

Johachidolite, $\text{CaAl}[\text{B}_3\text{O}_7]$, a mineralogical and structural peculiarity

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Abstract: The crystal structure of johachidolite, $\text{CaAl}[\text{B}_3\text{O}_7]$, (*Cmma*, $a = 9.767(2)$, $b = 11.723(3)$, $c = 4.3718(5)$ Å, $V = 408.3(1)$ Å³, $Z = 4$) has been refined ($R1 = 2.5\%$) from a light-green gem-quality crystal from the Mogok gem-mining district in Myanmar. A fragment from the same gem was measured by electron microprobe and Laser-Ablation Inductively-Coupled-Plasma Mass-spectrometry (LA-ICP-MS), and is almost end-member composition with ca. 0.3 wt.% ThO_2 and ca. 1000 ppm *Ln* probably replacing Ca. Johachidolite has a very dense structure with all cations in maximum oxygen coordination. Boron is tetrahedrally coordinated and the tetrahedra form four- and six-membered rings that link to give a sheet, the only borate layer-structure among minerals with only BO_4 tetrahedra. The interlayer space is filled by octahedrally coordinated Al and ten-coordinated Ca. Johachidolite, forming in boron-rich skarn or pegmatite, has never been synthesized. Other ternary compounds, synthesized from corresponding glass compositions, CaAlBO_4 and $\text{CaAl}_2\text{B}_2\text{O}_7$, are unknown as minerals and have B (three-coordinate), Al (tetrahedral), and Ca (octahedral) in their lowest known oxygen coordination. Johachidolite displays the structural characteristics of a mineral with high-pressure stability.

Key-words: johachidolite, $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ system, single crystal X-ray diffraction, LA-ICP-MS, crystal structure, borate.

Introduction

Synthesis in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$

The system $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ was investigated at 23 °C to understand the drastic increase of hardening time for Portland cements used for immobilization of nuclear waste containing boric acid. The stable crystalline phases are high-boro-ettringite, $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3 \cdot 39\text{H}_2\text{O}$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \frac{1}{2}\text{B}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$, with a LDH (layered double hydroxide) structure related to the mineral hydrocalumite (Bothe & Brown, 1998).

Phase relations in the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ (CAB) were studied by Schäfer & Kuzel (1967) using solid-state reactions (900–1500 °C) for high melting B_2O_3 -poor compositions and re-crystallization (800–1000 °C) of glasses for B_2O_3 -rich compositions (Fig. 1). The authors noted very sluggish crystallization behavior for the most B_2O_3 rich mixtures, and subsequent wetting and autoclave treatment at 600 °C became necessary to obtain crystalline products. Two ternary phases were detected, CaAlBO_4 and $\text{CaAl}_2\text{B}_2\text{O}_7$. The structure of CaAlBO_4 (*Ccc2*, $\rho = 2.60$ g/cm³, $a = 8.269$, $b = 15.227$, $c = 5.733$ Å) is characterized by low coordination numbers for all cations: Ca is six-coordinate, Al shows tetrahedral coordination and boron is three-coordinated by O (Schuckmann, 1968). Two modifications were assumed

for $\text{CaAl}_2\text{B}_2\text{O}_7$: α - $\text{CaAl}_2\text{B}_2\text{O}_7$ (below 830 °C, $R\bar{3}c$, $\rho = 2.44$ g/cm³, $a = 4.810$, $c = 46.633$ Å) with a structure of ABC-stacked modules of CaO_6 octahedra, AlO_4 tetrahedra and trigonal BO_3 groups (Chang & Keszler, 1998); β - $\text{CaAl}_2\text{B}_2\text{O}_7$ is assumed to be monoclinic (Schäfer & Kuzel, 1967). Solid-state reactions up to 900 °C of oxides of CaAlB_3O_7 bulk composition and slow cooling of corresponding melts from 1100 to 700 °C yielded β - $\text{CaAl}_2\text{B}_2\text{O}_7$ and $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ (Leonyuk & Shvanskiy, 1998). Besides application as ultra-low thermal-expansion glass ceramics (MacDowel, 1990), glasses in the system $\text{CaO}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$, named “CaBAI”, find use as seals in Li batteries due to their resistance to Li attack.

Johachidolite, a gem mineral

None of the synthetic products in the ternary CAB system has been described as a mineral. On the other hand, $\text{CaAl}[\text{B}_3\text{O}_7]$, johachidolite, occurs in boron-rich pegmatites and skarns but has never been synthesized (Leonyuk & Shvanskiy, 1998; Harding *et al.*, 1999). In contrast to the low-density synthetic CAB products formed at high temperature, johachidolite ($\rho = 3.4$ g/cm³) has an extremely dense-packed structure (Moore & Araki, 1972) as one would normally expect for high-pressure conditions.

