

The crystal structure of ginorite, $\text{Ca}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_6]\cdot 5\text{H}_2\text{O}$, and the analysis of dimensional reduction and structural complexity in the $\text{CaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system

YULIA A. PANKOVA¹, LIUDMILA A. GORELOVA^{1,2}, SERGEY V. KRIVOVICHEV^{1,2,*} and IGOR V. PEKOV³

¹ Department of Crystallography, Institute of Earth Sciences, Saint-Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia

*Corresponding author, e-mail: s.krivovichev@spbu.ru

² Nanomaterials Research Centre, Kola Science Centre, Russian Academy of Sciences, Fersmana 14, 184209 Apatity, Russia

³ Department of Mineralogy, Faculty of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia

Abstract: The crystal structure of ginorite, $\text{Ca}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_6]\cdot 5\text{H}_2\text{O}$, from the Chelkar salt dome, western Kazakhstan, has been refined at 150(2) and 296(2) K. The mineral is monoclinic, $P2_1/c$, unit-cell parameters are (at 150/296 K): $a = 12.738(1)/12.728(1)$, $b = 14.240(1)/14.303(1)$, $c = 12.750(1)/12.755(1)$ Å, $\beta = 101.163(2)/101.147(2)^\circ$, $V = 2268.9(4)/2278.3(4)$ Å³, $Z = 4$. The crystal structure is isotypic to that of strontiojinorite and is based upon 2-dimensional anionic layers with the composition $[\text{B}_{14}\text{O}_{20}(\text{OH})_6]^{4-}$. The layers are coplanar to (0 1 0) and are composed of BO_4 tetrahedra and BO_3 triangles. The fundamental building block (FBB) for the crystal structures of ginorite and strontiojinorite consists of eight BO_3 triangles and six BO_4 tetrahedra. The adjacent FBBs are linked by sharing O atoms to form layers that possess open nine-membered rings centered by the $M1$ and $M2$ metal atoms. In the crystal structure of strontiojinorite, the $M1$ and $M2$ sites are occupied by Sr and Ca, respectively, whereas, in ginorite, both sites are occupied by Ca. The $\text{Ca} \leftrightarrow \text{Sr}$ substitution affects the geometry of the $M1\text{O}_8$ polyhedron significantly, with the difference $|\Delta|$ between the Sr–O and Ca–O bond lengths up to 0.157 Å. The dimensional reduction, structural and chemical complexity of 45 minerals and inorganic compounds of the $\text{CaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system have been analyzed using ternary diagrams. The structures with 0-dimensional structural units (finite clusters) constitute 53.3% (24) of all structures in the system, whereas 1-, 2- and 3-dimensional borate polyanions have been observed in 15.6% (7), 20.0% (9) and 11.1% (5) of all structures in the system, respectively. The average structural complexity for the 42 B-bearing phases in the $\text{CaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system is 353 bits/cell and agrees well with the average complexity of 340 bits/cell for all boron minerals. Ginorite belongs to the class of very complex structures (1536.000 bits/cell) and is the second in complexity in the system after alfredstelnorite, $\text{Ca}_4(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6]_4\cdot 15\text{H}_2\text{O}$ (4026.707 bits/cell). In general, structural and chemical complexities correlate with each other and indicate the presence of the high-complexity areas in the H_2O dominant part of the diagram, in a band between ca. 10 and 20 mol% CaO.

Key-words: ginorite; crystal structure; calcium borates; dimensional reduction; structural complexity; chemical complexity; Shannon information; Chelkar salt dome.

1. Introduction

Natural borates constitute one of the most structurally diverse and complex mineral classes (Grew *et al.*, 2016, 2017), due to the possibility of both triangular and tetrahedral coordination of boron in the same crystal structure, large combinatorial variations of boron–oxygen fundamental building blocks (FBBs) and easy protonation of oxygen vertices of B-centered polyhedra (Burns *et al.*, 1995; Hawthorne *et al.*, 1996; Grice *et al.*, 1998; Filatov & Bubnova, 2000; Schindler & Hawthorne, 2001a, b, and c; Touboul *et al.*, 2003; Yuan & Xue, 2007; Bubnova & Filatov, 2013). According to the proposal by Benner (2004) and Ricardo *et al.* (2004), borate minerals may bear important

relevance to the formation of life on the early Earth, where they may act as ribose-stabilizing agents. This hypothesis was recently criticized by Grew *et al.* (2011), though it still remains viable (Holm, 2012; Mishima *et al.*, 2016).

Among natural borates, the minerals with species-defining Ca are especially diverse. Currently, there are twenty-one ternary borate mineral species containing Ca as the only metal cation, as well as three binary phases, *i.e.*, anhydrous Ca borates. They mainly form in calcic skarns (*e.g.*, Solongo, Buryatia, Russia, and Fuka, Okayama, Japan, feature the greatest diversity of borate minerals of skarn origin), continental evaporites (*e.g.*, numerous deposits in California, USA, and in Turkey), marine evaporites (*e.g.*, the Zechstein deposits), salt domes and

Table 1. Crystalline compounds in the CaO–B₂O₃–H₂O system: dimensionality of borate polyanions (*D*) and information-based parameters of chemical and structural complexity (in bits).

