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Natural Al-rich borosilicates – petrology, mineralogy, and crystal chemistry

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Abstract

Natural Al-rich borosilicates represent a specific group of minerals; they occur in diverse geological environments, in many cases they are associated with industrial minerals and they represent petrologically important minerals that record the evolution of the geological environment.

In my studies of natural Al-rich borosilicates, I focused on mineral assemblages, crystal chemistry, and structures of tourmaline-supergroup minerals (oxy-tourmalines), boron-rich mullite-type structure minerals (boralsilite, werdingite, vránaite, grandidierite, ominelite), and dumortierite-supergroup of minerals (dumortierite, As-rich holtite, As-rich dumortierite, Sb-rich dumortierite). Among other results, two new minerals of the tourmaline supergroup (oxy-schorl, lucchesiite), and one new mineral with mullite-type structure (vránaite) were defined.

Contents

List of papers

Part Tourmaline-supergroup minerals:

Paper 1) **Cempírek, J.,** Novák, M., Ertl, A., Hughes, J.M., Rossman, G.R., Dyar, M.D. (2006): Fe-bearing olenite with tetrahedrally coordinated Al from an abyssal pegmatite at Kutná Hora, Czech Republic: structure, crystal chemistry, optical and XANES spectra. *The Canadian Mineralogist* **44**, 1, 23–30.

Paper 2) Bačík, P., **Cempírek, J.,** Uher, P., Novák, M., Ozdín, D., Filip, J., Škoda, R. (2013): Oxy-schorl, $Na(Fe_2^{2+}Al)Al_6Si_6O_{18}(BO_3)_3(OH)_3O$, a new mineral from Zlatá Idka, Slovak Republic and Přibyslavice, Czech Republic. *American Mineralogist* **98**, 485–492.

Paper 3) Bačík, P., Uher, P., **Cempírek, J.,** Vaculovič, T. (2012): Magnesian tourmalines from plagioclase–muscovite–scapolite metaevaporite layers in dolomite marble near Prosetín (Olešnice Unit, Moravicum, Czech Republic). *Journal of Geosciences* **57**, 143–153.

Paper 4) **Cempírek, J.,** Houzar, S., Novák, M., Groat, L.A., Selway, J.B., Šrein, V. (2013): Crystal structure and compositional evolution of vanadium-rich oxy-dravite from graphite quartzite at Bítovánky, Czech Republic. *Journal of Geosciences* **58**, 149–162.

Paper 5) Gadas, P., Novák, M., **Cempírek, J.,** Filip, J., Vašinová-Galiová, M., Groat, L.A., Všianský, D. (2014): Mineral assemblages, compositional variation, and crystal structure of feruvitic tourmaline from a contaminated anatectic pegmatite at Mirošov near Strážek, Moldanubian Zone, Czech Republic. *The Canadian Mineralogist* **52**, 285–301.

Part Borosilicates with mullite-type structure:

Paper 6) **Cempírek, J.,** Novák, M., Dolníček, Z., Kotková, J., Škoda, R. (2010): Crystal chemistry and origin of grandidierite, ominelite, boralsilite and werdingite from the Bory Granulite Massif, Czech Republic. *American Mineralogist* **95**, 1533–1547.

Paper 7) Novák, M., **Cempírek, J.,** Gadas, P., Škoda, R., Vašinová-Galiová, M., Pezzotta, F., Groat, L.A. (2015): Boralsilite and Li,Be-bearing "boron mullite" $Al_8B_2Si_2O_{19}$, breakdown products of spodumene from the Manjaka pegmatite, Sahatany Valley, Madagascar. *The Canadian Mineralogist* **53**, 357–374.

Paper 8) **Cempírek, J.,** Grew, E.S, Kampf, A.R., Ma, C., Novák, M., Gadas, P., Škoda, R., Vašinová-Galiová, M., Pezzotta, F., Groat, L.A., Krivovichev, S.V. (2016) Vránaite, ideally $Al_{16}B_4Si_4O_{38}$, a new mineral related to boralsilite, $Al_{16}B_6Si_2O_{37}$, from the Manjaka pegmatite, Sahatany Valley, Madagascar. *American Mineralogist* **101**, 2108–2117.

Part Dumortierite-supergroup minerals:

Paper 9) Galliski, M.Á., Márquez-Zavalía, M.F., Lira, R., **Cempírek, J.,** Škoda, R. (2012): Mineralogy and origin of the dumortierite-bearing pegmatites of Virorco, San Luis, Argentina. *The Canadian Mineralogist* **50**, 873–894.

1. Introduction

Natural Al-rich borosilicates represent a specific group of minerals; they occur in diverse geological environments, and they represent petrologically important minerals that witness and record evolution of the geological environment. For example, boralsilite, werdingite, and vránaite typically indicate low water activity in melts (Grew et al. 1998a,b, Grew 2002, Cempírek et al. 2010, 2016, Novák et al. 2015 – [Papers 6–8]). Tourmaline-supergroup mineral occurrences can mark zones of fluid transport, and since they generally are highly resistant to weathering and alteration during erosion and diagenesis, zoning of their crystals may witness several events in evolution of the system (e.g., Dutrow et al. 1999, London 1999, London et al. 2002, Henry and Dutrow 2002, van Hinsberg et al. 2006, Kawakami 2007, Čopjaková et al. 2009, Trumbull et al. 2011, Dutrow and Henry 2011, van Hinsberg and Schumacher 2011, van Hinsberg et al. 2011, Marschall and Jiang 2011; also Bačík et al. 2012, 2013, Cempírek et al. 2006, 2013, Gadas et al. 2015 – [Papers 1-5]). In many cases they are associated with industrial minerals (e.g., dumortierite in epithermal gold deposits, tourmaline in volcanogenic massive sulphide deposits, both greisen and pegmatite deposits of Li, Sn, Ta, Nb, W, etc.; Slack et al. 1993, Slack 2002, Slack and Trumbull 2011). In some cases, they have important applications in the gemstone industry (particularly tourmaline, dumortierite, and grandidierite) and applications in technology (e.g., tourmaline piezoelectric pressure gauges).

The most common naturally occurring borosilicate minerals are members of the tourmaline-supergroup (Grew 2002), followed by dumortierite-supergroup minerals (mostly dumortierite as Ta-, Nb-, and As-members of the supergroup are very rare; e.g., Pieczka et al. 2013a,b); borosilicates with mullite-type structure represent a relatively new group of minerals that experiences a rapid development due to recent advances in analytical techniques (e.g., Grew et al. 2008, Buick et al. 2008, Cempírek et al. 2016 – [Paper 8]).

During our studies of borosilicates, we encountered complex mineral assemblages of several Al-rich borosilicates; the minerals of particular interest whose crystal chemistry, and structures were studied include tourmaline-supergroup minerals, borosilicates with mullite-type structure (boralsilite, werdingite, vránaite, grandidierite, ominelite), and dumortierite-supergroup of minerals (dumortierite, As-rich holtite, As-rich dumortierite, Sb-rich dumortierite). Among the results, two new minerals of the tourmaline supergroup (oxy-schorl, lucchesiite), and one new mineral with mullite-type structure (vránaite) were defined.