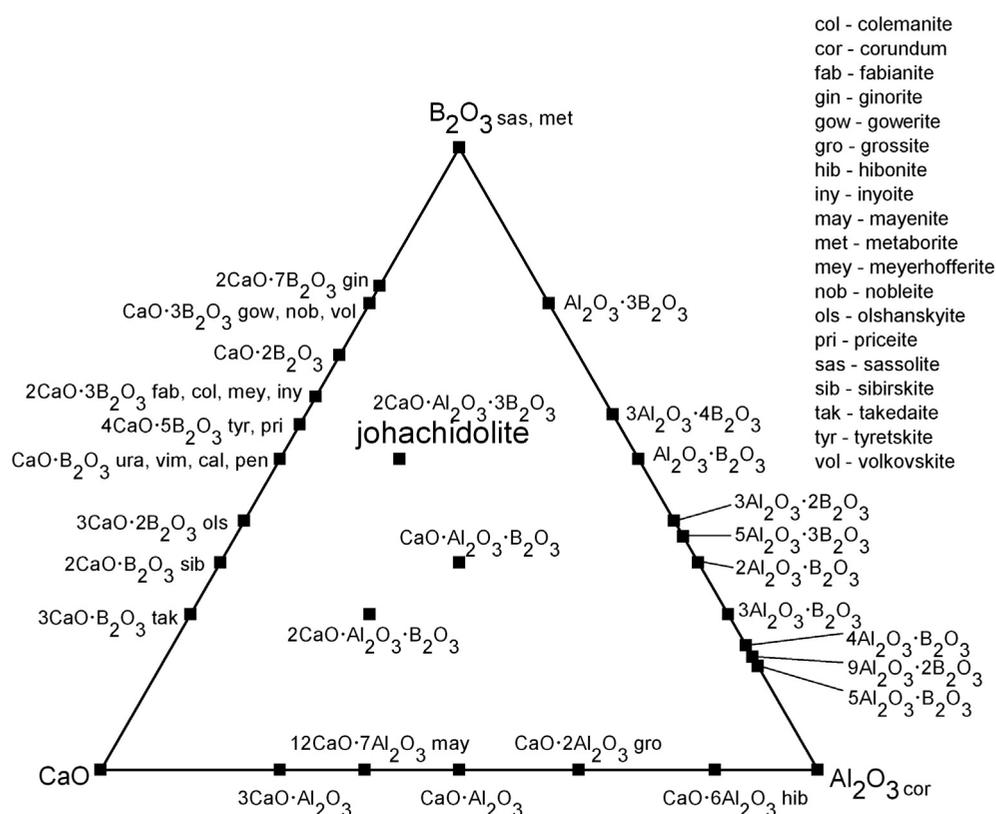


Fig. 1. Ternary plot in the system CaO–Al₂O₃–B₂O₃ after Werding & Schreyer (1996) and Schäfer & Kuzel (1967), showing johachidolite as the only natural product inside the ternary field of the diagram.

Johachidolite of gemological value (14.02 ct) was first described by Harding *et al.* (1999), suggesting that it is of natural origin. Until recently, johachidolite was extremely rare. However, in the last decade, the Pain Pyit mining province, *ca.* 5 km NE of Mogok in Myanmar (Peretti *et al.*, 2007) has produced several dozen johachidolite collector stones, many of purity and quality for faceting, although few cut stones exceed 10 ct (*e.g.*, Harding *et al.*, 1999). Johachidolite is associated with scapolite, orthoclase, hackmanite, phlogopite, muscovite, fluorapatite and thorianite-uraninite as xenomorphic masses, intergrown with other pegmatite minerals. It occasionally forms large crystals up to 5 cm long.

From complex formula to a ternary mineral

Described originally by Iwase & Saito (1942) as hydrous fluorborate H₆Na₂Ca₃Al₄F₅B₆O₂₀ from nepheline dykes cutting limestone at Johachido, North Korea, johachidolite passed several revisions. Johachidolite was named for the Japanese colonial-era name of the locality. According to Tsuda (1969) the recent name of the type locality is: Sangpal-tong, Changbaeng-myon, Kilchu-gun, North Hamgyong Province, North Korea.

Davies & Machin (1968) recalculated the original formula of Iwase & Saito (1942) to Na₄Ca₆Al₈B₁₀O₂₅(OH, F), using the same chemical analysis, but taking into account impurities due to nepheline and apatite in the studied

sample. Moore & Araki (1972) solved the structure and assigned the formula CaAl[B₃O₇] based on their structural analysis, presuming that impurities of nepheline, fluorite and villiamite, admixed in the original sample, adulterated previous results of chemical analysis. Later, Aristarain & Erd (1977) adopted the structure and chemical formula given by Moore & Araki (1972) and redefined johachidolite as a calcium aluminum borate. Peretti *et al.* (2007) have summarized occurrence, mining activities, and properties of gem-quality johachidolite from Myanmar. The revived interest in johachidolite motivated us to restudy crystal structure and chemical composition of this peculiar mineral from the Mogok gem-mining district of Myanmar. A structural reinvestigation seemed appropriate, because the only study by Moore & Araki (1972) was done with an isotropic atom-displacement model on material from the type locality in North Korea. The structural building blocks responsible for the high density will be compared with similar units in other minerals and synthetic compounds.

Experimental procedures

Electron-microprobe analysis

Chemical analysis was done on a JEOL JXA 8200 electron probe micro-analyzer (operating at 20 nA and 15 kV) equipped with five wavelength-dispersive spectrometers

Table 1. Main-element analyses of two differently coloured johachidolite samples.

elements	GRS-4583 light green LA-ICP-MS analysis*		GRS-4583 light green Electron probe microanalysis**, wt. %		GRS-5667-2 orange LA-ICP-MS analysis*, wt%	
	average of 3	RSD in %***	average of 18	RSD in %	average of 4	RSD in %
Cl	-	-	0.003	-	-	-
F	-	-	0.143	-	-	-
B ₂ O ₃	47.013	2.6	49.380	-	48.132	2.8
CaO	28.049	1.3	26.630	0.8	27.910	1.5
Al ₂ O ₃	24.328	4.4	22.940	0.8	23.645	1.3
Na ₂ O	0.004	4.7	0.004	-	0.002	5.1
MgO	0.062	4.0	0.074	20	0.066	3.2
SiO ₂	0.092	9.6	0.042	-	0.099	9.1
FeO	0.094	3.5	0.165	60	0.042	5.0
ThO ₂	0.259	4.2	0.319	3.1	0.003	2.0
Total	99.90		99.70		99.90	

* Normalized to a total of 99.90 oxide wt. %.

