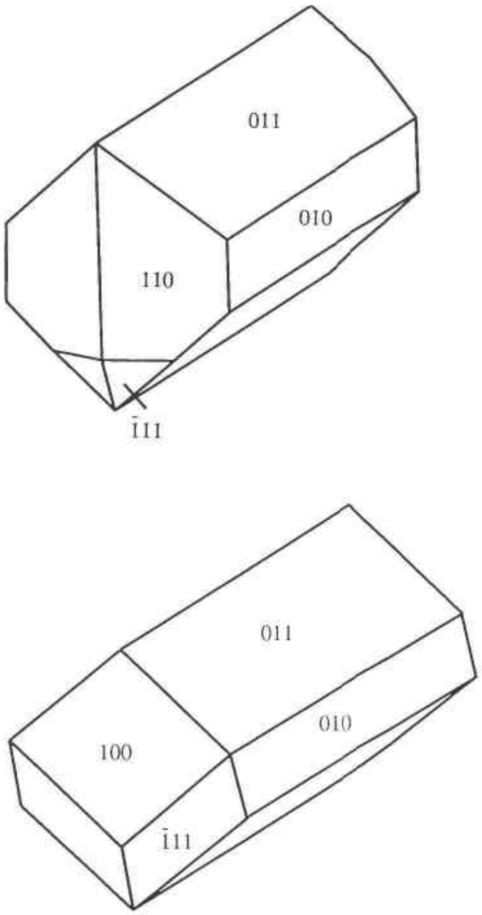

Fig. 1. Crystal morphology of tuzlaite from Tuzla salt mine.

TABLE 6. Selected interatomic distances (Å) and angles (°) for tuzlaite

Ca-O5	2.328(2)	Na-O13w	2.358(3)
Ca-O9	2.373(2)	Na-O6	2.431(2)
Ca-O10w	2.459(3)	Na-O7w	2.454(3)
Ca-O7w	2.481(3)	Na-O9	2.472(3)
Ca-O1	2.508(2)	Na-O3	2.552(3)
Ca-O8hy	2.534(2)	Na-O13w	2.705(3)
Ca-O3	2.593(2)	Na-O11hy	2.720(3)
Ca-O1	2.719(2)	mean	2.527
Mean	2.499		
B1-O5	1.355(4)	B3-O2	1.363(4)
B1-O6	1.362(4)	B3-O4	1.363(4)
B1-O3	1.365(4)	B3-O12	1.368(4)
Mean	1.361	mean	1.365
O3-B1-O5	121.5(3)	O2-B3-O4	123.3(3)
O3-B1-O6	116.8(3)	O2-B3-O12	115.9(3)
O5-B1-O6	121.7(3)	O4-B3-O12	120.8(3)
B2-O8hy	1.452(4)	B4-O9	1.440(4)
B2-O1	1.456(4)	B4-O6	1.460(4)
B2-O3	1.488(4)	B4-O11hy	1.484(4)
B2-O4	1.512(4)	B4-O2	1.487(4)
Mean	1.477	mean	1.468
O1-B2-O3	105.5(2)	O2-B4-O6	109.5(3)
O1-B2-O4	109.4(2)	O2-B4-O9	106.2(3)
O1-B2-O8hy	112.8(3)	O2-B4-O11hy	108.4(3)
O3-B2-O4	108.9(3)	O6-B4-O9	112.6(3)
O3-B2-O8hy	110.9(3)	O6-B4-O11hy	110.5(3)
O4-B2-O8hy	109.2(3)	O9-B4-O11hy	109.5(3)
B5-O9	1.446(4)		
B5-O1	1.467(4)		
B5-O12	1.475(4)		
B5-O5	1.481(4)		
Mean	1.467		
O1-B5-O5	106.0(2)		
O1-B5-O9	110.9(2)		
O1-B5-O12	111.0(2)		
O5-B5-O9	111.1(2)		
O5-B5-O12	106.3(2)		
O9-B5-O12	111.3(3)		
H7a-O7w	0.79(4)	H7b-O7w	0.84(4)
H7a-O12	2.24(4)	H7b-O4	1.93(4)
O7w-H7a-O12	161(4)	O7w-H7b-O4	174(4)
H7a-O7w-H7b	102(4)		
H10a-O10w	0.90(4)	H10b-O10w	0.87(4)
H10a-O12	1.83(4)	H10b-O11hy	1.94(4)
O10w-H10a-O12	169(4)	O10w-H10b-O11hy	157(4)
H10a-O10w-H10b	104(4)		
H8-O8hy	0.81(4)	H11-O11hy	0.69(4)
H8hy-O2	2.06(4)	H11-O6	2.42(4)
O8hy-H8-O2	174(4)	H11hy-O11	2.49(5)
		O11hy-H11-O6	82(4)
		O11hy-H11-O11hy	133(4)
H13a-O13w	0.81(4)	H13b-O13w	0.89(4)
H13a-O10w	2.07(4)	H13b-O4	2.11(4)
O13w-H13a-O10w	166(4)	O13w-H13b-O4	157(4)
H13a-O13w-H13b	98(4)		