2. Tourmaline-supergroup minerals

Tourmaline is an acentric rhombohedral (space group *R*3*m*) borosilicate mineral (Fig. 2.1) with the general formula $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$ where individual sites are typically occupied by following elements:

$X = \mathbf{R}^{+} > \mathbf{R}^{2+} > \square$ (vacancy)	$\mathbf{R}^{+}$: Na>>K; $\mathbf{R}^{2+}$: Ca
$Y = \mathbf{R}^{2+} > \mathbf{R}^{3+} > \mathbf{R}^{+} > \mathbf{R}^{4+}$	$\mathbf{R}^{2+}$: Fe~Mg>Mn>>>Zn, Ni, Co, Cu
	$\mathbf{R}^{3+}$: Al>>Fe>Cr>V; $\mathbf{R}^{+}$: Li; $\mathbf{R}^{4+}$: Ti
$Z = \mathbf{R}^{3+} >> \mathbf{R}^{2+}$	$\mathbf{R}^{3+}$: Al>>Fe>Cr>V; $\mathbf{R}^{2+}$: Mg
$T = \mathbf{R}^{4+} >> \mathbf{R}^{3+}$	$\mathbf{R}^{4+}$: Si; $\mathbf{R}^{3+}$: Al>B
$B = \mathbf{R}^{3+}$	$\mathbf{R}^{3+}$: B
$V = \mathbf{A}^{-} >> \mathbf{A}^{2-}$	$\mathbf{A}^{-}$: OH; $\mathbf{A}^{2-}$: O
$W = \mathbf{A}^{-} \sim \mathbf{A}^{2-}$	$\mathbf{A}^{-}$: OH~F; $\mathbf{A}^{2-}$: O

Additional minor to trace elements in natural and synthetic tourmaline include: Ag, Pb, Sr, Ba, Bi, Sb, Cl (Hawthorne and Henry 1999, Henry et al. 2011).

Classification and nomenclature of the tourmaline supergroup was recently published by Henry et al. (2011). Since the publication, 17 new tourmaline end members were added to the 15 previously known species (Table 2.1). The most prominent increase of species number was in the alkali-group (Table 2.1), where 15 new tourmaline species were described; four new minerals are fluorine-analogues of existing end members, another four are Cr- and V-derivatives from dravite coming from a single locality (Pereval quarry, Sludyanka, Russia). is Most remarkable of all the new species is probably the recent discovery of the first K-dominant end-member, maruyamaite, from ultra-high pressure rocks in the Kokchetav massif, northern Kazakhstan (Lussier et al. 2016); until now, the only tourmaline with significantly elevated potassium contents (up to 0.6 *apfu*; *apfu* = atoms per formula unit) was povondraite from its type locality (e.g., Žáček et al. 2000).

Out of the 17 recently described new species, 11 belong among oxy-tourmalines where the structural W-site is fully occupied by oxygen (Fig. 2.1, Table 2.1). During our recent studies, we focused on the group of oxy-tourmalines because they are rather poorly understood with regard to the analytically challenging way of their characterization (valence of Fe, presence of Li, occupational disorder in the structure); among other results, I structurally characterized two new oxy-tourmalines and co-authored their descriptions (Bačík et al. 2013 – [Paper 2], Bosi et al. 2016).

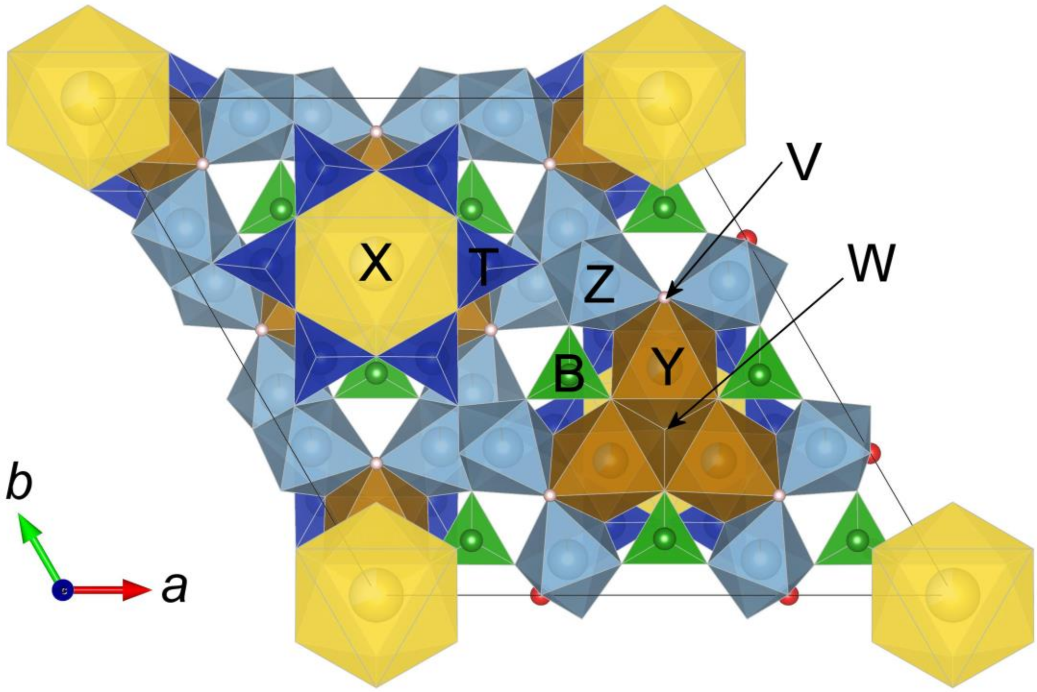

Figure 2.1: Crystal structure and structural sites of tourmaline-supergroup minerals. After Cempírek et al. (2013 – [Paper 4]).

Table 2.1: Current end-members in the tourmaline supergroup (site occupancies in ordered form)