No.	Mineral name	Chemical formula	Space group	<i>D</i>	Reference	Chemical complexity		Structural complexity	
						Per atom	Per formula	Per atom	Per cell
1	Lime	CaO	<i>Fm</i> $\bar{3}m$	0	Gerlach (1922)	1.000	2.000	1.000	2.000
2	–	B ₂ O ₃	<i>P</i> 3 ₁ 21	3	Effenberger <i>et al.</i> (2001)	0.971	4.855	1.522	22.829
3	Ice	H ₂ O	<i>P</i> 6 ₃ / <i>mmc</i>	0	Dowell & Rinfret (1960)	0.918	2.755	1.371	27.419
4	–	CaB ₂ O ₄	<i>Pnca</i>	1	Marezio <i>et al.</i> (1963)	1.379	9.651	1.950	54.606
5	Calciborite	CaB ₂ O ₄	<i>Pccn</i>	1	Shashkin <i>et al.</i> (1970)	1.379	9.651	2.807	157.212
6	Shimazakiite-4O	Ca ₂ B ₂ O ₅	<i>P</i> 2 ₁ / <i>c</i>	0	Kusachi <i>et al.</i> (2013)	1.436	12.920	3.170	114.117
7	Shimazakiite-4M	Ca ₂ B ₂ O ₅	<i>P</i> 2 ₁ 2 ₁ 2 ₁	0	Kusachi <i>et al.</i> (2013)	1.436	12.920	3.170	114.117
8	Takedaite	Ca ₃ B ₃ O ₆	<i>R</i> $\bar{3}c$	0	Schuckmann (1969)	1.435	15.789	1.435	31.578
9	–	α-CaB ₄ O ₇	<i>P</i> 2 ₁ / <i>n</i>	3	Zarakina & Brovkin (1977)	1.281	15.368	4.585	440.156
10	–	CaB ₆ O ₁₀	<i>P</i> 2 ₁ / <i>c</i>	3	Chen <i>et al.</i> (2008)	1.221	20.758	4.087	277.947
11	–	Ca ₂ B ₆ O ₁₁	<i>P</i> 2 ₁ / <i>b</i>	1	Zarakina & Brovkin (1976)	1.324	25.147	4.248	322.842
12	Clinometaborite	HBO ₂	<i>P</i> 2 ₁ / <i>a</i>	1	Demartin <i>et al.</i> (2011)	1.500	6.000	3.585	172.078
13	Metaborite	HBO ₂	<i>P</i> $\bar{4}3n$	3	Zachariasen (1963)	1.500	6.000	2.000	192.000
14	–	HBO ₂	<i>P</i> bnm	0	Tazaki (1940)	1.500	6.000	3.585	172.078
15	Sassolite	H ₃ BO ₃	<i>P</i> $\bar{1}$	0	Zachariasen (1954)	1.449	10.142	3.807	106.606
16	–	H ₃ BO ₃	<i>P</i> 32	0	Shuvalov & Burns (2003)	1.449	10.142	3.807	159.909
17	Portlandite	Ca(OH) ₂	<i>P</i> 3 ₁ m	0	Petch (1961)	1.522	7.610	1.522	7.610
18	Sibirskite	CaHBO ₃	<i>P</i> 2 ₁ / <i>a</i>	0	Miura & Kusachi (2008)	1.792	10.755	2.585	62.039
19	Parasibirskite	CaHBO ₃	<i>P</i> 2 ₁ / <i>m</i>	0	Takahashi <i>et al.</i> (2010)	1.792	10.755	2.236	31.303
20	Fabianite	Ca(B ₃ O ₃)(OH)	<i>P</i> 2 ₁ / <i>a</i>	2	Konnert <i>et al.</i> (1970b)	1.617	17.789	3.459	152.215
21	–	Ca(B ₃ O ₃)(OH)	<i>P</i> bn2 ₁	2	Clark <i>et al.</i> (1962)	1.617	17.789	3.459	152.216
22	Pentahydroborite	Ca[B ₂ O(OH) ₆]·2H ₂ O	<i>P</i> $\bar{1}$	0	Egorov-Tismenko <i>et al.</i> (1973)	1.562	34.359	4.459	196.215
23	Gowerite	Ca[B ₅ O ₈ (OH)] [B(OH) ₃]·3H ₂ O	<i>P</i> 2 ₁ / <i>a</i>	2	Konnert <i>et al.</i> (1972)	1.646	52.668	5.000	640.000
24	Hexahydroborite	Ca[B(OH) ₄] ₂ ·2H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	0	Ozol <i>et al.</i> (1964)	1.514	37.858	3.684	184.193
25	–	Ca[B(OH) ₄] ₂ ·2H ₂ O	<i>C</i> 2/ <i>c</i>	0	Kravchenko (1964)	1.514	37.858	3.684	184.193
26	–	Ca[B(OH) ₄] ₂ ·2H ₂ O	<i>P</i> 2 ₁ / <i>a</i>	0	Simonov <i>et al.</i> (1976a)	1.514	37.858	3.684	184.193
27	Inyoite	Ca[B ₃ O ₃ (OH) ₅]·4H ₂ O	<i>P</i> 2 ₁ / <i>n</i>	0	Rumanova & Genkina (1981)	1.552	45.001	4.858	563.526
28	Olshanskyite	Ca ₂ [B ₃ O ₃ (OH) ₆](OH)·3H ₂ O	<i>P</i> $\bar{1}$	0	Callegari <i>et al.</i> (2001)	1.633	50.614	4.954	307.160
29	Nifontovite	Ca ₃ [B ₃ O ₃ (OH) ₆] ₂ ·2H ₂ O	<i>B</i> 2/ <i>b</i>	0	Simonov <i>et al.</i> (1978)	1.698	76.430	4.514	406.267
30	–	Ca ₂ B ₆ O ₁₁ ·9H ₂ O	<i>P</i> $\bar{1}$	0	Clark & Christ (1957)	1.632	75.077	4.524	208.084
31	–	Ca ₂ [B ₈ O ₁₃ (OH) ₂]	<i>P</i> $\bar{1}$	3	Yamnova <i>et al.</i> (1976)	1.547	41.779	4.755	256.764
32	Jarandolite	Ca[B ₃ O ₄ (OH) ₃]	<i>P</i> 2 ₁ / <i>a</i>	1	Yamnova <i>et al.</i> (1994)	1.724	24.142	3.807	213.212
33	–	Ca[B ₅ O ₈ (OH)]·H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	2	Yamnova <i>et al.</i> (2003)	1.638	31.127	4.248	322.842
34	Uralborite	Ca(B ₂ O ₂ (OH) ₄)	<i>P</i> 2 ₁ / <i>n</i>	0	Shashkin <i>et al.</i> (1969)	1.706	25.584	4.170	300.235
35	Vimsite	Ca[B ₂ O ₂ (OH) ₄]	<i>B</i> 2/ <i>b</i>	1	Simonov <i>et al.</i> (1976b)	1.706	25.584	2.777	72.211
36	–	Ca[B ₈ O ₁₁ (OH) ₄]	<i>P</i> 2 ₁	2	Zarakina & Brovkin (1978)	1.572	44.003	4.807	269.212
37	Colemanite	Ca[B ₃ O ₄ (OH) ₃]·H ₂ O	<i>P</i> 2 ₁ / <i>a</i>	1	Christ <i>et al.</i> (1958)	1.713	29.122	4.087	277.947
38	Alfredstelnzerite	Ca ₄ (H ₂ O) ₄ [B ₄ O ₄ (OH) ₆] ₄ ·15H ₂ O	<i>P</i> ca2 ₁	0	Cooper <i>et al.</i> (2010)	1.549	218.441	7.140	4026.707
39	–	Ca ₂ [B ₅ O ₈ (OH)] ₂ B(OH) ₃ ·H ₂ O	<i>P</i> $\bar{1}$	2	Yamnova <i>et al.</i> (2009)	1.635	68.665	5.392	226.477
40	Meyerhofferite	Ca[B ₃ O ₃ (OH) ₅]·H ₂ O	<i>P</i> $\bar{1}$	0	Burns & Hawthorne (1993)	1.675	33.503	4.322	172.877
41	Priceite	Ca ₂ [B ₅ O ₇ (OH) ₅]·H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	2	Wallwork <i>et al.</i> (2002)	1.741	47.015	4.755	513.528
42	–	Ca[B(OH) ₄] ₂	<i>P</i> ban	0	Zeigan (1967)	1.616	30.711	3.301	250.842
43	Frolovite	Ca[B(OH) ₄] ₂	<i>P</i> $\bar{1}$	0	Simonov (1976)	1.616	30.711	4.248	161.421
44	Nobleite	Ca[B ₆ O ₉ (OH) ₂]·3H ₂ O	<i>P</i> 2 ₁ / <i>a</i>	2	Karanovic <i>et al.</i> (2004)	1.658	48.069	4.858	563.526
45	Ginorite	Ca ₂ [B ₁₄ O ₂₀ (OH) ₆]·5H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	2	This work	1.646	103.686	6.000	1536.000

their weathered zones exposed to near-surface conditions (e.g., Chelkar and Inder, Kazakhstan) and salt lakes (e.g., Searles Lake, USA) (Malinko *et al.*, 1991). In addition, there are seventeen synthetic Ca borates with known crystal structures (Grew *et al.*, 2017), so the total number of phases with determined crystal structures in the CaO–B₂O₃–H₂O system is forty-five, including B₂O₃ and ice I (the high-pressure phase β-CaB₄O₇ (Huppertz, 2003) has not been considered; Table 1).

Ginorite, Ca₂[B₁₄O₂₀(OH)₆]·5H₂O, is a relatively rare mineral with eight known localities (Grew *et al.*, 2017). It has first been described by D'Achiardi (1934) from

calcite-bearing hydrothermal veins in sandstones in Sasso Pisano, Tuscany, Italy, and named in honor of Ginori Conti (1865–1939), the founder of the borax industry in Tuscany. Later, ginorite was reported from the Death Valley, California, USA (Allen & Kramer, 1957), Inder and Chelkar salt domes in western Kazakhstan (Pekov & Abramov, 1993; Pekov, 1998), Tyretskoe salt deposit, Irkutsk Oblast, Russia (Garrett, 1998).

The ordered Ca–Sr analogue of ginorite, strontioGINORITE, CaSr[B₁₄O₂₀(OH)₆]·5H₂O, was first reported by Braitsch (1959) from Königshall-Hindenburg Mine, Lower Saxony, Germany (in general, there are five known

Table 2. Data collection and structure-refinement parameters for ginorite at 150 and 293 K.

<i>Crystallographic data</i>			
Crystal system		Monoclinic	
Space group		$P2_1/c$	
Unit-cell parameters	a , Å	12.738(1)	12.728(1)
	b , Å	14.240(1)	14.303(1)
	c , Å	12.750(1)	12.755(1)
	β , °	101.163(2)	101.147(2)
	V , Å ³	2268.9(4)	2278.3(4)
Z		4	
Crystal density (g/cm ³)		1.839	1.831
Absorption coefficient (mm ^{−1})		2.168	2.160
Crystal size (mm ³)		0.36 × 0.22 × 0.10	
<i>Data collection</i>			
Temperature, K		150(2)	296(2)
Radiation type, wavelength		MoK α , 0.71073	
θ angles range, deg.		1.629–37.478	1.631–39.371
h, k, l values range		−17 → 21, −23 → 20, −21 → 21	−20 → 22, −25 → 25, −22 → 22
Reflections collected		35 815	45 282
Unique reflections (R_{int})		11 027 (0.0343)	12 975 (0.0338)
Observed reflections ($>4\sigma F_o$)		8773	10 391
<i>Structure refinement</i>			
Refinement method		Full-matrix least-square analysis of F^2	
Weight coefficients a, b		0.0390, 0.6353	0.0415, 0.6239
R_1 [$F>4\sigma(F)$], wR_2 [$F>4\sigma(F)$]		0.0339, 0.0792	0.0350, 0.0823
R_1 [all data], wR_2 [all data]		0.0494, 0.0850	0.0502, 0.0885
S		1.026	1.024
$\rho_{\text{max}}, \rho_{\text{min}}, e \cdot \text{Å}^{-3}$		0.71, −0.57	0.78, −0.62

localities for strontioginorite listed by Grew *et al.*, 2017). Its crystal structure was determined by Konnert *et al.* (1970a) and refined by Grice (1995), who determined H positions that allowed to reveal the basic features of hydrogen bonding scheme in the mineral. However, the crystal structure of ginorite itself had never been reported and is the subject of this study. In addition, we provide the results of the analysis of dimensional reduction, structural and chemical complexities in the CaO–B₂O₃–H₂O system.