** B₂O₃ assumed as 49.38 wt. %, derived from Moore & Araki (1972).

*** Relative standard deviation.

Formula units normalized on 7 O; GRS-4583 (LA-ICP-MS): Ca_{1.08}Al_{1.03}B_{2.91}O₇; GRS-4583 (EMP): Ca_{1.01}Al_{0.96}B_{3.02}Si_{0.01}O₇; GRS-5667 (LA-ICP-MS): Ca_{1.07}Al_{0.99}B_{2.96}O₇.

(WDS) and an energy-dispersive detector (EDS). The standards used were synthetic Al₂O₃ for Al, wollastonite for Ca, synthetic F-phlogopite for F and synthetic thorium for Th. All measured elements were analyzed for 40 s, corrected for background and for the dead time of the detectors. All analyses were further corrected for excitation effects, inter-element absorption and fluorescence (Phi-Rho-Z procedure). Boron was not measured with this method. For the matrix correction, the B₂O₃ content was fixed to 49.38 wt. %, as derived from Moore & Araki (1972). The instrument has a detection limit of 0.1 wt. % for fluorine. Data from chemical analyses are given in Table 1.

Laser ablation ICP-MS

LA-ICP-MS analyses were done using a GeoLas Q-193 nm ArF excimer laser-ablation system (Lambda Physik, Göttingen, Germany) coupled to an Elan 6100 DRC ICP-MS mass spectrometer (Perkin Elmer, Norwalk, USA). NIST 610 glass standard was used as external calibration standard. The background signal was measured for 30 s for each analysis. The johachidolite samples were analyzed for 4–10 s using a 60 µm crater and 30 s using an 80 µm crater at 10 Hz, respectively. Data reduction was based on the protocol described by Longerich *et al.* (1996). The results are listed in Table 1 and 2.

Single crystal X-ray analysis

Three different coloured johachidolite crystals from Myanmar (collection of GRS: GemResearch Swisslab) were used to determine cell dimensions from 25 centered high-angle reflections using an Enraf Nonius CAD4 (MoK α)

diffractometer (Table 3). The cell dimensions of the three crystals are identical within 3 esd's.

An almost colorless (light-green hue) johachidolite crystal GRS-4583 was selected for collection of intensity data with an Enraf Nonius CAD4 diffractometer (graphite-monochromated MoK α radiation) at room temperature. Experimental details for data collection and structure refinements are given in Table 4. Intensity data were empirically corrected for absorption (ψ -scans). Data reduction, including background and Lorentz polarization corrections, was done using the WinGX software (Farrugia, 1999). Neutral atom scattering factors were used for the structure refinement using the SHELXTL package (Bruker, 1997). Starting parameters were taken from Moore & Araki (1972). As already indicated by the gem quality of the crystal and the sharpness of reflections, the crystal displayed a low degree of mosaicity and suffered from extinction, which was also refined. In addition, high crystal quality caused multiple-diffraction. To reduce the influence of altered reflection intensities due to multiple scattering, a half sphere of diffraction data in reciprocal space was collected. The refinement led to an *R* value of 2.5 % (Table 4). Atom coordinates, anisotropic and equivalent isotropic-displacement parameters for johachidolite are given in Table 5. Selected bond lengths and angles for johachidolite are listed in Table 6.

Results

Our structural and chemical analyses confirm the results of Moore & Araki (1972) that johachidolite has a CaAl[B₃O₇] composition with substitutions only in the range of trace amounts. Furthermore, the crystal structure is unusual for several reasons: (1) the extremely dense packing with high coordination number of all cations; (2) the fact that it is the only known layer structure among minerals built

Table 2. Trace-element analyses of two differently coloured johachidolite samples.

element	sample			
	GRS-4583 light green		GRS-5667-2 orange	
	ppm	RSD in %*	ppm	RSD in %
Li	0.27	27	n.d.**	-
Be	37.7	9.5	139	8
Na	26.2	4.7	n.d.	-
P	n.d.	-	n.d.	-
K	14.4	19	n.d.	-
Sc	n.d.	-	n.d.	-
Ti	15	23	2.48	17
V	43	3.3	7.29	3
Cr	14	18	n.d.	-
Mn	1.53	9.3	n.d.	-
Co	0.16	113	n.d.	-
Ni	0.55	65	n.d.	-
Cu	1.51	35	< 0.1	-
Zn	3	5.4	n.d.	-
Ga	n.d.	-	78.9	1.1
Rb	0.11	28	n.d.	-
Sr	177	5.6	73	0.8
Y	98	5.7	3.62	4.8
Zr	0.2	33	0	0
Sb	n.d.	-	0.13	20
Cs	0.2	83	n.d.	-
Ba	0.28	60	n.d.	-
Hf	0.01	56	< 0.7	-
Pb	9.13	2.9	1.58	13
Bi	0.33	33	0.16	28
U	2.9	4	2.21	4.2
La	252	6.3	5.77	13
Ce	428	6	11	11
Pr	47	5.6	1.3	11
Nd	171	2.5	4.96	14
Sm	36	3.1	1.48	11
Eu	6.94	7.2	0.09	8.7
Gd	38	3.3	1.22	6
Tb	6.53	5.9	0.21	3.7
Dy	28	3.7	0.94	5.6
Ho	4.06	7.4	0.13	10
Er	5.88	4.4	0.21	12
Tm	0.45	5.6	0.02	37
Yb	1.43	14	0.09	14
Lu	0.09	10	< 0.01	-

* Relative standard deviation.