Name / Site	X	Y	Z	T	B	V	W	Source
Alkali group								
Alkali-subgroup 1								
Dravite	Na	Mg_3	Al_6	Si_6	B_3	$(OH)_3$	OH	*
Schorl	Na	Fe^{2+}_3	Al_6	Si_6	B_3	$(OH)_3$	OH	*
Tsilaisite	Na	Mn^{2+}_3	Al_6	Si_6	B_3	$(OH)_3$	OH	Bosi et al. (2012b)
Chromium-dravite	Na	Mg_3	Cr_6	Si_6	B_3	$(OH)_3$	OH	** (renamed from chromdravite)*
Fluor-dravite	Na	Mg_3	Al_6	Si_6	B_3	$(OH)_3$	F	Clark et al. (2011)
Fluor-schorl	Na	Fe^{2+}_3	Al_6	Si_6	B_3	$(OH)_3$	F	Ertl et al. (2016b)
Fluor-tsilaisite	Na	Mn^{2+}_3	Al_6	Si_6	B_3	$(OH)_3$	F	Bosi et al. (2015)
Alkali-subgroup 2								
Elbaite	Na	$Li_{1.5},Al_{1.5}$	Al_6	Si_6	B_3	$(OH)_3$	OH	*
Fluor-elbaite	Na	$Li_{1.5},Al_{1.5}$	Al_6	Si_6	B_3	$(OH)_3$	F	Bosi et al. (2013)
Alkali-subgroup 3								
Povondraite	Na	Fe^{3+}_3	$Fe^{3+}_4Mg_2$	Si_6	B_3	$(OH)_3$	O	*
Bosiite	Na	Fe^{3+}_3	Al_4Mg_2	Si_6	B_3	$(OH)_3$	O	Ertl et al. (2016a)
Oxy-dravite	Na	Al_3	Al_4Mg_2	Si_6	B_3	$(OH)_3$	O	Bosi and Skogby (2013)
Oxy-schorl	Na	Al_3	Al_4Fe_2	Si_6	B_3	$(OH)_3$	O	Bačík et al. (2013)
Maruyamaite	K	Al_3	Al_4Mg_2	Si_6	B_3	$(OH)_3$	O	Lussier et al. (2016)
Chromo-alumino-povondraite	Na	Cr_3	Al_4Mg_2	Si_6	B_3	$(OH)_3$	O	Reznitskii et al. (2014)
Oxy-chromium-dravite	Na	Cr_3	Cr_4Mg_2	Si_6	B_3	$(OH)_3$	O	Bosi et al. (2012a)
Oxy-vanadium-dravite	Na	V_3	V_4Mg_2	Si_6	B_3	$(OH)_3$	O	**(renamed from vanadium-dravite)*
Vanadio-oxy-chromium-dravite	Na	V_3	Cr_4Mg_2	Si_6	B_3	$(OH)_3$	O	Bosi et al. (2014a)
Vanadio-oxy-dravite	Na	V_3	Al_4Mg_2	Si_6	B_3	$(OH)_3$	O	Bosi et al. (2014b)
Alkali-subgroup 4								
Darrellhenryite	Na	$LiAl_2$	Al_6	Si_6	B_3	$(OH)_3$	O	Novák et al. (2013)
Alkali-subgroup 5								
Fluor-buergerite	Na	Fe^{3+}_3	Al_6	Si_6	B_3	O_3	F	*
Olenite	Na	Al_3	Al_6	Si_6	B_3	O_3	OH	*
Monoclinic tourmaline								
Luinaite-(OH)	Na	Fe^{2+}_3	Al_6	Si_6	B_3	$(OH)_3$	OH	** Kolitsch et al. (2013)
Calcic group								
Calcic-subgroup 1								
Fluor-uvite	Ca	Mg_3	Al_5Mg	Si_6	B_3	$(OH)_3$	F	*
Feruvite	Ca	Fe^{2+}_3	Al_5Mg	Si_6	B_3	$(OH)_3$	OH	*
Uvite	Ca	Mg_3	Al_5Mg	Si_6	B_3	$(OH)_3$	OH	** Clark et al. (2010)
Calcic-subgroup 2								
Fluor-liddicoatite	Ca	Li_2Al	Al_6	Si_6	B_3	$(OH)_3$	F	*
Calcic-subgroup 3								
Lucchesiite	Ca	Fe^{2+}_3	Al_6	Si_6	B_3	$(OH)_3$	O	Bosi et al. (2016)
New calcic-subgroup								
Adachiite	Ca	Fe^{2+}_3	Al_6	Si_5Al	B_3	$(OH)_3$	OH	Nishio-Hamane et al. (2014)
X-site vacant group								
Vacant-subgroup 1								
Foitite	□	Fe^{2+}_2Al	Al_6	Si_6	B_3	$(OH)_3$	OH	*
Magnesio-foitite	□	Mg_2Al	Al_6	Si_6	B_3	$(OH)_3$	OH	*
Vacant-subgroup 2								
Rossmanite	□	$LiAl_2$	Al_6	Si_6	B_3	$(OH)_3$	OH	*

*listed as a valid species in Henry et al. (2011).
**The mineral description from its type locality is still missing and its validity status is unclear.

Table 2.1 (continued): Current end-members in the tourmaline supergroup ...

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2.1. Crystal structures of oxy-tourmalines

The studies provided in the [Papers 1, 2, 4, and 5] characterized crystal chemistry of four different oxy-tourmaline species – three members of the sodic group and one member of the calcic group (groups defined by Henry et al. 2011). In the first case, Cempírek et al. (2006 – [Paper 1]) studied Fe-bearing olenite with high contents of tetrahedral Al. The second paper (Bačík et al. 2013 – [Paper 2]) provides the definition of a new mineral oxy-schorl, whereas the third paper studied its Mg-analogue, oxy-dravite (Cempírek et al. 2013 – [Paper 4]). An unusual calcic tourmaline was structurally characterized by Gadas et al. (2014 – [Paper 5]), and described as a new tourmaline of the calcic group, lucchesiite by Bosi et al. (2016).

2.1.1 Oxy-tourmalines with high contents of ^{T}Al

Structure of Fe-rich olenite with high ^{T}Al was examined by Cempírek et al. (2006 – [Paper 1]); very high ^{T}Al contents were also found in oxy-schorl from Zlatá Idka, Slovakia (Bačík et al. 2013 – [Paper 2]).

Cempírek et al. (2006 – [Paper 1]) studied a pale blue olenite from an abyssal pegmatite (Černý 1991, Černý and Ercit 2005) at the locality Kuklík near Kutná Hora, Czech Republic; its structure refinement provided the optimized formula

$$^{X}(\mathrm{Na}_{0.54}\mathrm{Ca}_{0.14}\mathrm{K}_{0.01}\square_{0.31})\ ^{Y}(\mathrm{Al}_{2.15}\mathrm{Fe}^{2+}_{0.78}\mathrm{Mn}^{2+}_{0.06}\mathrm{Ti}^{4+}_{0.01})\ ^{Z}(\mathrm{Al}_{5.90}\mathrm{Mg}_{0.10})\ \boldsymbol{^{T}(\mathrm{Si}_{5.60}\mathrm{Al}_{0.40})}\ \mathrm{B}_{3}\mathrm{O}_{27}\ ^{V}[(\mathrm{OH})_{2.49}\mathrm{O}_{0.51}]\ ^{W}(\mathrm{O}_{0.99}\mathrm{F}_{0.01})$$

with a = 15.8838(3), c = 7.1056(2) Å. The relatively small <*Y*–O> bond-length with 1.992 Å confirms the high content of Al at the *Y* site (~2.1 *apfu*). It is similar to that of olenite from the type locality (Schreyer et al. 2002), though the olenite from Kuklík contains significant amounts of Fe at the *Y* site, and significant amounts of $^{[4]}$Al (~0.4 *apfu*) instead of $^{[4]}$B in the *T* site. This is supported by the crystal structure showing an enlarged <*T*–O> bond-length of ~1.626 Å. This olenite shows that non-stoichiometric content of Si does not always imply $^{[4]}$B in aluminous tourmaline. No H could be found at the *W* site by refinement. The (OH) content with ~2.5 (OH) *pfu* (*pfu* = per formula unit), which was calculated for a charge-balanced formula, is in a good agreement with these findings and with the integrated intensity of the OH overtones in the 7000 cm^{-1} region; OH seems to be ordered strongly into the O3 site. The composition of this olenite shows a trend towards the proposed olenite end-member formula, which contains only 1 OH group. The low content of F (0.01 *apfu*) is uncommon for a natural Al-rich and Mg-poor tourmaline from granitic pegmatites. Synchrotron micro-XANES was used to detect the valence state of Fe in this crystal, which was found to have 93±10% of the total Fe as Fe^{2+}. Optical absorption spectra show that the blue color is derived primarily from a combination of $^{[6]}Fe^{2+}$, together with $^{[6]}Fe^{2+}$ interaction with a minor amount of $^{[6]}Fe^{3+}$ (Cempírek et al. 2006 – [Paper 1]).