2. Materials and methods

2.1. Crystal-structure analysis

The sample of ginorite used in this study originates from the Chelkar salt dome borate deposit, western Kazakhstan, and was taken from the collection of the fourth author. Qualitative electron-microprobe analysis confirmed the absence of detectable amounts of elements heavier than B, except of O and Ca. The crystal of ginorite selected for data collection was mounted on a Bruker APEX II DUO X-ray diffractometer operated at 50 kV and 40 mA and equipped with the I μ S microfocus source (St. Petersburg State University). More than a hemisphere of 3-dimensional data was collected using monochromatic MoK α X-radiation, with frame widths of 0.5°, and with a 10 s count for each frame. The unit-cell parameters (Table 2) were refined using least-squares techniques. The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker

programs *APEX* and *XPREP*. An analytical multiscan absorption correction was performed using *SADABS*. The observed systematic absences were consistent with the space group $P2_1/c$, in agreement with the previous reports by Konnert *et al.* (1970a) and Grice (1995). The initial model included atom coordinates taken from Grice (1995) and the crystal structure was refined at 150 and 293 K in order to obtain more reliable data on hydrogen bonding system in the mineral. The refinements converged to $R_1=0.034$ and 0.035 on the basis of 8773 and 10 391 unique reflections for the 150 and 293 K data, respectively. The *SHELX* program package was used for all structural calculations (Sheldrick, 2008). The final atomic coordinates and displacement parameters are given in Tables S1 and S2 of the Supplementary Material (SM, freely available online as supplementary material linked to this article on the GSW website of the journal, <http://eurjmin.geoscienceworld.org>), selected interatomic distances in Tables 3 and 4. Geometrical parameters of the hydrogen bonding schemes in the crystal structure of ginorite at different temperatures are provided in Table S3 (SM).

2.2. Dimensional reduction

The composition–structure relationships for the crystalline compounds in the CaO–B₂O₃–H₂O system can be rationalized using the principle of dimensional reduction initially proposed by Long *et al.* (1996) for the description of decreasing dimensionality of chalcogenide structural units in Re sulfides and selenides. Later, this idea was

Table 3. B–O bond lengths (Å) in the crystal structure of ginorite at different temperatures.

Bond length		Temperature		Bond length		Temperature	
		293 K	150 K			293 K	150 K
B1	–O1	1.514(1)	1.518(1)	B7	–O11	1.461(1)	1.465(1)
	–O5	1.466(1)	1.467(1)		–O12	1.520(1)	1.520(1)
	–O6	1.460(1)	1.460(1)		–O16	1.446(1)	1.446(1)
	–O26	1.448(1)	1.449(1)		–O17	1.455(1)	1.455(1)
<B1–O>		1.472	1.474	<B7–O>		1.471	1.455
B2	–O1	1.497(1)	1.497(1)	B8	–O12	1.507(1)	1.508(1)
	–O2	1.461(1)	1.461(1)		–O13	1.457(1)	1.457(1)
	–O7	1.450(1)	1.452(1)		–O18	1.453(1)	1.455(1)
	–O9	1.454(1)	1.459(1)		–O20	1.460(1)	1.461(1)
<B2–O>		1.466	1.459	<B8–O>		1.469	1.461
B3	–O1	1.528(1)	1.529(1)	B9	–O12	1.511(1)	1.512(1)
	–O3	1.452(1)	1.456(1)		–O14	1.460(1)	1.463(1)
	–O4	1.460(1)	1.461(2)		–O15	1.455(1)	1.456(1)
	–O10	1.442(1)	1.444(1)		–O25	1.465(1)	1.468(1)
<B3–O>		1.471	1.444	<B9–O>		1.473	1.468
B4	–O6	1.367(1)	1.372(1)	B10	–O17	1.367(1)	1.370(1)
	–O7	1.368(1)	1.370(1)		–O18	1.362(1)	1.360(1)
	–O10	1.353(1)	1.353(1)		–O25	1.367(1)	1.370(1)
<B4–O>		1.363	1.353	<B10–O>		1.365	1.370
B5	–O2	1.361(1)	1.364(1)	B11	–O13	1.367(1)	1.370(1)
	–O3	1.365(1)	1.367(1)		–O14	1.377(1)	1.376(1)
	–O11	1.353(1)	1.356(1)		–O26	1.358(1)	1.361(1)
<B5–O>		1.360	1.356	<B11–O>		1.367	1.361
B6	–O4	1.351(1)	1.355(1)	B12	–O15	1.367(1)	1.370(1)
	–O5	1.359(1)	1.360(1)		–O16	1.357(1)	1.361(1)
	–O8	1.376(1)	1.379(2)		–O19	1.367(1)	1.371(2)
<B6–O>		1.362	1.379	<B12–O>		1.364	1.371
B13	–O20	1.356(1)	1.359(1)	B14	–O22	1.368(1)	1.355(1)
	–O21	1.362(1)	1.364(2)		–O23	1.351(1)	1.370(2)
	–O22	1.382(1)	1.385(1)		–O24	1.376(1)	1.379(1)
<B7–O>	<B13–O>	1.367	1.385	<B14–O>		1.365	1.379

generalized for a wide class of ternary compounds (Tulsky & Long, 2001) and was applied to inorganic oxysalts (Alekseev *et al.*, 2007; Krivovichev, 2009; Kovrugin *et al.*, 2012). The principle of dimensional reduction states that incorporation of an ionic reagent A_nX into the framework of a parent compound, MX_n , according to the reaction $kA_nX + MX_n \rightarrow A_{kn}MX_{n+k}$, results in the decreased dimensionality of the MX_{n+k} structural unit. The higher the k value, the lower the dimensionality of the MX_{n+k} unit. Herein dimensionality (D) is the number of dimensions in which a given structural unit has infinite extension. All compounds in the $\text{CaO–B}_2\text{O}_3\text{–H}_2\text{O}$ system have been analyzed from the viewpoint of the D value of their borate polyanions that may be equal to 0 (finite clusters), 1 (chains), 2 (layers) and 3 (frameworks) (Table 1).

2.3. Structural and chemical complexity calculations

In order to investigate variations in structural and chemical complexity of minerals and synthetic phases in the $\text{CaO–B}_2\text{O}_3\text{–H}_2\text{O}$ system the former was estimated as an amount of structural Shannon information per atom ($^{\text{str}}I_G$) and per unit cell ($^{\text{str}}I_{G,\text{total}}$). According to this approach developed by Krivovichev (2012, 2013, 2014, 2015, 2016), the

complexity of a crystal structure can be quantitatively characterized by the amount of Shannon information it contains measured in bits (binary digits) per atom (bits/atom) and per unit cell (bits/cell), respectively. The concept of Shannon information employed here, also known as Shannon entropy, originates from the information theory and its application to various problems in graph theory, chemistry, and biology. The amount of Shannon information reflects diversity and relative proportion of different objects, *e.g.*, the number and relative proportion of different sites in the elementary unit cell of a crystal structure. For a crystal structure, the calculation involves the use of the following equations:

$$^{\text{str}}I_G = -\sum_{i=1}^k p_i \log_2 p_i \quad (\text{bits/atom}), \quad (1)$$

$$^{\text{str}}I_{G,\text{total}} = -vI_G = -v\sum_{i=1}^k p_i \log_2 p_i \quad (\text{bits/cell}), \quad (2)$$

where k is the number of different crystallographic orbits (independent crystallographic Wyckoff sites) in the structure and p_i is the random choice probability for

Table 4. *M*–O bond lengths (Å) in the crystal structure of ginorite at different temperatures compared with strontioginorite.

Bond length		Strontioginorite (Grice, 2005)		Ginorite (this work)		Δ _{max}
		293 K		293 K	150 K	
<i>M</i> 1	–O6	2.620		2.585	2.582	0.038
	–O10	2.883		3.010	3.008	0.127
	–O13	2.691		2.570	2.561	0.130
	–O14	2.600		2.571	2.571	0.029
	–O18	2.610		2.469	2.466	0.144
	–O _h 21	2.706		2.590	2.587	0.119
	–O _h 23	2.657		2.557	2.550	0.107
	–O26	2.847		2.998	2.991	0.151
	–O _w 27	2.591		2.444	2.454	0.147
	–O _w 29	2.572		2.415	2.415	0.157
	< <i>M</i> 1–O>	2.678		2.621	2.619	0.059
<i>M</i> 2	–O2	2.511		2.495	2.497	0.016
	–O3	2.563		2.533	2.533	0.030
	–O7	2.612		2.606	2.617	0.011
	–O11	2.557		2.551	2.548	0.009
	–O17	2.577		2.574	2.566	0.011
	–O _h 24	2.398		2.388	2.383	0.015
	–O25	2.496		2.507	2.504	0.011
	–O _w 28	2.311		2.305	2.314	0.009
	< <i>M</i> 2–O>	2.503		2.495	2.495	0.008

an atom from the *i*th crystallographic orbit, that is:

$$p_i = m_i/v, \quad (3)$$

where m_i is a multiplicity of a crystallographic orbit (*i.e.*, the number of atoms of a specific Wyckoff site in the reduced unit cell), and v is the total number of atoms in the reduced unit cell. It has recently been shown (Krivovichev, 2016) that the I_G value provides a negative contribution to the configurational entropy (S^{cfig}) of crystalline solids in accordance with the general principle that the increase in structural complexity corresponds to the decrease of the S^{cfig} value.