** Not detected.

exclusively by [BO₄] tetrahedra forming six- and four-membered rings (Hawthorne *et al.*, 1996; Grice *et al.*, 1999): connectivity (6□) = (4□); (3) the strongly distorted coordination polyhedra (Table 6 and 7).

Johachidolite is constructed of extremely compact walls parallel to (010). The peculiar building units of these walls are dense infinite columns of [AlB₄O₁₂]⁹⁻ composition parallel to the *c* axis (Fig. 2). The columns are formed by four-membered rings of BO₄ tetrahedra linked to the trian-

Table 3. Cell dimensions of differently coloured johachidolite crystals.

Sample No.	<i>a</i> Å	<i>b</i> Å	<i>c</i> Å	<i>V</i> Å ³
GRS-4583 light green	7.967(2)	11.723(3)	4.3718(5)	408.32(14)
GRS-5648 yellow	7.966(1)	11.730(2)	4.3722(5)	408.6(1)
GRS-5667 orange	7.969(2)	11.728(3)	4.3711(6)	408.5(1)

Table 4. Parameters for X-ray data collection and crystal structure refinement of crystal GRS-4583.

Diffractometer	CAD-4
X-ray radiation	MoK α (0.71069 Å)
X-ray power	50 kV, 40 mA
Temperature	293 K
Crystal size (mm)	0.125 × 0.200 × 0.375
Space group	<i>Cmma</i> (Nr. 67)
Cell dimensions (Å)	7.967 11.723 4.3718
Cell volume (Å ³)	408.3
<i>Z</i>	4
Collection mode	ω -scans
Reflections collected	2762
Max. 2 θ	80.19
Index range	-14 ≤ <i>h</i> ≤ 14, -21 ≤ <i>k</i> ≤ 21, 0 ≤ <i>l</i> ≤ 7
Unique reflections	691
Reflections > 2 σ (<i>I</i>)	655
<i>R</i> _{int}	0.0419
<i>R</i> _{σ}	0.0262
Number of least squares parameters	38
Goof	1.193
<i>R</i> 1, <i>I</i> > 2 σ (<i>I</i>)	0.0251
<i>R</i> 1, all data	0.0263
w <i>R</i> 2 (on <i>F</i> ²)	0.0626
$\Delta\rho_{\min}$ (-e Å ⁻³)	-1.18; 0.61 Å from Ca1
$\Delta\rho_{\max}$ (e Å ⁻³)	0.66; 1.37 Å from Al2

gular face of an AlO₆ octahedron such that the connection is made by three tetrahedron corners and one tetrahedron edge (Fig. 3). Perpendicular to the walls, [BO₄] tetrahedra link to an adjacent wall, forming a layer structure where Al may be interpreted as an interlayer cation. Between the compact (010) walls, six-membered-ring channels are generated which are occupied by ten-coordinated Ca at the same level along *c* as interlayer Al.

All oxygen atoms in johachidolite are four-coordinated. However, the peculiar polyhedron distortion in this mineral is due to large differences in the sums of the incident bond strengths (valence/coordination number). O2 bonds twice to Ca (2 × 2/10 v.u. = valence units), once to B (3/4 v.u.), and once to Al (3/6 v.u.), adding up to 1.65 v.u. (Table 7). In contrast, O3 (Table 7) receives 2.20 v.u.. In order to have balanced bond valence-sums (close to 2.0 v.u.) at O2 and O3 (Table 7), bonds to O2 will be strengthened (shortened) whereas bonds to O3 will be weakened (lengthened). This leads to highly non-uniform bonds around tetrahedral B2 with B2–O2 of 1.395 and B2–O3 of 1.549 Å and octahedral Al with Al–O2 of 1.822 and Al–O3 of 1.954 Å (Table 6).

Table 5. Atom coordinates, anisotropic and equivalent isotropic displacement parameters for johachidolite GRS-4583.

	Ca	Al	B1	B2	O1	O2	O3
<i>x</i>	1/4	0	1/4	0	0	0	0.14664(5)
<i>y</i>	1/4	0	0	0.13658(6)	1/4	0.13131(5)	0.07316(3)
<i>z</i>	0	0	1/2	0.45836(19)	0.32945(18)	-0.22291(12)	0.29975(9)
<i>U</i> ₁₁	0.00840(12)	0.00491(16)	0.0041(4)	0.0054(3)	0.0102(3)	0.0073(2)	0.00406(15)
<i>U</i> ₂₂	0.00811(12)	0.00432(16)	0.0047(4)	0.0046(3)	0.0032(2)	0.0053(2)	0.00546(16)
<i>U</i> ₃₃	0.00752(13)	0.00333(17)	0.0042(4)	0.0043(2)	0.0045(3)	0.00346(19)	0.00460(16)
<i>U</i> ₂₃	0	0.00016(8)	0	0.00001(19)	0	0.00031(13)	0.00028(9)
<i>U</i> ₁₃	0.00273(5)	0	0	0	0	0	-0.00018(9)
<i>U</i> ₁₂	0.000	0	0	0	0	0	0.00092(9)
<i>U</i> _{equ}	0.00801(9)	0.00419(10)	0.00436(18)	0.00479(13)	0.00599(14)	0.00538(12)	0.00471(10)

Table 6. Bond lengths (Å) and angles (°) for johachidolite GRS-4583.