tals. Crystals faces often gave multiple signals because of parallel intergrowths, and thus the values given in Table 2 have possible errors of 1–2°. Figure 1 shows the most prominent crystal habits. Particular attention was paid to the identification of twinning. However, goniometric and microscopic universal stage measurements on five crystals revealed no specific twin plane. The crystallographic **a** axes are diverted by an angle of 1–2°, whereas the **b** and **c** axes, as well as the principal vibrational directions *X, Y,* and *Z,* are practically subparallel. Only one single group of crystals gave an angle between the **b** axes of 26°, but examination of the zero-level precession photograph indicated no reason for the crystals to be regarded as twins.

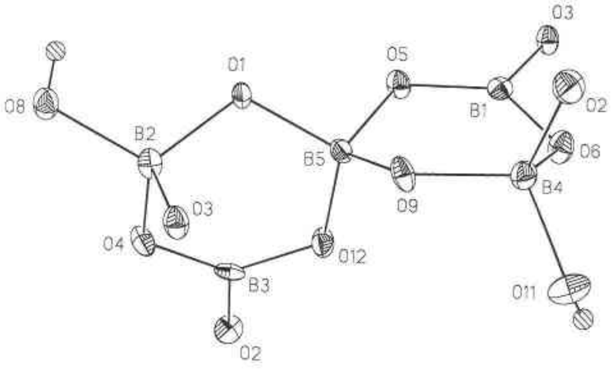

Fig. 2. Pentaborate group in tuzlaite composed of three BO_4 tetrahedra (B2, B4, and B5) and two planar BO_3 units (B1 and B3). All atoms except H are displayed with anisotropic displacement parameters using ellipsoids of 80% probability.

Physical and optical properties

Tuzlaite is white to colorless, with a white streak and perfect cleavage parallel to {001}. The hardness is between 2 and 3 on the Mohs scale, and the luster is silky to pearly and depends on crystal size and growth conditions. It is inert under short- and long-wave UV light. The measured specific gravity of tuzlaite is 2.21(2) g/cm^3; the calculated density is 2.23 g/cm^3. Tuzlaite is insoluble in H_2O but easily decomposes in hydrochloric acid, leaving a transparent solution without residue.

Tuzlaite has refractive indices n_x = 1.532(2), n_y = 1.544(2), and n_z = 1.561(2). The optical orientation is $Y = b$, $Z{:}a$ = 14° (in acute angle β). It is optically positive with Δ = 0.029(1), measured with a compensator and calculated from refractive indices. The optic axial angle was measured as $2V_z$ = 82(1)°; $2V_z$ = 80.9° was calculated from refractive indices. Indicatrix dispersion was not observed.

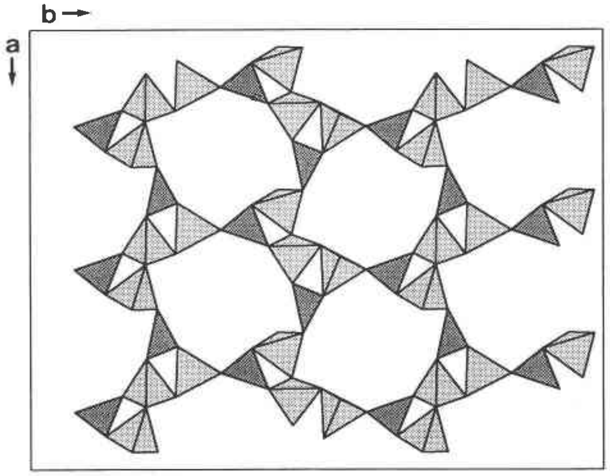

Fig. 3. Polyhedral model of ten-membered borate rings connected to a pentaborate sheet, as found in tuzlaite. Triangular borate units have darker shading than the tetrahedra.