The calculation of the information-based structural complexity parameters using equations (1)–(3) implies that the positions of all atoms in the crystal structures are known. However, it is not always the case in the crystal structures of hydrated oxysalt minerals, as very frequently the H atom positions could not be determined due to the experimental problems associated with crystal quality and low scattering power of H. The exclusion of the H sites from the calculations significantly affects the complexity parameters. In particular, Krivovichev (2013) calculated structural complexity parameters for all structurally characterized minerals without taking into account that the H sites had not been determined, that is, the analysis of complexity in a particular system is difficult because crystal structures with determined H sites are being compared to structures in which the H sites were not determined. For instance, in the CaO–B₂O₃–H₂O system, H sites were determined for nobleite, Ca[B₆O₉(OH)₂]₃·3H₂O (Karanovic *et al.*, 2004), and not determined for alfredstelnznerite, Ca₄(H₂O)₄[B₄O₄(OH)₆]₄·15H₂O (Cooper *et al.*, 2010). In order to calculate structural complexity parameters more correctly, we have introduced into the structure data for hydrated

borates with no experimentally determined H sites “dummy” H atoms with fictitious atom coordinates, taking into account multiplicities of the respective O atoms of OH and H₂O groups. For instance, for the H₂O group in a general position, two general positions of “dummy” H atoms have been introduced into the structure data. It was observed that the structural complexity parameters for the structures corrected with “dummy” H atoms may differ significantly from the uncorrected data. For instance, the crystal structure of alfredstelnznerite, Ca₄(H₂O)₄[B₄O₄(OH)₆]₄·15H₂O (Cooper *et al.*, 2010), with no H sites determined in the original study, has $v=316$ atoms ($Z=4$) in the unit cell and its complexity parameters are: $^{\text{str}}I_G=6.304$ bits/atom and $^{\text{str}}I_{G,\text{total}}=1991.995$ bits/cell [note that Krivovichev (2013) and Grew *et al.* (2016) significantly underestimated the complexity of this mineral as $^{\text{str}}I_G=5.858$ bits/atom and $^{\text{str}}I_{G,\text{total}}=1359.052$ bits/cell]. Since the structure contains 24 symmetrically independent (OH)[–] groups and 19 symmetrically independent H₂O molecules, $24+19\times 2=62$ “dummy” H sites have been introduced into the structure data. This results in the increase of the number of atoms per unit cell from 316 to 564 (by $62\times 4=248$ atoms) and the “corrected” structural complexity parameters $^{\text{str}}I_G=7.140$ bits/atom and $^{\text{str}}I_{G,\text{total}}=4026.707$ bits/cell. Note that, due to the H-correction, the total structural complexity has increased by the factor of 2. The H-corrected structural complexity parameters for the crystalline phases the CaO–B₂O₃–H₂O system are provided in Table 1.

By analogy with structural complexity, chemical complexity can be evaluated by the amount of chemical information per atom ($^{\text{chem}}I_G$) and per formula unit, f.u. ($^{\text{chem}}I_{G,\text{total}}$), as suggested by Siidra *et al.* (2014). Following this approach, for the idealized chemical formula of a mineral or inorganic compound,

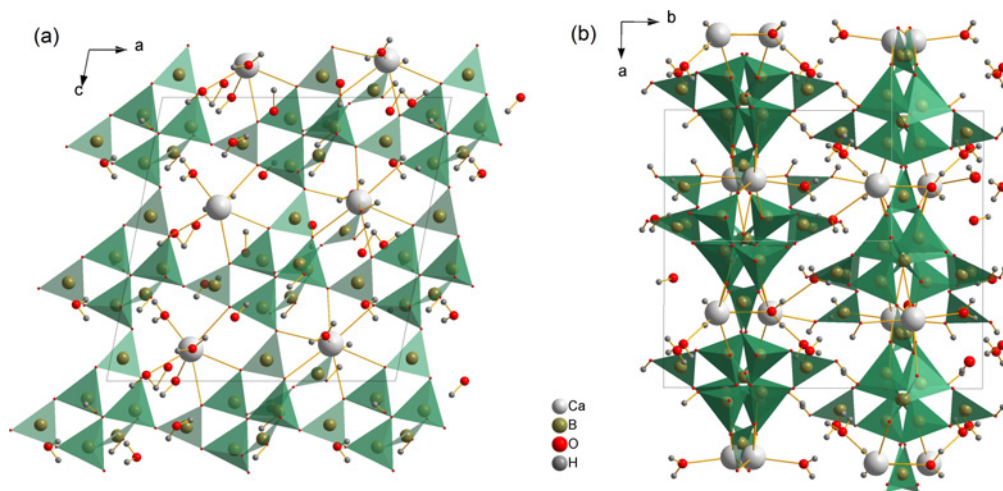


Fig. 1. The crystal structure of ginorite projected along the **b** axis (a) and $[001]$ (b). Boron–oxygen polyhedra are shown in green.

$E_{c1}^{(1)} E_{c2}^{(2)} \dots E_{ck}^{(k)}$, where $E^{(i)}$ is an i th chemical element in the formula and c_i is its integer coefficient, the chemical information can be calculated as follows:

$$^{\text{chem}}I_G = -\sum_{i=1}^k p_i \log_2 p_i \quad (\text{bits/atom}), \quad (4)$$

$$^{\text{chem}}I_{G,\text{total}} = -eI_G = -v \sum_{i=1}^k p_i \log_2 p_i \quad (\text{bits/f.u.}), \quad (5)$$

where k is the number of different elements in the formula and p_i is the random choice probability for an atom of the i th element, that is:

$$p_i = c_i/e, \quad (6)$$

where e is the total number of atoms in the chemical formula:

$$e = \sum_{i=1}^k c_i. \quad (7)$$

For instance, for ginorite, $\text{Ca}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_6] \cdot 5\text{H}_2\text{O}$, its chemical formula can be re-written as $\text{Ca}_2\text{B}_{14}\text{O}_{31}\text{H}_{16}$ with $e=63$ and $c_{\text{Ca}}=2$, $c_{\text{B}}=14$, $c_{\text{O}}=31$, $c_{\text{H}}=16$. This results in $^{\text{chem}}I_G=1.646$ bits/atom and $^{\text{chem}}I_{G,\text{total}}=103.686$ bits/f.u.

The information-based parameters of chemical of minerals and synthetic phases in the $\text{CaO-B}_2\text{O}_3\text{-H}_2\text{O}$ system are provided in Table 1.

3. Results

3.1. Crystal structure

The crystal structure of ginorite is isotypic to that of strontioginorite described in detail by Konnert *et al.* (1970a) and Grice (1995) (Fig. 1). It is based upon two-

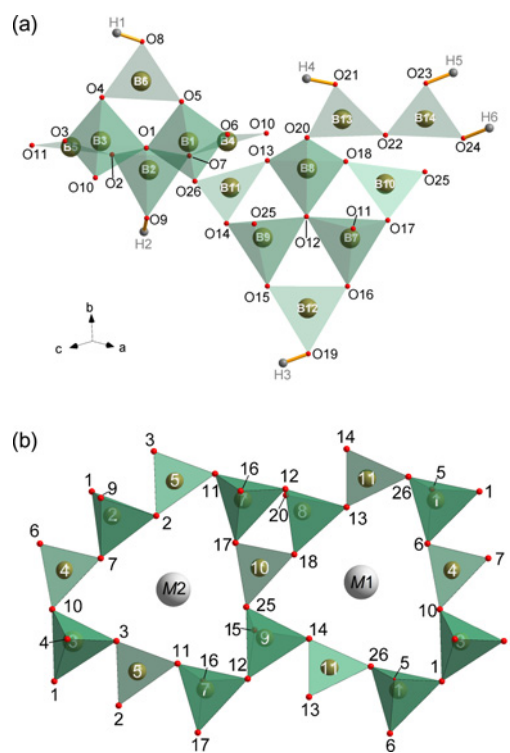


Fig. 2. Fundamental building block in the crystal structure of ginorite (a) and arrangement of nine-membered rings (b; O atoms numbered according to the crystal-structure data). Borate polyhedra are shown in green.

dimensional anionic layers with the composition $[\text{B}_{14}\text{O}_{20}(\text{OH})_6]^{4-}$. The layers are coplanar to the (010) plane and consist of BO_4 tetrahedra and BO_3 triangles.