Ca	Distance	Angles						
O1_8	2.4580(5)							
O1	2.4580(5)	180.00						
O3_14	2.5872(4)	56.31(1)	123.69(1)					
O3_16	2.5872(4)	123.69(1)	56.31(1)	180.00(2)				
O3_8	2.5872(4)	56.31(1)	123.69(1)	106.51(2)	73.49(2)			
O3	2.5872(4)	123.69(1)	56.31(1)	73.49(2)	106.51(2)	180.00		
O2	2.6178(3)	113.48(2)	66.52(2)	68.14(1)	111.86(1)	118.65(1)	61.35(1)	
O2_8	2.6178(3)	66.52(2)	113.48(2)	111.86(1)	68.14(1)	61.35(1)	118.65(1)	
O2_10	2.6178(3)	66.52(2)	113.48(2)	61.35(1)	118.65(1)	111.86(1)	68.14(1)	
O2_5	2.6178(3)	113.48(2)	66.52(2)	118.65(1)	61.35(1)	68.14(1)	111.86(1)	
Mean	2.5736	O1_8	O1	O3_14	O3_16	O3_8	O3	O2
Al	Distance	Angles						
O2	1.8219(5)							
O2_9	1.8219(5)	180.00(2)						
O3	1.9539(4)	89.31(2)	90.69(2)					
O3_9	1.9539(4)	90.69(2)	89.31(2)	180.00(2)				
O3_11	1.9539(4)	90.69(2)	89.31(2)	106.56(2)	73.443(2)			
O3_13	1.9539(4)	89.31(2)	90.69(2)	73.44(2)	106.56(2)	180.00(2)		
Mean	1.9099	O2	O2_9	O3	O3_9	O3_11		
B1	Distance	Angles						
O3_15	1.4765(4)							
O3_4	1.4765(4)	112.20(3)						
O3_12	1.4765(4)	107.27(3)	108.98(3)					
O3	1.4765(4)	108.98(3)	107.27(3)	112.20(3)				
Mean	1.4765	O3_15	O3_4	O3_12				
B2	Distance	Angles						
O2_2	1.3949(10)							
O1	1.4441(8)	115.51(7)						
O3_13	1.5487(6)	115.22(4)	105.50(4)					
O3	1.5487(6)	115.22(4)	105.50(4)	97.94(5)				
Mean	1.4841	O2_2	O1	O3_13				

Symmetry codes: \$2 x, y, z + 1; \$4 $-x + 1/2, -y, z$; \$5 $-x, -y + 1/2, z$; \$8 $-x + 1/2, -y + 1/2, -z$; \$9 $-x, -y, -z$; \$10 $x + 1/2, y, -z$; \$11 $x, -y, -z$; \$12 $x, -y, -z + 1$; \$13 x, y, z ; \$14 $-x + 1/2, y, -z$; \$15 $-x + 1/2, y, -z + 1$; \$16 $x, -y + 1/2, z$

Table 7. Bond valences for johachidolite GRS-4583 using the parameters of Brown & Altermatt (1985) and Pauling bond-strength sums (P) given by Moore & Araki (1972).

	O1	O2	O3	Total
Ca	0.265 ($\times 2 \downarrow \rightarrow$)	0.172 ($\times 4 \rightarrow$) ($\times 2 \downarrow$)	0.187 ($\times 4 \rightarrow$) ($\times 1 \downarrow$)	1.966
Al		0.579 ($\times 2 \rightarrow$) ($\times 1 \downarrow$)	0.406 ($\times 4 \rightarrow$) ($\times 1 \downarrow$)	2.782
B1			0.752 ($\times 4 \rightarrow$) ($\times 1 \downarrow$)	3.008
B2	0.821 ($\times 2 \downarrow$)	0.937	0.619 ($\times 2 \rightarrow$) ($\times 1 \downarrow$)	2.996
Total v.u.	2.172	1.86	1.964	
Total v.u. (P)	1.9	1.65	2.20	