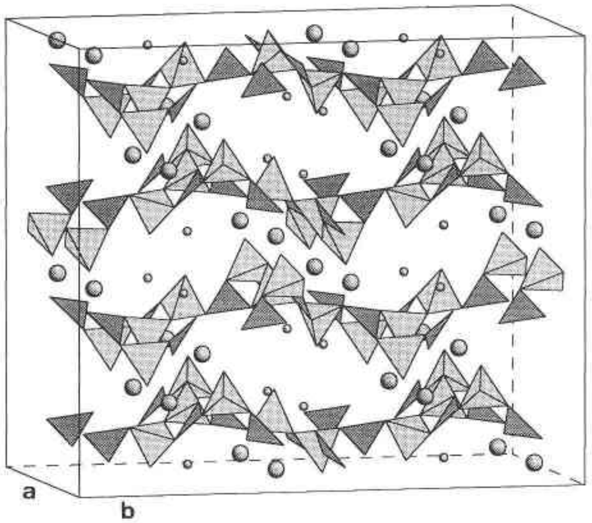

Fig. 4. Polyhedral model of the stacking of undulated pentaborate sheets. Small spheres represent Na; large spheres represent Ca.

Calculation of the Gladstone-Dale relationship using the constants of Mandarino (1976) yields K_c = 0.2388 for the chemical composition, compared with K_p = 0.2449 for the physical properties, thus providing excellent agreement based on the compatibility relationship proposed by Mandarino (1979).

Chemical composition

Results of the chemical analyses are given in Table 3. The following chemical formula (based on B + Al = 5)

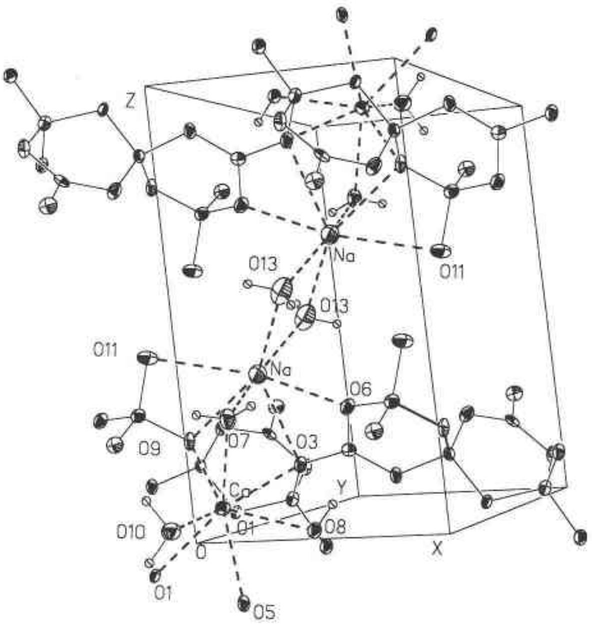

Fig. 5. Undulated pentaborate sheets are connected by CaO_8 and NaO_7 polyhedral chains. Two neighboring NaO_7 units share two H_2O molecules (O13). B-O bonds are solid; Na-O and Ca-O bonds are dashed.