The FBB for the crystal structures of ginorite and strontioginorite was described by Grice *et al.* (1998) and Grice (1995) as follows: $8\Delta 6\square: [\varphi] < \Delta 2\square > | < \Delta 2\square > | < \Delta 2\square > - [\varphi] < \Delta 2\square > | < \Delta 2\square > | < \Delta 2\square > - 2\Delta$. This means that FBB consists of eight BO_3 triangles, 8Δ , and six BO_4 tetrahedra, $6\square$ (Fig. 2a). The very basic unit of the

Table 5. Comparison of the B–O–B bond angles (degrees) in strontioginorite and ginorite at 293 and 150 K.*

Angle	Strontioginorite (Grice, 2005)	$ \Delta_{\text{Sr-Ca}} $	Ginorite (this work)			$ \Delta_{\text{max}} $
			293 K	$ \Delta_{\text{T}} $	150 K	
B2–O1–B1	120.91	0.55	120.36	0.03	120.33	0.58
B2–O1–B3	120.55	0.19	120.36	0.11	120.25	0.30
B1–O1–B3	117.78	0.05	117.73	0.17	117.56	0.22
B5–O2–B2	119.79	0.45	119.34	0.03	119.37	0.45
B5–O3–B3	125.60	0.10	125.50	0.20	125.30	0.30
B6–O4–B3	120.87	0.51	120.36	0.27	120.09	0.78
B6–O5–B1	124.53	0.10	124.63	0.12	124.75	0.22
B4–O6–B1	125.73	1.72	124.01	0.02	124.03	1.72
B4–O7–B2	121.95	0.42	122.37	0.08	122.45	0.50
B4–O10–B3	124.20	0.07	124.13	0.20	123.93	0.27
B5–O11–B7	124.09	0.24	123.85	0.59	123.26	0.83
B8–O12–B9	120.05	0.31	119.74	0.15	119.59	0.46
B8–O12–B7	119.79	0.50	119.29	0.07	119.22	0.57
B9–O12–B7	117.50	0.10	117.60	0.07	117.53	0.10
B11–O13–B8	123.78	0.18	123.96	0.18	123.78	0.18
B11–O14–B9	124.22	0.90	123.32	0.15	123.17	1.05
B12–O15–B9	124.28	0.29	124.57	0.21	124.36	0.29
B12–O16–B7	121.49	0.03	121.52	0.12	121.40	0.12
B10–O17–B7	124.43	0.03	124.46	0.33	124.13	0.33
B10–O18–B8	121.53	0.53	121.00	0.03	120.97	0.56
B13–O20–B8	130.29	0.32	129.97	0.67	129.30	0.99
B14–O22–B13	129.83	1.04	128.79	0.18	128.61	1.22
B10–O25–B9	124.52	0.25	124.27	0.56	123.71	0.81
B11–O26–B1	124.87	0.12	124.99	0.41	124.58	0.41

* $|\Delta_{\text{Sr-Ca}}|$ = absolute angular difference between strontioginorite and ginorite at 293 K; $|\Delta_{\text{T}}|$ = absolute angular difference between ginorite at 293 and 150 K; $|\Delta_{\text{max}}|$ = maximal angular difference between different structures.

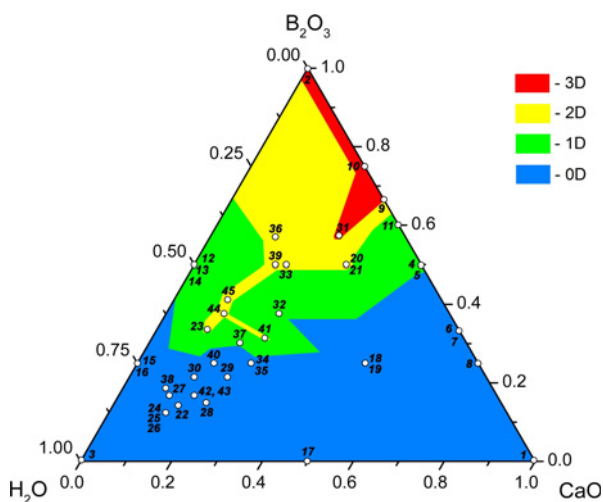


Fig. 3. Composition (molar)–dimensionality diagram for the CaO–B₂O₃–H₂O system. Numbers correspond to the numbers of crystalline compounds in Table 1.

structure is a $\langle \Delta 2 \square \rangle$ ring shown in $\langle \text{brackets} \rangle$, each consisting of one BO₃ triangle, Δ , and two BO₄ tetrahedra, $\square$. Three such rings are united into a hexameric unit, $[\varphi] \langle \Delta 2 \square \rangle \langle \Delta 2 \square \rangle \langle \Delta 2 \square \rangle$, and share an O atom denoted as $[\varphi]$. There are two different hexameric units in the FBB and one is decorated by two additional triangles, BO₂(OH) and BO(OH)₂, denoted as 2Δ .

The adjacent FBBs are linked by sharing O atoms to form layers that possess open nine-membered rings centered by the M1 and M2 metal atoms (Fig. 2b). In the crystal structure of strontioginorite, the M1 and M2 sites are occupied by Sr and Ca, respectively, whereas in ginorite both sites are occupied by Ca. Table 4 provides comparison of M–O bond lengths in strontioginorite and ginorite studied at 293 and 150 K. It can be seen that Ca $\leftrightarrow$ Sr substitution affects the geometry of the M1O₈ polyhedron significantly, with the difference $|\Delta|$ between the Sr–O and Ca–O bond lengths reaching 0.157 Å.

3.2. Flexibility of borate polyanion: thermal and chemical deformations

It is of interest to compare geometrical parameters of the borate polyanions as a function of chemical (induced by the Ca $\leftrightarrow$ Sr substitution) and thermal deformations. It was pointed out by Filatov & Bubnova (2000) and Bubnova & Filatov (2013) that, in borates, small rings are relatively rigid and act as rigid units, with bridging anions between them being soft points that sometimes act as hinges. Table 5 provides a comparison of the interpolyhedral B–O–B angles for strontioginorite and ginorite at 293 and 150 K. Inspection of the data in Table 5 and its comparison with Fig. 2 show that there are seven O sites with $|\Delta_{\text{max}}| > 0.75^\circ$ ($|\Delta_{\text{max}}|$ = maximal angular difference between identical bond angles in different structures) that

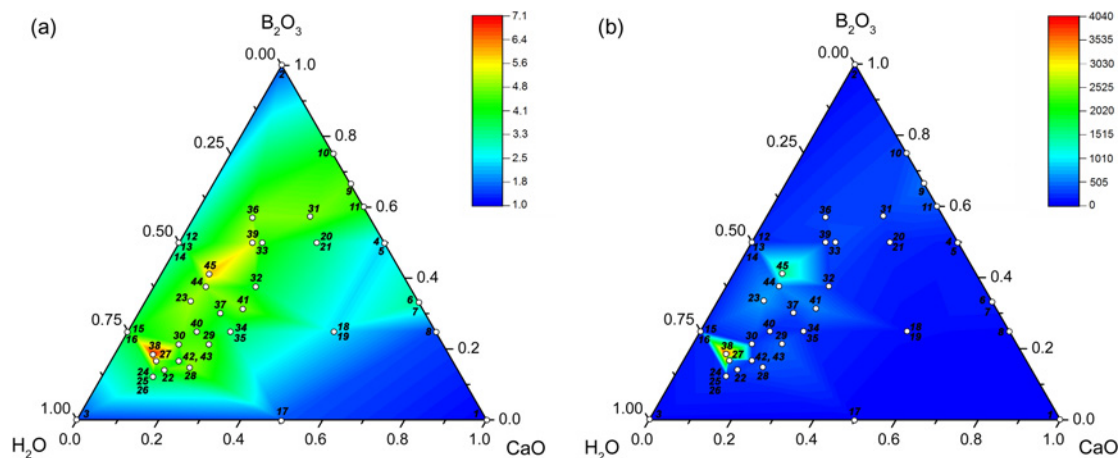


Fig. 4. Structural complexity vs. chemical composition diagram for the CaO–B₂O₃–H₂O system: structural information (in bits) per atom (a) and per unit cell (b). Numbers correspond to the numbers of crystalline compounds in Table 1.