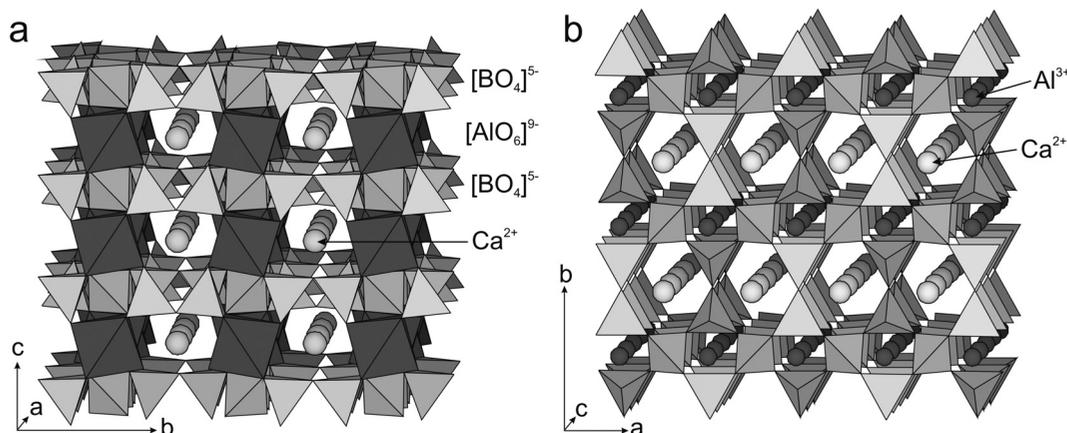


Fig. 2. Polyhedral arrangement in the structure of johachidolite: a) layers of BO_4 tetrahedra, perpendicular to the c axis, linked by octahedral Al and ten-coordinated Ca (spheres); b) the $\langle 6\Box \rangle = \langle 4\Box \rangle$ connectivity of the boron tetrahedral layer with Al (dark spheres) in the four-membered rings and Ca (light spheres) in the six-membered rings.

Discussion

In general, B occurs in two coordinations: (1) the three-coordinated anion $[\text{BO}_3]^{3-}$, and (2) as four-coordinated anion $[\text{BO}_4]^{5-}$. The structure of many borate minerals is characterized by a combination of linked borate tetrahedra and triangles contributing to very complex crystal chemistry (Hawthorne *et al.*, 1996; Grice *et al.*, 1999). In johachidolite $\text{CaAl}[\text{B}_3\text{O}_7]$, borate tetrahedra are only linked in two dimensions, forming a layer structure of tetrahedra. Johachidolite is the only mineral with an uninterrupted, corrugated sheet formed by only BO_4 tetrahedra (Fig. 2a, b). The single sheets are strongly bonded to each other by the interlayer cations Al and Ca. In particular, AlO_6 octahedra sharing edges with BO_4 (Fig. 3) are responsible for strong bonds perpendicular to the borate sheet, and thus the mineral has no pronounced cleavage, as one would expect for a layer structure. The arrangement in the structure of johachidolite is very dense, which accounts for its high mean refractive index of 1.720. In the structure of johachidolite all cations occur in their maximum coordination numbers: [4]-coordinated boron, [6]-coordinated aluminum, and [10]-coordinated calcium. In contrast, the other two phases known in the ternary CAB system, CaAlBO_4 (Schuckmann, 1968) and $\alpha\text{-CaAl}_2\text{B}_2\text{O}_7$ (Chang & Keszler, 1998) have all cations in their lowest coordination numbers: [3] boron, [4] aluminum, and [6]-coordinated calcium.

Crystallization of glass melts to produce CaAlB_3O_7 probably failed because such low-density glasses ($\rho \approx$

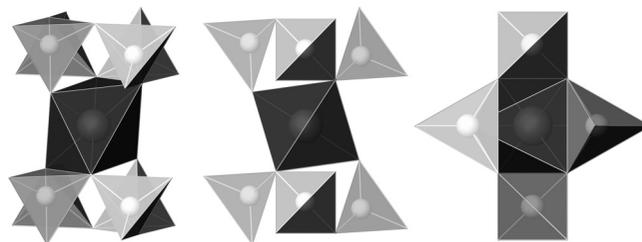


Fig. 3. Selected projections of the highly compact $[\text{AlB}_4\text{O}_{12}]^{9-}$ columns in johachidolite, with a distorted AlO_6 octahedron sharing apices and edges with four-membered rings of BO_4 tetrahedra. Left and middle: columns projected sidewise; right: column projected parallel to their extension.

2.75 g/cm^3) do not provide appropriate nuclei for a high density compound like johachidolite ($\rho = 3.4 \text{ g/cm}^3$). The structure of glass (Bunker *et al.*, 1991a, b) of composition close to that of johachidolite has *ca.* 85 % BO_3 and 15 % BO_4 ; Al is mainly in tetrahedral coordination (*ca.* 55 %), with minor five-coordinated (*ca.* 21 %) and octahedral Al (*ca.* 17 %).

Solid-state reactions of oxides below 1000°C seem too sluggish to investigate phase relations in the boron-rich part of the system $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ (Schäfer & Kuzel, 1967; Leonyuk & Shvanskiy, 1998). Also, slow cooling of melts and flux growth (Leonyuk & Shvanskiy, 1998) were not successful in synthesizing johachidolite. All unsuccessful attempts to synthesize johachidolite under ambient pres-