Oxy-schorl, ideally $Na(Fe^{2+}{}_2Al)Al_6Si_6O_{18}(BO_3)_3(OH)_3O$, was described as a new mineral species by Bačík et al. (2013 – [Paper 2]) from Zlatá Idka, Slovak Republic (type locality) and Přibyslavice, Czech Republic. Oxy-schorl has the unit cell parameters of a = 15.916(3) Å, c = 7.107(1) Å (Zlatá Idka) and a = 15.985(1) Å, c = 7.154(1) Å (Přibyslavice). A combination of EMPA, Mössbauer spectroscopy, and crystal-structure refinement yields the empirical formulae

$$^{X}(Na_{0.591}Ca_{0.103}\square_{0.306})\ ^{Y}(Al_{1.885}Fe^{2+}{}_{1.108}Mn_{0.005}Ti_{0.002})\ ^{Z}(Al_{5.428}Mg_{0.572})\ ^{\boldsymbol{T}}\mathbf{(Si_{5.506}Al_{0.494})}$$
$$O_{18}(BO_3)_3\ ^{V}(OH)_3\ ^{W}(O_{0.625}OH_{0.236}F_{0.136}Cl_{0.003})$$

for the holotype sample from Zlatá Idka, and

$$^{X}(Na_{0.586}Ca_{0.017}K_{0.006}\square_{0.391})\ ^{Y}(Fe^{2+}{}_{1.879}Mn_{0.015}Al_{1.013}Ti_{0.093})\ ^{Z}(Al_{5.732}Mg_{0.190}Fe^{3+}{}_{0.078})$$
$$^{\boldsymbol{T}}\mathbf{(Si_{5.944}Al_{0.056})}\ O_{18}(BO_3)_3\ ^{V}(OH)_3\ ^{W}(O_{0.579}F_{0.307}OH_{0.115})$$

for Přibyslavice (Bačík et al. 2013 – [Paper 2]). Their contents of tetrahedral Al are strikingly different and correlate with the <T–O> bond-length in their structures: the 0.494 *apfu* ^{T}Al and <T–O> ~1.632 Å at Zlatá Idka, and 0.056 *apfu* ^{T}Al and <T–O> ~ 1.622 Å at Přibyslavice.

The two ^{T}Al contents and long <T–O> distances found in olenite and oxy-schorl belong among the highest values found in the tourmaline supergroup. However, the highest amount of ^{T}Al in tourmaline was found in the new mineral **adachiite** (Nishio-Hamane et al. 2014), with holotype sample cell parameters a = 15.9290(2), c = 7.1830(1) Å, the <T–O> ~ 1.634 Å, and the refined empirical formula $^{X}(Ca_{0.62}Na_{0.28}\square_{0.10})\ ^{Y}(Fe_{1.58}Al_{0.81}Mg_{0.55}Ti^{4+}{}_{0.01})\ ^{Z}(Al_{5.81}Fe_{0.14}Mg_{0.05})\ ^{\boldsymbol{T}}\mathbf{(Si_{5.15}Al_{0.85})}\ O_{18}\ B_{3.01}\ O_9\ ^{V}(OH)_3\ ^{W}[(OH)_{0.56}O_{0.44}]$. Adachiite forms rims on schorl-dravite crystals associated with margarite, chlorite, and diaspore in hydrothermal veins cutting the emery (corundum+hercynite metalaterite) from Kiura mine, Japan.

The average <T–O> distance in adachiite, although very high, seems still quite low compared to the sample from Zlatá Idka; this can be explained either by an unaccounted presence of ^{T}B which would lower the <T–O> value in adachiite, or by structural strain artificially increasing the <T–O> value in the Zlatá Idka sample. The problem requires more attention in future studies of high-^{T}Al tourmalines.

2.1.2 *Crystal structures of oxy-schorl and oxy-dravite*

Oxy-schorl and oxy-dravite are tourmaline end-members reported in the first tourmaline classification proposal of Hawthorne and Henry (1999), and therefore the two names were frequently used before the official nomenclature was published (Henry et al. 2011). Therefore, Bačík et al. (2013 – [Paper 2]) and Bosi and Skogby (2013) described the two species under their old names; in case of other new oxy-tourmaline end members, new root names are used (e.g., darrellhenryite, lucchesiite, maruyamaite – see Table 2.1).

Oxy-schorl, ideally $Na(Fe^{2+}_2Al)Al_6Si_6O_{18}(BO_3)_3(OH)_3O$, a new mineral species of the tourmaline supergroup, was described from Zlatá Idka, Slovakia (type locality) and Přibyslavice, Czech Republic (co-type locality) (Bačík et al. 2013 – [Paper 2]). It is trigonal, space group $R3m$, Z = 3, a = 15.916(3) Å, c = 7.107(1) Å, V = 1559.1(4) Å^3 (Zlatá Idka) and a = 15.985(1) Å, c = 7.154(1) Å, V = 1583.1(2) Å^3 (Přibyslavice). A combination of EMPA, Mössbauer spectroscopy, and crystal-structure refinement yielded empirical formulae

$$^{X}(Na_{0.591}Ca_{0.103}\square_{0.306})\ ^{Y}(Al_{1.885}Fe^{2+}_{1.108}Mn_{0.005}Ti_{0.002})\ ^{Z}(Al_{5.428}Mg_{0.572})\ ^{T}(Si_{5.506}Al_{0.494})$$

$$O_{18}(BO_3)_3\ ^{V}(OH)_3\ ^{W}(O_{0.625}OH_{0.236}F_{0.136}Cl_{0.003})\text{ for Zlatá Idka, and}$$

$$^{X}(Na_{0.586}Ca_{0.017}K_{0.006}\square_{0.391})\ ^{Y}(Fe^{2+}_{1.879}Mn_{0.015}Al_{1.013}Ti_{0.093})\ ^{Z}(Al_{5.732}Mg_{0.190}Fe^{3+}_{0.078})$$

$$^{T}(Si_{5.944}Al_{0.056})\ O_{18}(BO_3)_3\ ^{V}(OH)_3\ ^{W}(O_{0.579}F_{0.307}OH_{0.115})\text{ for Přibyslavice.}$$

The studied crystals of oxy-schorl represent two distinct ordering mechanisms: disorder of R^{2+} and R^{3+} cations in octahedral sites and all O ordered in the *W* site (Zlatá Idka), and R^{2+} and R^{3+} cations ordered in the *Y* and *Z* sites and O disordered in the *V* and *W* sites (Přibyslavice); the disorder of *Y* and *Z* sites is characteristic for solid solutions of Fe-Mg tourmalines (e.g., Grice and Ercit 1993, Hawthorne et al. 1993, Bloodaxe et al. 1999, Ertl et al. 2003, Bosi and Lucchesi 2004, Bosi and Lucchesi 2007, Bosi 2011, Bačík et al. 2012, Bačík 2015). Oxy-schorl is derived from schorl end-member by the $AlOFe_{-1}(OH)_{-1}$ substitution, or from foitite by the $^{X}Na^{+} + {}^{W}O^{2-} \leftrightarrow {}^{X}\square^{+} + {}^{W}(OH)^{1-}$ substitution.