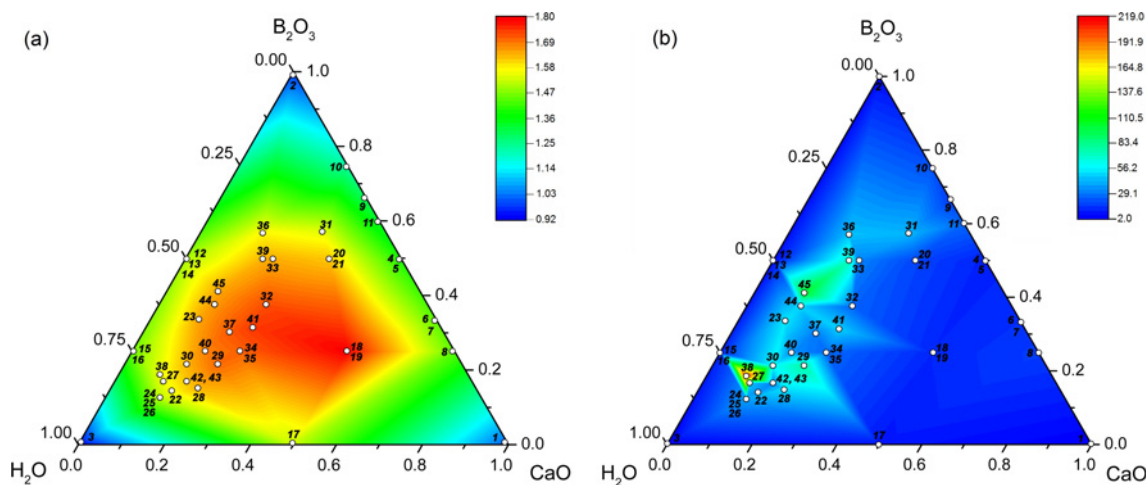


Fig. 5. Chemical complexity vs. chemical composition diagram for the CaO–B₂O₃–H₂O system: chemical information (in bits) per atom (a) and per formula unit (b). Numbers correspond to the numbers of crystalline compounds in Table 1.

can be considered as soft points in the borate layers: O4, O6, O11, O14, O20, O22 and O25. Among them, O4, O6 and O14 are internal O atoms within the three-membered rings that constitute the FBBs. The O11 and O25 are bridging atoms between adjacent FBBs, whereas the O20 and O22 sites belong to the 2 Δ that decorate one of two hexameric units within the FBB (see above). Therefore, neither three-membered rings nor FBBs can be considered as rigid units within the borate layers in the gonorite structure type.

4. Discussion

4.1. Dimensional reduction in the CaO–B₂O₃–H₂O system

Figure 3 shows the diagram of dimensionality of borate polyanions in the CaO–B₂O₃–H₂O system. Each point in the diagram corresponds to a particular chemical composition (particular crystal structure) to which the given dimensionality of borate polyanion is assigned. The diagram was

produced by applying the Ternary Contour Graph procedure within the Origin 9.0 program package (Origin, 2015). It should be noted that borders between different dimensionality fields are drawn automatically and should not be taken as exact borders, but rather they reflect a general tendency of changing dimensionality depending upon changing chemical composition. It should be noted that, in their original paper, Tulskey & Long (2001) considered only ionic reagent as a dimensionality-reducing agent in binary systems A_aX-MX_n (see above), whereas Krivovichev (2009) and Kovrugin *et al.* (2012) added H₂O as another dimensionality-reducing agent in agreement with the proposal made by Hawthorne (1992) that (OH)[–] and H₂O as components of the structural unit control its dimensionality due to the asymmetric nature of hydrogen-bond interactions. Therefore, in H₂O-bearing systems with the general formula $A_aX-MX_n-H_2O$, there are two dimensionality-reducing agents: the ionic reagent A_aX and H₂O. In the CaO–B₂O₃–H₂O system, the parent framework compound with predominantly covalent bonding is boron oxide, B₂O₃, whereas CaO plays the role of an ionic reagent.

The analysis of the diagram shown in Fig. 3 indicates that incorporation of both CaO and H₂O results in the decreasing dimensionality of boron-oxide structural units in Ca borates. This agrees well with the observation made by Schindler & Hawthorne (2001c) that, with increasing activity of H₂O, structural units trend from frameworks → sheets → chains → clusters → isolated polyhedra. The diagram, however, has a strong mirror asymmetry as H₂O seems to have less influence upon the dimensionality compared to CaO. In general, structures with 0-dimensional structural units (finite clusters) constitute 53.3% (24) of all structures, whereas 1-, 2- and 3-dimensional borate polyanions have been observed in 15.6% (7), 20.0% (9) and 11.1% (5) of all structures in the CaO–B₂O₃–H₂O system, respectively. It is noteworthy that the natural phases (minerals) generally have low dimensionality, whereas most 2D and 3D phases are synthetic products. The predominance of 0-dimensional structural units in the system may be the result of crystallization of most Ca borate minerals from aqueous solutions, where borate species occur as isolated hydrated and/or protonated complexes. This kind of crystallization is observed for various geochemical environments such as salt lakes and evaporites (direct deposition from low-temperature solutions) or skarns (where Ca borate minerals most likely formed from low-temperature alteration by aqueous solutions but under temperatures higher than those in salt lakes). For instance, inyoite, Ca [B₃O₃(OH)₅]₄·4H₂O, based upon 0D structural units (Rumanova & Genkina, 1981), has been found in both skarn and evaporitic environments (Grew *et al.*, 2017).

4.2. Structural and chemical complexity in the CaO–B₂O₃–H₂O system

On the basis of the information-based structural complexity measures (see Section 2.3), Krivovichev (2013) classified crystal structures of minerals into very simple (0–20 bits/cell), simple (20–100 bits/cell), intermediate (100–500 bits/cell), complex (500–1000 bits/cell) and very complex (>1000 bits/cell), which are represented by 15%, 28%, 46%, 8%, and 3% of all structurally characterized minerals, respectively. Grew *et al.* (2016) analyzed 256 boron minerals according to their complexity and observed the following distribution of structures among different complexity groups: 2%, 14%, 64%, 14%, and 7%, respectively, which demonstrates an essential shift of structural complexity toward more complex structures in boron minerals compared to all minerals. For the CaO–B₂O₃–H₂O system, the similar distribution is 0%, 14%, 71%, 10%, and 5%, respectively, very similar to the general trend observed for all boron minerals (Grew *et al.*, 2016). The average structural complexity of 353 bits/cell for the 42 B-bearing phases in the CaO–B₂O₃–H₂O system agrees well with the average complexity of 340 bits/cell for all boron minerals (Grew *et al.*, 2016), which is essentially higher than the average structural complexity of 228 bits/cell for all minerals reported by Krivovichev (2013).

There are two structurally very complex minerals in the system: alfredstelnznerite, Ca₄(H₂O)₄[B₄O₄(OH)₆]₄·15H₂O (4026.707 bits/cell) and ginorite, Ca₂[B₁₄O₂₀(OH)₆]₅·5H₂O (1536.000 bits/cell), which is the subject of this study. Grew *et al.* (2016) identified the following mechanisms responsible for the appearance of complex structures in boron minerals: (1) modularity induced by complex chemistry; (2) combinatorial modularity in simple borates; (3) modularity of borate polyanions; (4) complexity of hydrogen bonding networks. It is noteworthy that alfredstelnznerite and ginorite belong to different groups according to the origin of their structural complexity: the complexity of the crystal structure of alfredstelnznerite is due to its exceptional hydration state and, as a consequence, the presence of complicated hydrogen bonding network (see also Grew *et al.*, 2016), whereas the complexity of ginorite is controlled by the presence in its crystal structure of 14-nuclear borate FBB (see above).

Ternary diagrams of structural and chemical complexity of crystalline phases in the CaO–B₂O₃–H₂O system are shown in Figs. 4 and 5 (produced by means of the Origin 9.0 program package). The distribution of chemical complexity per atom (Fig. 5a) is very straightforward and reflects the fact that the system with equal amounts of each component has the highest information content.

The remarkable observation on the system is that minerals dominate in both structural and chemical complexity relative to synthetic compounds. In our opinion, this reflects the more complex physical and chemical environments that exist in Nature compared to those created under laboratory conditions. Another interesting observation is the distribution of structural information (Fig. 4) and of chemical information per formula (Fig. 5b). All three distributions show the presence of high-complexity areas in the H₂O-dominant part of the diagram in a band between *ca.* 10 mol% and *ca.* 20 mol% CaO. This observation leads to the conclusion that, at least in the CaO–B₂O₃–H₂O system, very complex structures occur at low Ca contents in the crystalline phases.

Acknowledgments: We are grateful to Joel Grice, an anonymous reviewer and Associate Editor Edward Grew for useful and constructive comments on the manuscript. This work was supported by the Russian Foundation for Basic Research (17-05-01027), St. Petersburg State University (grant 3.38.243.2015) and Presidium of the Russian Academy of Sciences. The XRD studies have been performed at the X-ray Diffraction Centre of St. Petersburg State University.

References

- Alekseev, E.V., Krivovichev, S.V., Armbruster, T., Depmeier, W., Suleimanov, E.V., Chuprunov, E.V., Golubev, A.V. (2007): Dimensional reduction in alkali metal uranyl molybdates: synthesis and structure of Cs₂[(UO₂)O(MoO₄)]. *Z. Anorg. Allg. Chem.*, **633**, 1979–1984.