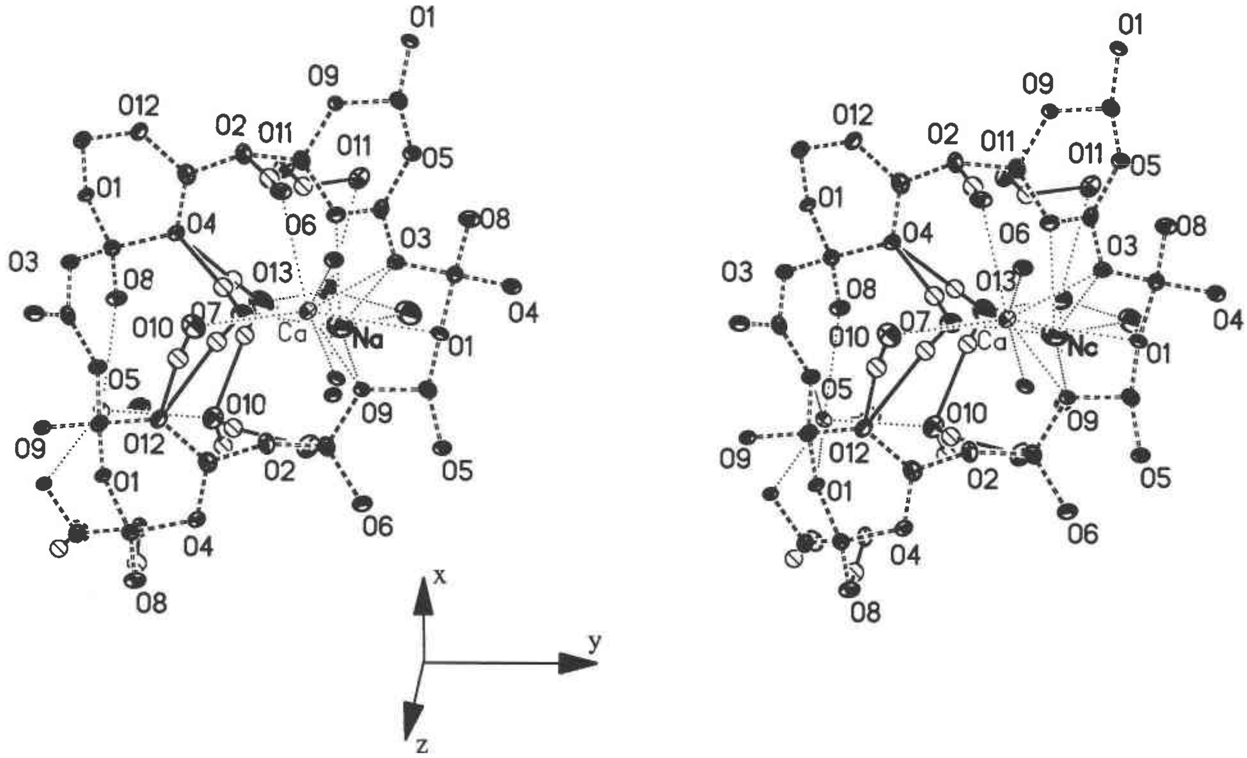

Fig. 6. Stereo figure displaying H bonds (solid lines) between the NaO_7 and CaO_8 polyhedra (Na-O and Ca-O bonds dotted) and the pentaborate sheet (B-O bonds dashed). NaO_7 and CaO_8 polyhedral chains penetrate the ten-membered borate rings. H atoms are drawn as open circles with a diagonal bar.

was derived for the new mineral: $(Ca_{0.87}Na_{0.10}Sr_{0.01})Na_{1.00}(B_{4.98}Al_{0.02})O_{7.92}(OH)_2 \cdot 3H_2O$ or ideally, $NaCa[B_5O_8(OH)_2] \cdot 3H_2O$.

A thermogravimetric measurement for tuzlaite showed that the mineral lost H_2O in three steps during heating in air: between 153 and 220 °C (10.69 wt%), at about 280 °C (1.44 wt%), and at about 610 °C (9.53 wt%). The three intervals in which H_2O is lost result from the multiple H_2O and OH groups in the tuzlaite structure. The exothermic peak at 610 °C is probably due to a dehydroxylation reaction and H_2O loss by condensation of two OH^- ions, leaving O^{2-}. A resultant rearrangement of the B coordination polyhedra or bridging groups possibly occurs as a consequence of the OH decompensation. Melting occurred at 850 °C. A total loss of ignition (LOI) of 21.66 wt% correlates well with 21.63 wt% H_2O obtained from the structure refinement.