On the other hand, Cempírek et al. (2013 – [Paper 4]) studied two types of V-rich dravitic tourmaline (oxy-dravite to dravite), distinct in their colour, morphology, paragenesis and composition from graphite quartzite at Bítovánky near Třebíč, Moldanubicum, Bohemian Massif, were studied by means of electron microprobe and single-crystal X-ray diffraction. Green **oxy-dravite** (GVD) from graphite quartzite is sporadically zoned with V-enriched rims; brown **oxy-dravite to dravite** (BVD) from mobilized quartz-rich nests is characterized by such V-enriched rims. The formulae derived from chemical and structure data of the two oxy-dravite varieties are

$$^{X}(\mathrm{Na}_{0.534}\mathrm{Ca}_{0.284}\square_{0.164}\mathrm{K}_{0.018})\ ^{Y}(\mathrm{Mg}_{1.461}\mathrm{V}_{0.679}\mathrm{Al}_{0.771}\mathrm{Fe}_{0.042}\mathrm{Mn}_{0.003}\mathrm{Ti}_{0.043})$$

$$^{Z}(\mathrm{Al}_{5.074}\mathrm{V}_{0.237}\mathrm{Mg}_{0.689})\ ^{T}(\mathrm{Si}_{5.782}\mathrm{Al}_{0.218}\mathrm{O}_{18})\ (\mathrm{BO}_3)_3\ ^{V,W}[(\mathrm{OH})_{3.058}\mathrm{O}_{0.75}\mathrm{F}_{0.192}] \text{ for GVD,}$$

and

$$^{X}(\mathrm{Na}_{0.539}\mathrm{Ca}_{0.148}\square_{0.297}\mathrm{K}_{0.017})\ ^{Y}(\mathrm{Mg}_{0.992}\mathrm{V}_{0.302}\mathrm{Al}_{1.039}\mathrm{Fe}_{0.582}\mathrm{Mn}_{0.011}\mathrm{Ti}_{0.068}\mathrm{Cr}_{0.007})$$

$$^{Z}(\mathrm{Al}_{5.339}\mathrm{V}_{0.082}\mathrm{Mg}_{0.578})\ ^{T}(\mathrm{Si}_{5.864}\mathrm{Al}_{0.136}\mathrm{O}_{18})\ (\mathrm{BO}_3)_3\ ^{V,W}[(\mathrm{OH})_{3.209}\mathrm{O}_{0.621}\mathrm{F}_{0.171}] \text{ for BVD.}$$

Both types of V-rich oxy-dravite feature Al–Mg–V disorder between the *Y* and *Z* sites; V and Cr are preferentially located at the *Y* site. The V-rich oxy-dravite from Bítovánky has unusually high Ca contents and high proportion of vacancy at the *X* site.

2.1.3 Lucchesiite – a new calcic oxy-tourmaline

Lucchesiite, ideally $\mathrm{CaFe^{2+}{}_3Al_6(Si_6O_{18})(BO_3)_3(OH)_3O}$, is a new mineral of the tourmaline supergroup (Bosi et al. 2016); its structure, refined formula, and Mössbauer spectra were published by Gadas et al (2014 – [Paper 5]) under provisional name "feruvitic tourmaline". Lucchesiite crystals are black with a vitreous luster, conchoidal fracture, and grey streak; it has a Mohs hardness of approximately 7, and a calculated density of 3.209 g/cm^3 (Sri Lanka) to 3.243 g/cm^3 (Czech Republic). In plane-polarized light, lucchesiite is pleochroic (O = very dark brown and E = light brown) and uniaxial negative. Lucchesiite is rhombohedral, space group $R3m$, $a \sim 16.00$ Å, $c \sim 7.21$ Å, $V \sim 1599.9$ Å^3, $Z = 3$. Crystal-chemical analysis for the Sri Lanka (holotype; Bosi et al. 2016) and Czech Republic (co-type; Gadas et al. 2014 – [Paper 5]) samples resulted in the empirical formulae, respectively:

$$^{X}(\mathrm{Ca}_{0.69}\mathrm{Na}_{0.30}\mathrm{K}_{0.02})_{\Sigma 1.01}\ ^{Y}(\mathrm{Fe^{2+}}_{1.44}\mathrm{Mg}_{0.72}\mathrm{Al}_{0.48}\mathrm{Ti^{4+}}_{0.33}\mathrm{V^{3+}}_{0.02}\mathrm{Mn}_{0.01}\mathrm{Zn}_{0.01})_{\Sigma 3.00}$$

$$^{Z}(\mathrm{Al}_{4.74}\mathrm{Mg}_{1.01}\mathrm{Fe^{3+}}_{0.25})_{\Sigma 6.00}\ [^{T}(\mathrm{Si}_{5.85}\mathrm{Al}_{0.15})_{\Sigma 6.00}\ \mathrm{O}_{18}]\ (\mathrm{BO}_3)_3\ ^{V}(\mathrm{OH})_3\ ^{W}[\mathrm{O}_{0.69}\mathrm{F}_{0.24}(\mathrm{OH})_{0.07}]_{\Sigma 1.00}$$

and

$$^{X}(\mathrm{Ca}_{0.49}\mathrm{Na}_{0.45}\square_{0.05}\mathrm{K}_{0.01})_{\Sigma 1.00}\ ^{Y}(\mathrm{Fe^{2+}}_{1.14}\mathrm{Fe^{3+}}_{0.95}\mathrm{Mg}_{0.42}\mathrm{Al}_{0.37}\mathrm{Mn}_{0.03}\mathrm{Ti^{4+}}_{0.08}\mathrm{Zn}_{0.01})_{\Sigma 3.00}$$

$$^{Z}(\mathrm{Al}_{5.11}\mathrm{Fe^{3+}}_{0.38}\mathrm{Mg}_{0.52})_{\Sigma 6.00}\ [^{T}(\mathrm{Si}_{5.88}\mathrm{Al}_{0.12})_{\Sigma 6.00}\mathrm{O}_{18}]\ (\mathrm{BO}_3)_3\ ^{V}[(\mathrm{OH})_{2.66}\mathrm{O}_{0.34}]_{\Sigma 3.00}\ ^{W}(\mathrm{O}_{0.94}\mathrm{F}_{0.06})_{\Sigma 1.00}$$

Lucchesiite is an oxy-species belonging to the calcic group of the tourmaline supergroup. The closest end-member composition of a valid tourmaline species is that of feruvite, to which lucchesiite is ideally related by the heterovalent coupled substitution $^{Z}\mathrm{Al}^{3+} + {}^{W}\mathrm{O}^{2-} \leftrightarrow {}^{Z}\mathrm{Mg}^{2+} + {}^{W}(\mathrm{OH})^{1-}$, or schorl, related by the $^{X}\mathrm{Ca}^{2+} + {}^{W}\mathrm{O}^{2-} \leftrightarrow {}^{X}\mathrm{Na}^{+} + {}^{W}(\mathrm{OH})^{1-}$ coupled substitution.

Lucchesiite is the first known oxy-endmember in the calcic group of the tourmaline supergroup (*cf*. Table 2.1).

2.2. Mineral parageneses of oxy-tourmalines

The paragenetic studies in the [Papers 3 and 5] focused also on mineral assemblages in which oxy-tourmalines can be found in various geological environments. More data on oxy-tourmaline parageneses in different rock types are provided in the [Papers 1, 2 and 4]. The studied oxy-tourmalines and geological environments include:

- olenite in an abyssal pegmatite (Cempírek et al. 2006 – [Paper 1])
- oxy-schorl occurs in metarhyolite and in metagranite (Bačík et al. 2013 – [Paper 2])
- lucchesiite in a contaminated granitic pegmatite (Gadas et al. 2014 – [Paper 5])
- oxy-dravite and dravite with high oxy-dravite component in metacarbonate (Bačík et al. 2012 – [Paper 3])
- oxy-dravite in graphite quartzite (Cempírek et al. 2013 – [Paper 4])

2.2.1 Occurrences in granitic systems

Oxy-tourmalines are rather common constituents of granitic pegmatites and granitic rocks (e.g., Henry and Dutrow 2001; Buriánek and Novák 2004, 2007; Novák et al. 2004; Ertl et al. 2010a, 2010b; Baksheev et al. 2011; Bosi 2011, Gadas et al. 2012). [Papers 1, 2, and 5] describe occurrences of oxy-tourmalines (olenite, oxy-schorl, and lucchesiite) in two uncommon types of granitic pegmatites and in metarhyolite and metagranite.