- Allen, R.D. & Kramer, H. (1957): Ginorite and sassolite from Death Valley, California. *Am. Mineral.*, **42**, 56–61.
- Benner, S.A. (2004): Understanding nucleic acids using synthetic chemistry. *Acc. Chem. Res.*, **37**, 784–797.
- Braitsch, O. (1959): Über Strontioginorit, eine neu Ginorit-Varietät aus dem Zechsteinsalz. *Beitr. Mineral. Petrogr.*, **6**, 366–370.
- Bubnova, R.S. & Filatov, S.K. (2013): High-temperature borate crystal chemistry. *Z. Kristallogr.*, **228**, 395–428.
- Burns, P.C. & Hawthorne, F.C. (1993): Hydrogen bonding in meyerhofferite: an X-ray and structure energy study. *Can. Mineral.*, **31**, 305–312.
- Burns, P.C., Grice, J.D., & Hawthorne, F.C. (1995): Borate minerals I: polyhedral clusters and fundamental building blocks. *Can. Mineral.*, **33**, 1131–1151.
- Callegari, A., Mazzi, F., Tadini, C. (2001): The crystal structure of olshanskyite. *Can. Mineral.*, **39**, 137–144.
- Chen X.A., Li, M., Chang, X.N., Zang, H., Xiao, W.Q. (2008): Synthesis and crystal structure of a new calcium borate, $\text{CaB}_6\text{O}_{10}$. *J. Alloys Compd.*, **464**, 332–336.
- Christ, C.L., Clark, J.R., Evans, H.T. Jr. (1958): Studies of borate minerals(III): the crystal structure of colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3\text{H}_2\text{O}$. *Acta Crystallogr.*, **11**, 761–770.
- Clark, J.R. & Christ, C.L. (1957): The crystal structure of $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$. *Acta Crystallogr.*, **10**, 776–777.
- Clark, J.R., Christ, C.L., Appleman, D.E. (1962): Studies of borate minerals (X): the crystal structure of $\text{CaB}_3\text{O}_5(\text{OH})$. *Acta Crystallogr.*, **15**, 207–213.
- Cooper, M.A., Hawthorne, F.C., Galliski, M.A., Marquez-Zavalia, M.F. (2010): The crystal structure of alfredstelnzerite, $\text{Ca}_4(\text{H}_2\text{O})_4(\text{B}_4\text{O}_4(\text{OH})_6)_4(\text{H}_2\text{O})_{15}$, a complex hydroxy-hydrated calcium borate mineral. *Can. Mineral.*, **48**, 129–138.
- D'Achiardi, G. (1934): Ginorite, nuovo borato di calcio di Sasso Pisano. *Per. Mineral.*, **5**, 22–32.
- Demartin, F., Gramaccioli, C.M., Camprostrini, I. (2011): Clinometaborite, natural beta-metaboric acid, from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.*, **49**, 1273–1279.
- Dowell, L.G. & Rinfret, A.P. (1960): Low-temperature forms of ice as studied by X-ray diffraction. *Nature*, **188**, 1144–1148.
- Effenberger, H., Lengauer, C.L., Parthe, E. (2001): Trigonal B_2O_3 with higher space-group symmetry: results of a reevaluation. *Monatsh. Chem.*, **132**, 1515–1517.
- Egorov-Tismenko, Yu.K., Barishnikov, J.M., Shashkin, D.N., Simonov, M.A., Belov, N.V. (1973): The crystal structure of calciumpentahydroborate $\text{CaB}_2\text{O}_4(\text{H}_2\text{O})_5 = \text{Ca}(\text{B}_2\text{O}(\text{OH})_6)(\text{H}_2\text{O})_2$. *Dokl. Akad. Nauk SSSR*, 208, 1082–1085 (in Russian).
- Filatov, S.K. & Bubnova, R.S. (2000): Borate crystal chemistry. *Phys. Chem. Glass.*, **41**, 216–224.
- Garrett, D.E. (1998): Borates. Handbook of deposits, processing, properties, and use. Academic Press, San Diego, CA.
- Gerlach, W. (1922): Die Gitterstruktur der Erdalkalioxyde. *Z. Phys.*, **9**, 184–192.
- Grew, E.S., Bada, J.L., Hazen, R.M. (2011): Borate minerals and origin of the RNA world. *Orig. Life Evol. Biosph.*, **41**, 307–316.
- Grew, E.S., Krivovichev, S.V., Hazen, R.M., Hystad, G. (2016): Evolution of structural complexity in boron minerals. *Can. Mineral.*, **54**, 125–143.
- Grew, E.S., Hystad, G., Hazen, R.M., Krivovichev, S.V., Gorelova, L.A. (2017): How many boron minerals occur in Earth's upper crust? *Am. Mineral.*, **102**, 1573–1578.
- Grice, J.D. (1995): Strontioginorite: crystal-structure analysis and hydrogen bonding. *Can. Mineral.*, **43**, 1019–1026.
- Grice, J.D., Burns, P.C., Hawthorne, F.C. (1998): Borate minerals II: a hierarchy of structures based upon the borate fundamental building block. *Can. Mineral.*, **37**, 731–762.
- Hawthorne, F.C. (1992): The role of OH and H_2O in oxide and oxysalt crystals. *Z. Kristallogr.*, **201**, 183–206.
- Hawthorne, F.C., Burns, P.C., Grice, J.D. (1996): The crystal chemistry of boron. *Rev. Mineral.*, **33**, 41–116.
- Holm, N.G. (2012): The significance of Mg in prebiotic geochemistry. *Geobiology*, **10**, 269–279.
- Huppertz, H. (2003): $\beta\text{-CaB}_4\text{O}_7$: a new polymorph synthesized under high-pressure/high-temperature conditions. *Z. Naturforsch.*, **58b**, 257–265.
- Karanovic, L., Rosic, A., Poleti, D. (2004): Crystal structure of nobleite, $\text{Ca}[\text{B}_6\text{O}_9(\text{OH})_2] \cdot 3\text{H}_2\text{O}$, from Jarandol (Serbia). *Eur. J. Mineral.*, **16**, 825–833.
- Konnert, J.A., Clark, J.R., Christ, C.L. (1970a): Crystal structure of strontioginorite, $(\text{Sr}, \text{Ca})_2\text{B}_{14}\text{O}_{20}(\text{OH})_6(\text{H}_2\text{O})_5$. *Am. Mineral.*, **55**, 1911–1931.
- , —, — (1970b): Crystal structure of fabianite, $\text{CaB}_3\text{O}_5(\text{OH})$, and comparison with the structure of its synthetic dimorph. *Z. Kristallogr.*, **132**, 241–254.
- , —, — (1972): Gowerite, $\text{CaB}_5\text{O}_8(\text{OH})\text{B}(\text{OH})_3(\text{H}_2\text{O})_3$: crystal structure and comparison with related borates. *Am. Mineral.*, **57**, 381–396.
- Kovrugin, V.M., Gurzhiy, V.V., Krivovichev, S.V. (2012): Structural topology and dimensional reduction in uranyl oxysalts: eight novel phases in the methylamine- $(\text{UO}_2)(\text{NO}_3)_2\text{-H}_2\text{SeO}_4\text{-H}_2\text{O}$ system. *Struct. Chem.*, **23**, 2003–2017.
- Kravchenko, V.B. (1964): The crystal structure of $\text{CaB}_2\text{O}_4(\text{H}_2\text{O})_6 = \text{Ca}(\text{B}(\text{OH})_4)_2(\text{H}_2\text{O})_2$. *J. Struct. Chem.*, **5**, 77–82.
- Krivovichev, S.V. (2009): Structural crystallography of inorganic oxysalts. Oxford University Press, Oxford.
- (2012): Topological complexity of crystal structures: quantitative approach. *Acta Crystallogr.*, **A68**, 393–398.
- (2013): Structural complexity of minerals: information storage and processing in the mineral world. *Mineral. Mag.*, **77**, 275–326.
- (2014): Which inorganic structures are the most complex? *Angew. Chem. Int. Ed.*, **53**, 654–661.
- (2015): Structural complexity of minerals and mineral parageneses: information and its evolution in the mineral world. in "Highlights in mineralogical crystallography", R. Danisi & T. Armbruster, eds. Walter de Gruyter GmbH, Berlin/Boston, 31–73.
- (2016): Structural complexity and configurational entropy of crystalline solids. *Acta Crystallogr.*, **B72**, 274–276.
- Kusachi, I., Kobayashi, S., Takechi, Y., Nakamuta, Y., Nagase, T., Yokoyama, K., Momma, K., Miyawaki, R., Shigeoka, M., Matsubara, S. (2013): Shimazakiite-4M and shimazakiite-4O, $\text{Ca}_2\text{B}_2\text{O}_5$, two polytypes of a new mineral from Fuka, Okayama prefecture, Japan. *Mineral. Mag.*, **77**, 93–105.
- Long, J.R., McCarty, L.S., Holm, R.H. (1996): A solid state route to molecular clusters: access to the solution chemistry of $[\text{Re}_6\text{Q}_8]^{2+}$ (Q = S, Se) core-containing clusters via dimensional reduction. *J. Am. Chem. Soc.*, **118**, 4603–4616.
- Malinko, S.V., Khalturina, I.I., Ozol, A.A., Bocharov, V.M. (1991): Minerals of boron. Nedra Publishing, Moscow (in Russian).
- Marezio, M., Plettinger, H.A., Zachariasen, W.H. (1963): Refinement of the calcium metaborate structure. *Acta Crystallogr.*, **16**, 390–392.
- Mishima, S., Ohtomo, Y., Kakegawa, T. (2016): Occurrence of tourmaline in metasedimentary rocks of the Isua Supracrustal Belt, Greenland: implications for ribose stabilization in Hadean marine sediments. *Orig. Life Evol. Biosph.*, **46**, 247–271.