Table 7. Calculated bond valences for all atoms except H

	Ca	Na	B1	B2	B3	B4	B5	Total
O1	0.232 0.131			0.795			0.771	1.929
O2					1.022	0.731		1.753
O3	0.184	0.132	1.016	0.729				2.061
O4				0.683	1.022			1.705
O5	0.377		1.044				0.743	2.164
O6		0.183	1.025			0.786		1.994
O7w	0.249	0.172						0.421
O8hy	0.216			0.803				1.019
O9	0.334	0.164				0.830	0.817	2.145
O10w	0.265							0.265
O11hy		0.084				0.737		0.821
O12					1.008		0.775	1.783
O13w		0.223 0.087						0.310
Total	1.988	1.045	3.085	3.010	3.052	3.084	3.106	

Crystal structure

All atoms including H were located and refined (Table 4). Suffixes are used to distinguish OH groups (Ohy) and H_2O molecules (Ow) from O positions. Anisotropic displacement parameters are given in Table 5,[1] and selected interatomic distances and angles are summarized in Table 6. Tuzlaite possesses a pentaborate sheet structure with layers parallel to (001). The pentaborate polyanion is characterized by three borate tetrahedra and two triangular borate groups (Fig. 2); according to the classification of Christ and Clark (1977), 5:2Δ + 3*T*. The pentaborate groups are linked to form a new type of undulated ten-membered ring of borate polyhedra (Figs. 3 and 4). Corners (O11hy, O8hy) of two borate tetrahedra (B2 and B4) are terminated by OH groups. The sheets are connected by Na and Ca coordinated with three additional H_2O (O7w, O10w, O13w). Ca is eightfold coordinated by six borate O atoms and two H_2O molecules (O7w and O10w).

TABLE 8. X-ray powder pattern data for tuzlaite from the Tuzla salt mine

I_{meas}	I_{calc}	d_{meas}	d_{calc}	*hkl*
100	100	8.638	8.670	011
30	29	6.617	6.640	020
3	2	6.482	6.498	100
11	15	5.709	5.723	002
12	2	5.234	5.300	$11\bar{1}$
		5.234	5.256	012
2	17	4.328	4.360	$12\bar{1}$
		4.328	4.335	022
2	<1	4.238	4.249	121
17	4	4.179	4.188	102
		4.179	4.185	$11\bar{2}$
8	15	4.122	4.129	031
2	<1	3.986	3.994	112
4	12	3.660	3.667	013
		3.660	3.658	130
6	1	3.539	3.542	122
6	1	3.501	3.501	032
2	<1	3.456	3.455	131
3	<1	3.317	3.320	040
8	2	3.257	3.264	$11\bar{3}$
		3.257	3.249	200
12	2	3.123	3.128	113
		3.123	3.124	$13\bar{2}$
4	2	3.081	3.082	$21\bar{1}$
2	<1	3.040	3.042	132
6	<1	3.008	3.003	$12\bar{3}$
1	<1	2.912	2.918	220
29	24	2.868	2.890	$20\bar{2}$
		2.868	2.872	042
		2.868	2.860	$22\bar{1}$
14	4	2.845	2.846	141
11	3	2.821	2.824	$21\bar{2}$
6	2	2.795	2.797	014
3	<1	2.763	2.764	202
7	2	2.705	2.706	212
6	1	2.666	2.670	$10\bar{4}$
4	6	2.626	2.628	024
3	1	2.601	2.602	142
15	8	2.586	2.587	051
		2.586	2.577	$23\bar{1}$
		2.586	2.570	104
1	<1	2.549	2.552	222
2	<1	2.520	2.523	114
3	1	2.499	2.505	043
		2.499	2.494	$21\bar{3}$
13	2	2.409	2.420	$23\bar{2}$
		2.409	2.409	052
2	<1	2.371	2.374	213
		2.371	2.372	$22\bar{3}$
3	1	2.345	2.345	232
1	4	2.259	2.259	241
		2.259	2.256	015
<1	<1	2.244	2.243	152
9	5	2.224	2.223	134
		2.224	2.213	060
9	3	2.204	2.205	$20\bar{4}$
		2.204	2.203	$23\bar{3}$
3	<1	2.164	2.164	025
2	1	2.136	2.138	310
6	2	2.085	2.085	$15\bar{3}$
		2.085	2.084	$12\bar{5}$
		2.085	2.082	311
14	7	2.065	2.069	214
		2.065	2.067	$16\bar{1}$
		2.065	2.064	062
		2.065	2.061	$30\bar{2}$
		2.065	2.059	320
		2.065	2.055	161
8	6	2.033	2.037	$31\bar{2}$
		2.033	2.037	$25\bar{1}$
		2.033	2.034	035
		2.033	2.032	144
7	3	2.014	2.024	125
		2.014	2.012	251
		2.014	2.009	321
3	1	1.9926	1.9917	302
6	2	1.9795	1.9781	$16\bar{2}$
3	1	1.9689	1.9697	312
		1.9689	1.9666	$13\bar{5}$
7	2	1.9481	1.9556	$25\bar{2}$
		1.9481	1.9517	243
		1.9481	1.9454	330
4	1	1.9156	1.9153	252
		1.9156	1.9145	063
4	2	1.9088	1.9078	006
		1.9088	1.9077	322
		1.9088	1.9033	331
8	2	1.8990	1.8990	$21\bar{5}$
3	1	1.8351	1.8366	$24\bar{4}$
		1.8351	1.8354	$25\bar{3}$
3	1	1.8152	1.8163	332
		1.8152	1.8139	340
4	1	1.8038	1.8054	106
9	8	1.7442	1.7508	064
		1.7442	1.7421	126
		1.7442	1.7341	055
6	5	1.6589	1.6600	080
		1.6589	1.6593	155
		1.6589	1.6541	046