Mineral assemblages in the abyssal pegmatite at **Kuklík near Kutná Hora**, Czech Republic were studied in detail by Cempírek (2003); detailed characterization of green dumortierite and olenite from the locality was done by Cempírek and Novák (2005) and Cempírek et al. (2006 – [Paper 1]). The pegmatite is characterized by presence of several Al-rich assemblages:

1) border zone consists of coarse-grained quartz + oligoclase + K-feldspar + tourmaline I (Al-rich schorl) + muscovite;
2) the core zone is enriched in quartz and black to dark green tourmaline I (schorl-olenite), commonly rimmed by pale blue tourmaline II (olenite), which also can form small individual crystals, together with abundant colorless to green prismatic crystals of dumortierite I. The crystallization finished with skeletal dumortierite II and finely fibrous dumortierite III.

The crystallization sequence of borosilicates in abyssal pegmatites (Al-rich schorl → schorl-olenite → dumortierite → olenite → dumortierite) is distinct from those typically observed in Li-poor pegmatites (dumortierite → Mg-schorlitic tourmaline, Al-rich schorlitic tourmaline), and in complex Li-pegmatites (dumortierite → Mg-schorlitic tourmaline, Al-rich schorlitic tourmaline → Fe-rich elbaite → elbaite ± rossmanite, liddicoatite; e.g., Selway et al. 1999, Dixon et al. 2014). The trend observed in abyssal pegmatites is similar to that in the Stoffhütte pegmatite, Austria (Mg-rich schorl → Al-rich schorl to schorl-olenite → lithian olenite with tetrahedral boron; Kalt et al. 2001, Ertl and Hughes 2002). The progressive increase of Al in tourmaline during crystallization can be attributed to several factors, e.g., removal of Fe and Mg by crystallization of micas along with an increase of Al/Si ratio in melt by gradual crystallization of quartz.

Most of the work on the Kuklík pegmatite was done more than 10 years ago; with regard to recent discoveries in the field of minerals with the mullite-type structure (Chapter 3) and dumortierite supergroup of minerals (Chapter 4), the material revision using advanced analytical techniques that were not easily available at the time (e.g., field-emission scanning electron microscope, micro-Raman spectroscopy, analysis of light elements using LA-ICP-MS) can potentially provide new, very interesting results.

Similar to the oxy-tourmaline occurrences in pegmatites, the rocks at the type localities of oxy-schorl are characterized by an Al-rich environment and metamorphic overprint – at Zlatá Idka, it is associated with muscovite and occurs in hydrothermal veins in metarhyolite pyroclastics, whereas in the Přibyslavice muscovite-tourmaline alkali-feldspar metagranite, tourmaline magmatic composition was modified by metamorphic overprint (Bačík et al. 2013 – [Paper 2]). In both cases, primary reason for tourmaline deprotonation was the bulk composition of the system.

On the other hand, the mineral assemblage of the abyssal pegmatite hosting the calcic oxy-tourmaline lucchesiite at Mirošov, Czech Republic, is characterized by a reaction with its host, a calc-silicate rock which resulted in melt contamination by Ca and Mg. Crystallization of tourmaline commences by interstitial Ca-rich schorl-dravite to Na-Mg-rich feruvite in an outer granitic unit, graphic intergrowths of Ca-rich schorl to Na-rich lucchesiite with quartz in the central parts of the pegmatite, and volumetrically subordinate Ca-rich dravite occasionally replacing both previous tourmaline types (Gadas et al. 2014 – [Paper 5], Bosi et al. 2016). Compared to common anatectic pegmatites present in the SE part of the Moldanubian Zone where tourmaline ranges among Al-rich schorl, foitite, Al-bearing dravite, and magnesiofoitite compositions (Gadas et al. 2012), the high tourmaline deprotonation observed at Mirošov seems to result from excess cation charges due to combination of Ca-enrichment [substitution $CaO(NaOH)_{-1}$] and iron oxidation to Fe^{3+} [substitution $Fe^{3+}O(Fe^{2+}OH)_{-1}$] in the tourmaline structure.

2.2.2 Occurrences in metasedimentary rocks

[Papers 3 and 4] describe occurrences of dravitic tourmalines (oxy-dravite and dravite) in two types of metasedimentary rocks – in graphitic quartzites (Cempírek et al. 2013 – [Paper 4]), and in a metacarbonate (Bačík et al. 2012 – [Paper 3]).

The mineral assemblages in graphitic rocks at Bítovánky include accessory green V-bearing muscovite, sillimanite, V-rich tourmaline, zircon, apatite, V-rich rutile, schreyerite, monazite-(Ce), xenotime-(Y), pyrrhotite, and molybdenite, some of them in several varieties distinct in composition and mineral assemblage (Houzar and Šrein 2000; Houzar and Cempírek 2011). The V-rich tourmaline occurs in two types, distinct in their color, morphology, and paragenesis; Cempírek et al. (2013 – [Paper 4]) studied their composition, trace elements, and crystal structures. Green oxy-dravite (GVD) from graphite quartzite is sporadically zoned with V-enriched rims; brown oxy-dravite to dravite (BVD) from mobilized quartz-rich nests is characterized by such V-enriched rims. Most common trace elements include Ti, Cr, Mn, Zn, Sc, Ga, Sr, Ni, Sn, and LREE. High concentrations of V, Cr, and Ti (as well as elevated Mn, Zn, Sc, Sn, and Sr) in the GVD and late BVD most probably result from hydrothermal dissolution of (Ti,V)-oxides and other accessory phases during a high-grade metamorphic overprinting of the host graphite quartzite assemblage.

At Prosetín, Czech Republic, radial aggregates of blue-grey dravitic tourmaline were found in plagioclase-muscovite-scapolite metaevaporite layers in dolomite marble (Bačík et al. 2012 – [Paper 3]). The tourmaline occurs in association with plagioclase ($An_{15–37}$), muscovite, scapolite, phlogopite, vermiculite, pumpellyite-(Al), and clinozoisite. Electron-microprobe analyses of tourmaline showed that tourmaline is essentially dravite with very high content of Mg (1.92 to 2.77 *apfu*), Al (≤6.71 *apfu*), low content of Fe (max. 0.39 *apfu*) and variable amounts of vacancies (0.09 to 0.47 *apfu*) and Ca (0.03 to 0.29 *apfu*) in the *X*-site. Some analyses correspond to “oxy-dravite” and some almost attain magnesio-foitite compositions. The *X*-site vacancy decreases from the crystal cores to their rims whereas Ca content increases. The tourmaline is relatively poor in trace elements; only Ti, Sr, and Ga attain more than 100 ppm according to LA-ICP-MS. Trace-elements, assemblage and compositional zoning of tourmalines as well as host-rock mineral association suggest prograde metamorphic conditions and supports metaevaporitic origin of the plagioclase-muscovite-scapolite rocks, as suggested by Opletal et al. (2007).

3. Borosilicates with mullite-type structure

Minerals with mullite-type structures (Table 3.1, for definition of the mullite-type structure, see Fischer and Schneider 2008) belong to the most common accessory minerals, especially in metamorphic rocks; on the other hand, mineral assemblages containing borosilicates with mullite-type structure are rather rare in nature. The most common is grandidierite whereas ominelite, werdingite, and boralsilite each have less than ten localities worldwide; boromullite and vránaite were found at their type localities only (e.g., Grew 2002, Buick et al. 2008, Grew et al. 2008, 2011, Cempírek et al. 2010, Novák et al. 2015, Cempírek et al. 2016 – [Papers 6–8]).