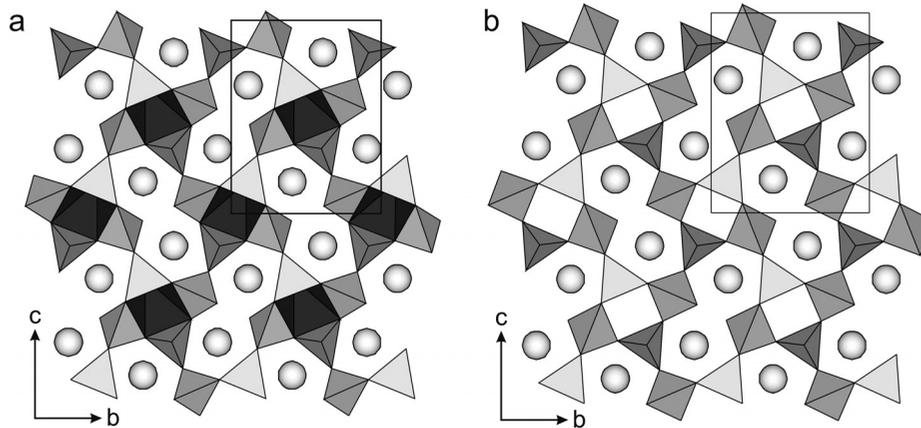


Fig. 4. Gadolinite structure type with $\langle 8\Box \rangle = \langle 4\Box \rangle$ connectivity: a) tetrahedral BO_4 sheet in synthetic $\text{CuLn}_2\text{B}_4\text{O}_{10}$ and $\text{NiHo}_2\text{B}_4\text{O}_{10}$, Cu or Ni are octahedrally coordinated and Ln occupies the eight-membered ring channels; b) tetrahedral sheet in bakerite, datolite and synthetic $\beta\text{-HfB}_2\text{O}_5$ and $\beta\text{-ZrB}_2\text{O}_5$ with vacant octahedral sites and Ca, Hf or Zr in the eight-membered rings.

sure conditions and the very dense structure of this mineral suggest a high-pressure stability field.

Topologically equivalent columns to those forming the compact walls in johachidolite are known in the structure of the rare skarn mineral borcarite $\text{Ca}_4\text{Mg}[\text{B}_4\text{O}_6(\text{OH})_6](\text{CO}_3)_2$ (Yamnova *et al.*, 1976; Burns & Hawthorne, 1995). However, in borcarite these columns are isolated, are hydroxylated on its surface, have composition $[\text{MgB}_4\text{O}_6(\text{OH})_6]^{4-}$, and occur as a molecule-like moiety. The similar periodicity parallel to *c* in borcarite (4.445 Å) and johachidolite (4.374 Å) is due to those columns. Another important difference between the two types of columns is the valence of the octahedrally coordinated cation. Trivalent cations (Al) in johachidolite seem more unfavorable than divalent cations (Mg) in borcarite due to edge-sharing between the octahedron and the BO_4 tetrahedron, leading to strong repulsion of the adjacent cations. The octahedron has two opposite edges common with a small BO_4 tetrahedron. Thus the rectangular cross-section of the octahedron is strongly distorted, with common edges as the shortest dimension and the vector perpendicular to those edges as the longest dimension.

Recently, the new mineral numanoite $\text{Ca}_4\text{Cu}[\text{B}_4\text{O}_6(\text{OH})_6](\text{CO}_3)_2$, isotypic with borcarite, was described (Ohnishi *et al.*, 2007) with mainly Cu^{2+} (minor Mg and Zn) occupying the distorted octahedron. Thus Jahn-Teller distorted octahedral Cu^{2+} seems appropriate for this type of octahedron.

Preference of octahedral Cu^{2+} sandwiched between two four-membered rings of BO_4 tetrahedra is also supported by the series of synthetic $\text{CuLn}_2\text{B}_4\text{O}_{10}$ (*Ln* = Ho, Er, Tm, Lu) phases (Wiesch & Bluhm, 1998; Schaefer & Bluhm, 1995a and b), which belong to the gadolinite structure type (Fig. 4a). In addition, $\text{NiHo}_2\text{B}_4\text{O}_{10}$ (Wiesch & Bluhm, 1995) is also a member of the same group. Gadolinite-(*Ln*) [*Ln*: Y, Ce] does not contain boron but tetrahedral sites linked to four-membered rings are occupied half by Be and half by Si with octahedral (Fe^{2+} ,

Mg). Homilite, $\text{Ca}_2\text{Fe}[\text{B}_2\text{Si}_2]\text{O}_{10}$, also a member of the gadolinite group, has half of the tetrahedra occupied by boron. In the $\text{CuLn}_2\text{B}_4\text{O}_{10}$ compounds cited above, four-membered rings of boron tetrahedra are connected to a layer of tetrahedra with connectivity $\langle 8\Box \rangle = \langle 4\Box \rangle$. Very recently $\beta\text{-HfB}_2\text{O}_5$ (and $\beta\text{-ZrB}_2\text{O}_5$) was synthesized (Knyrim & Huppertz, 2007) at 7.5 GPa and 1100° with a structure related to $\text{CuLn}_2\text{B}_4\text{O}_{10}$ (the same borate layer) but with vacant octahedral sites. $\beta\text{-HfB}_2\text{O}_5$ is similar to datolite and bakerite, $\text{Ca}_4\text{B}_4\text{Si}_4\text{O}_{16}(\text{OH})_4$ and $\text{Ca}_4\text{B}_5\text{Si}_3\text{O}_{15}(\text{OH})_5$ (Perchiazzi *et al.*, 2004), respectively, because the latter two mineral structures are also characterized by empty octahedra and a layer of tetrahedra with connectivity $\langle 8\Box \rangle = \langle 4\Box \rangle$ (Fig. 4b).

A mixed borate-silicate mineral with layer structure different to the gadolinite group ($\langle 8\Box \rangle = \langle 4\Box \rangle$) and johachidolite ($\langle 6\Box \rangle = \langle 4\Box \rangle$) is okayamalite $\text{Ca}_2[\text{B}_2\text{SiO}_7]$, a member of the melilite group with $\langle 5\Box \rangle = \langle 5\Box \rangle$ connectivity of rings formed by tetrahedra (Fig. 5a, b). The structure of okayamalite (Giuli *et al.*, 2000) shows an ordered arrangement of Si and B.