Note: pattern indexed on the basis of a calculated X-ray pattern based on refined coordinates and displacement parameters.

Na is sevenfold coordinated by four borate O atoms and three H_2O molecules (2 × O13w, O7w). Na and Ca polyhedra form continuous chains with a Ca-Ca-Na-Na-Ca-Ca sequence. Two neighboring Na polyhedra share 2 × O13w (Fig. 5), and two neighboring Ca polyhedra share 2 × O1. Face sharing occurs between Ca and Na polyhedra (O7w, O3, O9). Na and Ca polyhedral chains penetrate the ten-membered borate rings (Fig. 3) excentrically; thus the remaining space is filled by H_2O molecules (O7w, O10w, and O13w), which are linked by H bonds to the borate sheets (Fig. 6). Average B-O distances for triangular B are ca. 1.36 Å, and average tetrahedral B-O distances are ca. 1.47 Å. Distances between H and O vary between 0.7 and 0.9 Å, which is satisfactory for X-ray data. Except for H11, all H atoms are fixed by one fairly short H bridge (H·O between 1.9 and 2.2 Å). H11 has two O neighbors, O6 and O11 at ca. 2.45 Å. However, the acute O11hy-H11-O6 angle of 82° is not consistent with a H bond (Table 6). Bond valences (Table 7) (Brown and Altermatt, 1985) were calculated for all atoms except H using the constants of Brese and O'Keefe (1991). The O valence sums can be subdivided into four types. Those with sums below 0.5 represent H_2O molecules (O7w, O10w, and O13w); those with sums between 0.8 and 1.0 represent OH groups (O8hy, O11hy). Valence sums above 1.9 (O1, O3, O5, O6, O9) are characteristic of O^{2-} without additional H bonds, whereas valence sums between 1.7 and 1.8 (O2, O4, and O12) are characteristic of O^{2-} linked by additional H bonds. All cations show valence sums in good agreement with their corresponding ionic charge.

TABLE 9. Cell dimensions (Å) of tuzlaite and related minerals

	a	*b*	*c*	α	β	γ
Tuzlaite						
Monocrystal	6.503(4)	13.278(2)	11.445(2)	90	92.91(2)	90
Powder	6.506(1)	13.280(3)	11.462(3)	90	92.97(2)	90
Probertite*	13.43	12.57	6.589	90	100.25	90
Ulexite**	8.816	12.870	6.678	90.36	109.05	104.98

* Menchetti et al. (1982).
** Ghose et al. (1978).

X-ray powder diffraction pattern

The powder pattern is given in Table 8. The difference between observed and calculated intensities is probably caused by preferred orientation. Unit-cell dimensions calculated from the indexed pattern, as well as those obtained from measurements on a monocrystal, are given in Table 9 and compared with the corresponding cell dimensions of probertite (Menchetti et al., 1982) and ulexite (Ghose et al., 1978), which have the same Na:Ca:B ratio and the same pentaborate building block.

The IR spectrum

The infrared spectrum of tuzlaite appears to be typical for a borate mineral (Fig. 7). Prominent features in the spectrum are H_2O and OH group vibrations. Since tuzlaite is a phylloborate, unshared O atoms attract protons to form discrete OH groups. The three absorption peaks in the range of 3700–3200 cm^{-1} (3635, 3480, and 3420 cm^{-1}) are OH stretching or H_2O vibrations. The complexity of this pattern results from the fact that H_2O coordinates Ca and Na separately but also concurrently. The single strong peak at 3230 cm^{-1} is probably the ν(OH) stretching band, whereas the 1680-cm^{-1} peak is the H_2O bending mode. The large number of bands in the range of 1500–300 cm^{-1} are anionic lattice vibrations due to the complex B coordination.