The most common and the best known borosilicates with mullite-type structure are grandidierite and ominelite; structures of their end members and intermediate compositions of their solid solution series was structurally and chemically characterized by Dzikowski et al. (2007). The Mg-endmember of the series, grandidierite, is rather common and has more than 40 localities worldwide, mostly in pegmatites, migmatites, pelitic hornfelses, and calc-silicate rocks (Grew 2002). On the other hand, ominelite (Fe-endmember) occurrences are restricted to six localities only (e.g., Grew 2002, Grew et al. 1998b, Dzikowski et al. 2007, Cempírek et al. 2010 – [Paper 6]). The newest ominelite occurrence from leucocratic granulites at Horní Bory, Czech Republic (Cempírek et al. 2010 – [Paper 6]) provided a complex assemblage of ominelite with grandidierite, boralsilite, werdingite, Sb-rich dumortierite and secondary Al-rich tourmaline.

Werdingite was originally described from boron-rich granulite-facies rocks at Bok de Puts, Namaqualand, South Africa (Moore et al. 1990); it was later found in analogous rock type in Urungwe district, Zimbabwe (Grew et al. 1997). Werdingite was also discovered in silica-undersaturated grandidierite-bearing pegmatites in Andrahomana, Madagascar (Grew et al. 1998b), and Almgjotheii, Norway (Huijsmans et al. 1982, Grew et al. 1998a, 1998b, 2011), and in leucocratic granulite-facies rocks at Mount Stafford, Australia, and Larsemann Hills, Antarctica (Greenfield et al. 1998, Buick et al. 2008, Wadoski et al. 2011). At all localities, werdingite was associated with grandidierite, and in two cases (Almgjotheii and Larsemann Hills) also with boralsilite. Third occurrence of the werdingite + boralsilite assemblage was reported by Cempírek et al. (2010 – [Paper 6]) from Horní Bory, Czech Republic, where Fe-rich werdingite forms intergrowths with boralsilite.

Boromullite has a single locality at Mount Stafford, Australia, where it was found as a replacement product after werdingite or as sillimanite overgrowths; it was also frequently intergrown with sillimanite (Buick et al. 2008). Boromullite-forming process at the type locality is rather unique (werdingite breakdown), it can potentially be widespread as intergrowths with sillimanite in B-rich assemblages (Buick et al. 2008). Systematic analytical work on sillimanite associated with B-rich phases is required to uncover petrological potential of boromullite + sillimanite assemblages.

Boralsilite was discovered in pegmatite samples with grandidierite-ominelite and werdingite (± prismatine, tourmaline, and dumortierite) from Larsemann Hills, Antarctica, and Almgjotheii, Norway (Grew et al. 1998a,b). At Larsemann Hills, boralsilite occurs as a patch of fibrous of fine prisms in a quartz-rich part of a tourmaline-quartz intergrowth consisting of black tourmaline grains up to 1 cm long and gray quartz, with minor feldspar present through the intergrowth (Grew et al. 1998a); the stable assemblage with tourmaline is very unusual and has not been found elsewhere yet. At Almgjotheii, boralsilite occurs either in parallel growth with grandidierite, or as aggregates of prisms intergrown with werdingite; dumortierite, grandidierite, and andalusite occur in stable boralsilite assemblages (Grew et al. 1998a,b). Third world occurrence of boralsilite, paragenetically and texturally very similar to that in Almgjotheii, was discovered by Cempírek et al. (2010 – [Paper 6]) from Horní Bory, Czech Republic. All boralsilite occurrences above are present in environments formed at high temperature and at elevated pressure (T > 600°C, P > 3–4 kbar); a very exceptional occurrence in a low-pressure, low-temperature mineral assemblage in the Manjaka pegmatite, Madagascar (Novák et al. 2015, Cempírek et al. 2016 – [Papers 7–8]).

Vránaite has a single locality in the Manjaka pegmatite, Madagascar; its occurrence and properties are described in [Papers 7–8] (Novák et al. 2015, Cempírek et al. 2016).

Table 3.1: Minerals with mullite-type structures, and their structural properties

Mineral	*Vránaite*	*Boralsilite*	*Boromullite*	*Grandidierite – ominelite*	*Werdingite*	*Sillimanite*	*Andalusite*	*Mullite*
Formula	$Al_{16}B_4Si_4O_{38}$	$Al_{16}B_6Si_2O_{37}$	$Al_9BSi_2O_{19}$	$(Mg,Fe^{2+})Al_3SiBO_9$	$Mg_2Al_{14}Si_4B_4O_{37}$	Al_2SiO_5	Al_2SiO_5	$Al_2(Al_{2+x}Si_{2-2x})O_{10-x}$
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	triclinic	orthorhombic	orthorhombic	orthorhombic
Space group	*I*2/*m*	*C*2/*m*	$Cmc2_1$	*Pbnm*	*P –1*	*Pbnm*	*Pnnm*	*Pbam*
Z	1	2	2	4	1	4	4	1
a (Å)	10.383(1)	14.767(1)	5.717(2)	10.3631(4)	7.995(2)	7.4883(7)	7.7980(7)	7.5785(6)
b (Å)	5.6682(7)	5.574(1)	15.023(5)	11.0627(5)	8.152(1)	7.6808(7)	7.9031(10)	7.6817(7)
c (Å)	10.823(1)	15.079(1)	7.675(3)	5.7778(2)	11.406(4)	5.7774(5)	5.5566(5)	2.8864(3)
α (°)	90	90	90	90	110.45(2)	90	90	90
β (°)	90.11(1)	91.96(1)	90	90	110.85(2)	90	90	90
γ (°)	90	90	90	90	84.66(2)	90	90	90
Source of data	Cempírek et al. (2016)	Grew et al. (1998a)	Buick et al. (2008)	Dzikowski et al. (2007)*	Moore et al. (1990)	Winter and Ghose (1979)	Winter and Ghose (1979)	Angel and Prewitt (1986)

**Note:* sample G2 with Fe/(Fe+Mg) ~ 0.45

3.1. Occurrences of borosilicates with mullite-type structure in leucocratic granulites at Horní Bory, Czech Republic, and in the Manjaka pegmatite, Madagascar

In the [Paper 6] (Cempírek et al. 2010), we studied a mineral assemblage that contained four minerals with mullite-type structure: grandidierite, ominelite, boralsilite, and werdingite. They occur associated with dumortierite, and secondary Al-rich tourmaline and corundum in a thin veinlet formed by dry [i.e., with low $a(H_2O)$] partial melting of a leucocratic granulite at Horní Bory, Czech Republic. The prevailing mineral assemblage of the veinlet is Kfs + Qtz ± Pl (mineral abbreviations after Whitney and Evans 2010); early magmatic grandidierite-ominelite forms compositionally zoned skeletal crystals with Mg-rich cores [Fe/(Mg+Fe) ~ 0.34–0.47] and Fe-rich rims [Fe/(Mg+Fe) ~ 0.62–0.71] enclosed in K-feldspar and quartz. In some cases, ominelite is overgrown by aggregates formed by prismatic crystals of boralsilite and werdingite (Fig. 3.1.A); similar aggregates also form isolated cross-shaped intergrowth enclosed in quartz (Fig. 3.1.B). Fine intergrowths of boralsilite and werdingite observed at Horní Bory (Fig. 3.1.B) are similar to their other occurrences (Grew et al. 1998a, 1998b, 2011) and might indicate breakdown of a high-temperature solid solution mineral. Large compositional variation of both minerals indicates either a solid solution or sub-microscopic inclusion with other minerals with mullite-type structure (e.g., boralsilite-vránaite).