A similar tetrahedral layer built up from 4- and 6-membered rings has been described by Huminicki & Hawthorne (2002) for aminoffite, $\text{Ca}_3\text{Be}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$, where tetrahedrally coordinated Si and Be link into a sheet of tetrahedra. However, the connectivity between the B and Si tetrahedra causes a different layer topology, compared to the one observed for johachidolite.

If we summarize the composition of the infinite columns built by four-membered rings of BO_4 tetrahedra linked to the triangular face of an octahedron, the following substitutions are observed. Ni, Cu^{2+} , Fe^{2+} , Mg and vacancies occur at the octahedral site; johachidolite is the only structure with a trivalent ion (Al) occupying the octahedron (Fig. 6). The tetrahedral sites may partly be substituted by Si and Be. Charge balance may be achieved by replacement of Ca by Ln^{3+} or Zr^{4+} , Hf^{4+} . Deficit of cations, *e.g.*, due to octahedral vacancies, may be balanced by OH^- or F^- replacing O^{2-} . Without knowing about structures with similar columns, Moore & Araki (1972) suggested, based on

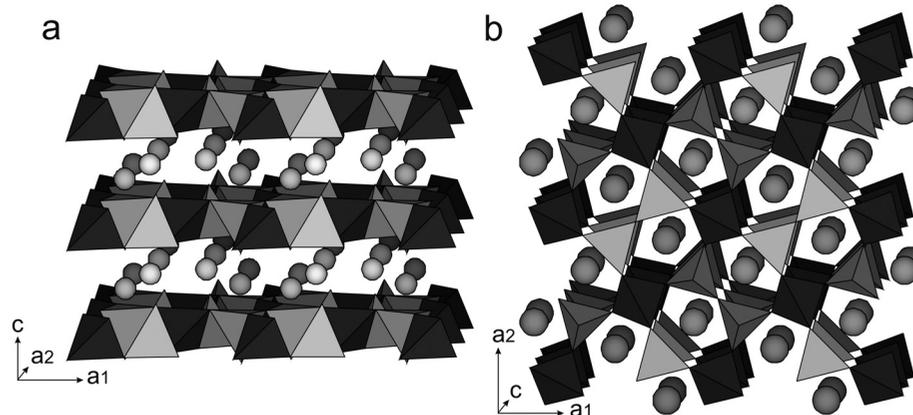


Fig. 5. Polyhedral model of the structure of okayamalite (melilite structure-type): a) layers of SiO_4 and BO_4 tetrahedra interconnected by Ca atoms (spheres); b) pairs of BO_4 tetrahedra (light) tied to a SiO_4 tetrahedron (dark), giving the specific $\langle 5\Box \rangle = \langle 5\Box \rangle$ connectivity with Ca atoms above and below the five-membered rings.

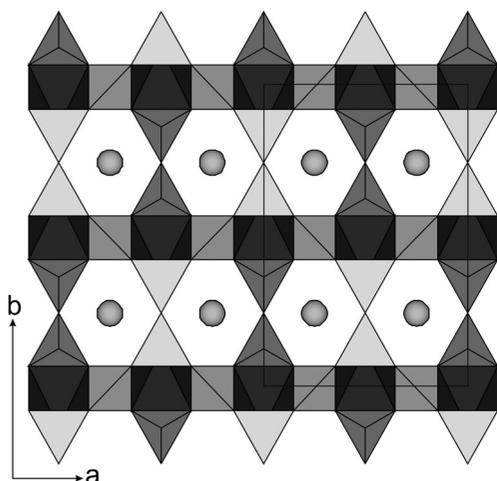


Fig. 6. The unique $\langle 6\Box \rangle = \langle 4\Box \rangle$ connectivity in johachidolite is characterized by columns of $[\text{AlB}_4\text{O}_{12}]^{9-}$ composition connected to produce layers with six-membered rings of BO_4 tetrahedra. Ten-fold coordinated Ca (spheres) occupies the interlayer space.

crystal-chemical principles, that $\text{YAl}[\text{BeB}_2\text{O}_7]$ would be a possible composition for a johachidolite-like structure. The structure of johachidolite is unique, without any other example in which the infinite characteristic columns are condensed to massive walls.

Surprisingly, the orange johachidolite GRS-5667-2 contained lower trace-element concentrations than the light-green one (GRS-4583; Table 2). The latter crystal displayed high concentrations of thorium and lanthanide. Analyses (Tables 1 and 2) do not offer an unambiguous clue as to how charge balance is achieved if Th^{4+} and Ln^{3+} substitute for Ca. The structural examples discussed above may suggest octahedral vacancies to balance excess charge at the Ca site. Chondrite-normalized (Peretti *et al.*, 2007), light Ln^{3+} with a slightly larger ionic radius than heavy Ln^{3+} are enriched in johachidolite, which fits the ten-coordination for Ca. In addition, a significant negative europium anomaly is obvious (Peretti *et al.*, 2007). FTIR

spectra of several johachidolite samples (Peretti *et al.*, 2007) showed that significant hydroxylation does not occur. Thus analyses of both samples (Table 1 and 2) indicate that johachidolite is a ternary compound in the CAB system.

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