DISCUSSION

The chemical composition of tuzlaite implies that it is a characteristic evaporite mineral, genetically related to a chemically homogeneous environment. There seem to be no important substitutions for any major constituent element. Only minor substitutions of Al for B and Sr for Ca are observed. The slight excess of Na (Table 3) could be caused by minor halite inclusions in the material used for analyses.

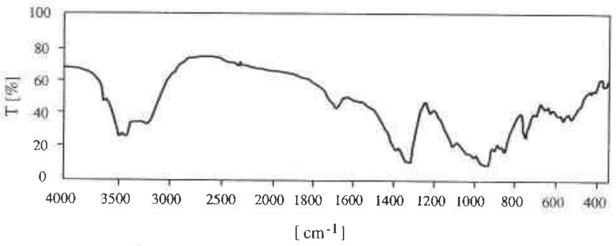

Fig. 7. Infrared powder spectrum of tuzlaite.

Ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$, probertite, $NaCaB_5O_7(OH)_4 \cdot 3H_2O$, and tuzlaite, $NaCaB_5O_8(OH)_2 \cdot 3H_2O$, have a Na:Ca:B ratio of 1:1:5 in common but are chemically distinct in their OH and H_2O content (Table 3). All three minerals consist of the pentaborate molecule ($5{:}2\Delta + 3T$) (Christ and Clark, 1977).

In ulexite the $[B_5O_6(OH)_6]^{3-}$ molecule occurs isolated. The first dehydroxylation step leads to $[B_5O_7(OH)_4]^{3-}$, as found in probertite, where pentaborate groups form continuous chains. In tuzlaite the OH content is further decreased to $[B_5O_8(OH)_2]^{3-}$, leading to a condensation of chains to sheets. The same building unit was found in heidornite, $Na_2Ca_3Cl(SO_4)_2[B_5O_8(OH)_2]$ (Burzlaff, 1967) and synthetic $Na_3[B_5O_8(OH)_2] \cdot H_2O$ (Menchetti and Sabelli, 1977), which have different sheet structure types. The OH-free end-member $NaCa[B_5O_9]$, which may possess a framework structure, has not been found as yet. A zeolite-like framework structure with a pentaborate building block $5{:}2\Delta + 3T$, however, was found for minerals of the hilgardite, $Ca_2B_5O_9Cl \cdot H_2O$, and tyretskite, $Ca_2B_5O_9OH \cdot H_2O$, groups (Ghose, 1985) and for synthetic bromoborate, $Ca_2B_5O_9Br$ (Lloyd et al., 1973). Sheet structures among pentaborates are fairly common; however, such sheets have a pentaborate unit $[B_5O_8(OH)]^{2-}$ composed of two tetrahedra and three triangular groups, $5{:}3\Delta + 2T$. The most prominent sheet type for $3\Delta + 2T$ pentaborates consists of condensate nine-membered rings, as found in nasinite, $Na_2[B_5O_8(OH)] \cdot 2H_2O$ (Corazza et al., 1975), synthetic $K_2[B_5O_8(OH)] \cdot 2H_2O$ (Marezio, 1969), veatchite, $Sr_2[B_5O_8(OH)]_2B(OH)_3 \cdot H_2O$ (Clark and Christ, 1971), gowerite, $Ca[B_5O_8(OH)]B(OH)_3 \cdot 3H_2O$ (Konnert et al., 1972), and biringuccite, $Na_4[B_5O_8(OH)OB_5O_7(OH)] \cdot 2H_2O$ (Corazza et al., 1974).

Ghose (1982) and Wan and Ghose (1983) noticed that there are two pentaborate ($2\Delta + 3T$) stereoisomeric configurations, left-handed and right-handed. In all known structures with a center of symmetry, both types occur equally. Even in examples without a center of symmetry, as hilgardite (Ghose and Wan, 1979) or parahilgardite (Wan and Ghose, 1983), both types are present. A sheet in heidornite and tuzlaite is composed of only one type, but the configuration alters from sheet to sheet.

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