- Miura, H. & Kusachi, I. (2008): Crystal structure of sibirskite (CaHBO_3) by Monte Carlo simulation and Rietveld refinement. *J. Mineral. Petrol. Sci.*, **103**, 156–160.
- Origin (2015): Origin 9.0. OriginLab, Northampton, MA.
- Ozol, Y., Vimba, S., Levin'sh, A.F. (1964): The crystal structure of calcium monoborate. *Kristallografiya*, **9**, 32–36 (in Russian).
- Pekov, I.V. (1998): Minerals first discovered on the territory of the Former Soviet Union. Ocean Pictures, Moscow.
- Pekov, I.V. & Abramov, D.V. (1993): Boron deposit of the Inder and its minerals. *World Stones*, **1**, 23–30.
- Petch, H.E. (1961): The hydrogen positions in portlandite, $\text{Ca}(\text{OH})_2$, as indicated by the electron distribution. *Acta Crystallogr.*, **14**, 950–957.
- Ricardo, A., Carrigan, M.A., Olcott, A.N., Benner, S.A. (2004): Borate minerals stabilize ribose. *Science*, **303**, 196.
- Rumanova, I.M. & Genkina, E.A. (1981): Precise structure of inyoite $\text{Ca}(\text{H}_2\text{O})_3(\text{B}_2(\text{t})\text{B}(\delta)\text{O}_3(\text{OH})_5)(\text{H}_2\text{O})$. Study of hydrogen bonds. *Latv. PSR Zin. Akad. Vest. Khim. Ser.*, **1981**, 643–653.
- Schindler, M. & Hawthorne, F.C. (2001a): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. I. Theory. *Can. Mineral.*, **39**, 1225–1242.
- , — (2001b): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. II. Crystal structure and chemical composition of borate minerals. *Can. Mineral.*, **39**, 1243–1256.
- , — (2001c): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. III. Paragenesis of borate minerals. *Can. Mineral.*, **39**, 1257–1274.
- Schuckmann, W. (1969): Zur Kristallstruktur des calcium-Borates $\text{Ca}_3(\text{BO}_3)_2$. *N. Jb. Mineral. Mh.*, **1969**, 142–143.
- Shashkin, D.N., Simonov, M.A., Belov, N.V. (1969): The crystal structure of uralborite $\text{Ca}_2(\text{B}_4\text{O}_4(\text{OH})_8)$. *Dokl. Akad. Nauk SSSR*, **189**, 532–535 (in Russian).
- , —, — (1970): Crystal structure of calciborite $\text{CaB}_2\text{O}_4 = \text{Ca}_2(\text{BO}_3\text{BO})_2$. *Dokl. Akad. Nauk SSSR*, **195**, 345–349 (in Russian).
- Sheldrick, G.M. (2008): A short history of SHELX. *Acta Crystallogr.*, **A64**, 112–122.
- Shuvalov, R.R. & Burns, P.C. (2003): A new polytype of orthoboric acid, $\text{H}_3\text{BO}_3\cdot 3\text{T}$. *Acta Crystallogr.*, **C59**, i47–i49.
- Siidra, O.I., Zenko, D.S., Krivovichev, S.V. (2014) Structural complexity of lead silicates: crystal structure of $\text{Pb}_{21}[\text{Si}_7\text{O}_{22}]_2[\text{Si}_4\text{O}_{13}]$ and its comparison to hyttsjoite. *Am. Mineral.*, **99**, 817–823.
- Simonov, M.A. (1976): The refined crystal structure of frolovite $\text{Ca}(\text{B}(\text{OH})_4)_2$. *Dokl. Akad. Nauk SSSR*, **230**, 91–94.
- Simonov, M.A., Yamnova, N.A., Kazanskaya, E.V., Egorov Tismenko, Yu.K., Belov, N.V. (1976a): Crystal structure of $\text{Ca}(\text{B}(\text{OH})_4)_2(\text{H}_2\text{O})_2$. *Dokl. Akad. Nauk SSSR*, **228**, 1337–1340.
- Simonov, M.A., Egorov-Tismenko, Yu.K., Belov, N.V. (1976b): Refined crystal structure of vimsite $\text{Ca}(\text{B}_2\text{O}_2(\text{OH})_4)$. *Kristallografiya*, **21**, 592–594 (in Russian).
- Simonov, M.A., Egorov-Tismenko, Yu.K., Kazanskaya, E.V., Belokoneva, E.L., Belov, N.V. (1978): The hydrogen bonds in the crystal structure of the niphontovite $\text{Ca}_3(\text{B}_3\text{O}_3(\text{OH})_6)_2(\text{H}_2\text{O})_2$. *Dokl. Akad. Nauk SSSR*, **239**, 326–329 (in Russian).
- Takahashi, R., Kusachi, I., Miura, H. (2010): Crystal structure of parasibirskite (CaHBO_3) and polymorphism in sibirskite and parasibirskite. *J. Mineral. Petrol. Sci.*, **105**, 70–73.
- Tazaki, H. (1940): The structure of orthorhombic metaboric acid, HBO_2 (alpha). *J. Sci. Hiroshima Univ. Ser. A*, **10**, 55–61.
- Touboul, M., Penin, N., Nowogrocki, G. (2003): Borates: a survey of main trends concerning crystal-chemistry, polymorphism and dehydration process of alkaline and pseudo-alkaline borates. *Solid State Sci.*, **5**, 1327–1242.
- Tulsky, E.G. & Long, J.R. (2001): Dimensional reduction: a practical formalism for manipulating solid structures. *Chem. Mater.*, **13**, 1149–1166.
- Wallwork, K.S., Pring, A., Taylor, M.R., Hunter, B.A. (2002): The structure of priceite, a basic hydrated calcium borate, by ab initio powder-diffraction methods. *Can. Mineral.*, **40**, 1199–1206.
- Yamnova, N.A., Simonov, M.A., Belov, N.V. (1976): Refined crystal structure of the framework Ca-borate $\text{Ca}_2(\text{B}_8\text{O}_{13}(\text{OH})_2)$. *Zh. Strukt. Khim.*, **17**, 489–495 (in Russian).
- Yamnova, N.A., Egorov Tismenko, Yu.K., Malinko, S.V., Pushcharovskii, D.Yu., Dorokhova, G.I. (1994): Crystal structure of a new natural calcium hydroborate $\text{Ca}(\text{B}_3\text{O}_4(\text{OH})_3)$. *Kristallografiya*, **39**, 991–993 (in Russian).
- Yamnova, N.A., Egorov Tismenko, Yu.K., Zubkova, N.V., Dimitrova, O.V., Kantor, A.P., Danian, Y., Ming, X. (2003): Crystal structure of new synthetic calcium pentaborate $\text{Ca}(\text{B}_5\text{O}_8(\text{OH}))\text{H}_2\text{O}$ and its relation to pentaborates with similar boron-oxygen radicals. *Kristallografiya*, **48**, 608–613 (in Russian).
- Yamnova, N.A., Zubkova, N.V., Dimitrova, O.V., Mochenova, N.N. (2009): Crystal structure of a new synthetic calcium pentaborate, $\text{Ca}_2[\text{B}_5\text{O}_8(\text{OH})]_2\cdot[\text{B}(\text{OH})_3]\cdot\text{H}_2\text{O}$, and modular crystal chemistry of pentaborates with polar boron-oxygen layers. *Kristallografiya*, **54**, 846–849 (in Russian).
- Yuan, G. & Xue, D. (2007): Crystal chemistry of borates: the classification and algebraic description by topological type of fundamental building blocks. *Acta Crystallogr.*, **B63**, 353–362.
- Zachariasen, W.H. (1954): The precise structure of orthoboric acid. *Acta Crystallogr.*, **7**, 305–310.
- (1963): The crystal structure of cubic metaboric acid. *Acta Crystallogr.*, **16**, 380–384.
- Zarakina, N.V. & Brovkin, A.A. (1976): Crystal structure of $\text{Ca}_2\text{B}_6\text{O}_{11}$. *Kristallografiya*, **21**, 502–506 (in Russian).
- , — (1977): Crystal structure of CaB_4O_7 . *Kristallografiya*, **22**, 275–280 (in Russian).
- , — (1978): Crystal structure of $\text{CaO}(\text{B}_2\text{O}_3)_4(\text{H}_2\text{O})_2 = \text{CaB}_8\text{O}_{11}(\text{OH})_4$. *Kristallografiya*, **23**, 1167–1170 (in Russian).
- Zeigan, D. (1967): Zur Struktur einer neuen Modifikation von Calcium (1/1/4)-borathydrat. *Z. Chem.*, **7**, 241–242.

Received 20 January 2017

Modified version received 16 June 2017

Accepted 27 June 2017