Other borosilicates in the assemblage feature rather unusual composition – the Al-rich tourmaline replacing grandidierite-ominelite has high contents of oxy-schorl and foitite components (oxy-schorl was formally described 3 years after the publication – Bačík et al. 2013 – [Paper 2]), whereas the tourmaline that rarely replaces boralsilite and werdingite probably represents a new species (*Al-excess foitite*). Dumortierite forms zoned grains with lamellae of Sb,Ti-rich dumortierite with up to 0.46 *apfu* Sb and 0.25 *apfu* Ti (Cempírek et al. 2010 – [Paper 6]).

In the [Paper 7] (Novák et al. 2015), we reported a discovery of boralsilite and "boron-mullite" in a low-pressure, low-temperature assemblage in the elbaite-subtype (Černý 1991, Černý and Ercit 2005) Manjaka granitic pegmatite, Sahatany Valley, Madagascar. We characterized properties of the "boron-mullite" in the subsequent [Paper 8] (Cempírek et al. 2016), and defined it as the new mineral vránaite. Boralsilite and vránaite occur as breakdown products of spodumene in the wall zone of the pegmatite (Figs. 3.1.C, 3.1.D). The pegmatite mineral assemblage is relatively simple (Ab + Qz > Kfs > Tur + Spd > Ap +

several accessory B-rich phases). This pegmatite is emplaced in an Mg-rich, calc-silicate rock; its exocontact locally contains thin reaction zones (Tur+Phl±Brl). Boralsilite assemblages are closely associated with prismatic spodumene crystals; long prismatic crystals and fibers of boralsilite, up to 200 µm long, and rare elongated grains of vránaite, up to 100 µm long, are mostly enclosed in albite and rarely in K-feldspar. The EMP and LA-ICP-MS data yielded relatively variable Al/Si ratios (~5.4–9.8; ~3.2–4.6) and high concentrations of Li (688–1433; 3339–4287 ppm), and Be (288–1082; 1017–2728 ppm), in boralsilite and vránaite, respectively.

The anhydrous borosilicate assemblages in the Horní Bory veinlet formed by partial melting of the host granulite; the observed mineral assemblages indicate that the associated fluid was rich in B_2O_3 but poor in H_2O. The estimated pressure-temperature conditions for the origin of the assemblage are T = 750 °C, and P = 6–8 kbar (Cempírek et al. 2010 – [Paper 6]) which generally matches the conditions at the boralsilite and werdingite occurrence in Larsemann hills, Antarctica (3–4 kbar, 600–700 °C; Grew et al. 2008). On the other hand, the estimated *PT*-conditions of origin for the newly discovered boralsilite + vránaite assemblage in the Manjaka pegmatite (Novák et al. 2015 – [Paper 7], Cempírek et al. 2016 – [Paper 8]) are significantly lower ($T \sim$ 350–450 °C at $P < \sim$ 2–3 kbar) and indicate that the stability fields of boralsilite and vránaite in silica-undersaturated assemblages extend to a relatively low temperature and pressure; presence of Li (and Be) which may further enhance their stabilities to lower P-T conditions (Novák et al. 2015 – [Paper 7]). Assemblages with vránaite and boralsilite are inferred to represent initial reaction products of a residual liquid rich in Li, Be, Na, K, and B during a pressure and chemical quench, but at low H_2O activities due to early melt contamination by carbonate in the host rocks. The two phases are interpreted to have crystallized metastably in lieu of dumortierite in accordance with Ostwald Step Rule, possibly first as "boron mullite", then as monoclinic phases (Cempírek et al. 2016 – [Paper 8]).

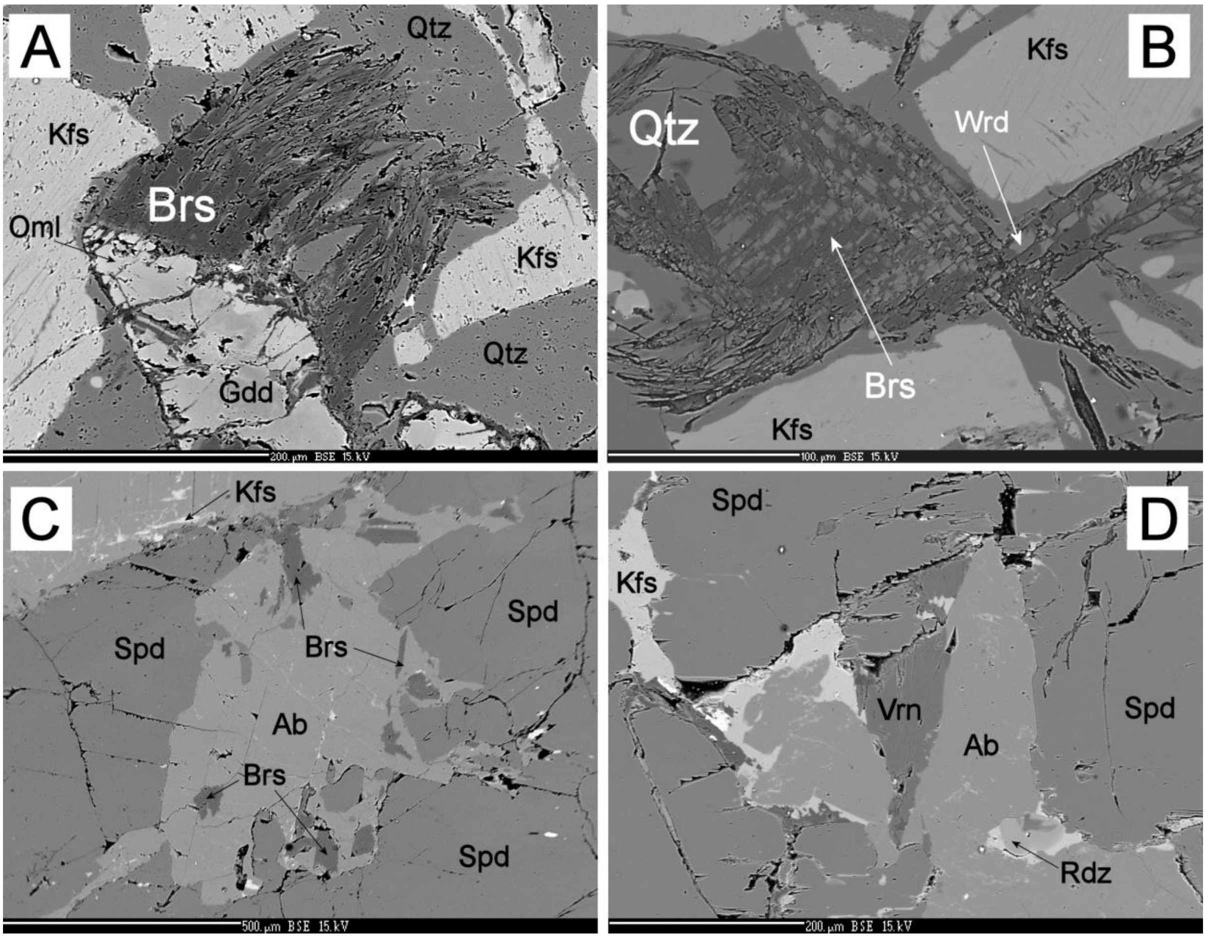


Figure 3.1: BSE images of grandidierite, ominelite, boralsilite, and werdingite from Horní Bory (A, B) and boralsilite and vránaite from Manjaka (C, D). Mineral abbreviations: Gdd = grandidierite, Oml = ominelite, Brs = boralsilite, Wrd = werdingite, Kfs = K-feldspar, Qtz = quartz, Ab = albite, Spd = spodumene, Vrn = vránaite.

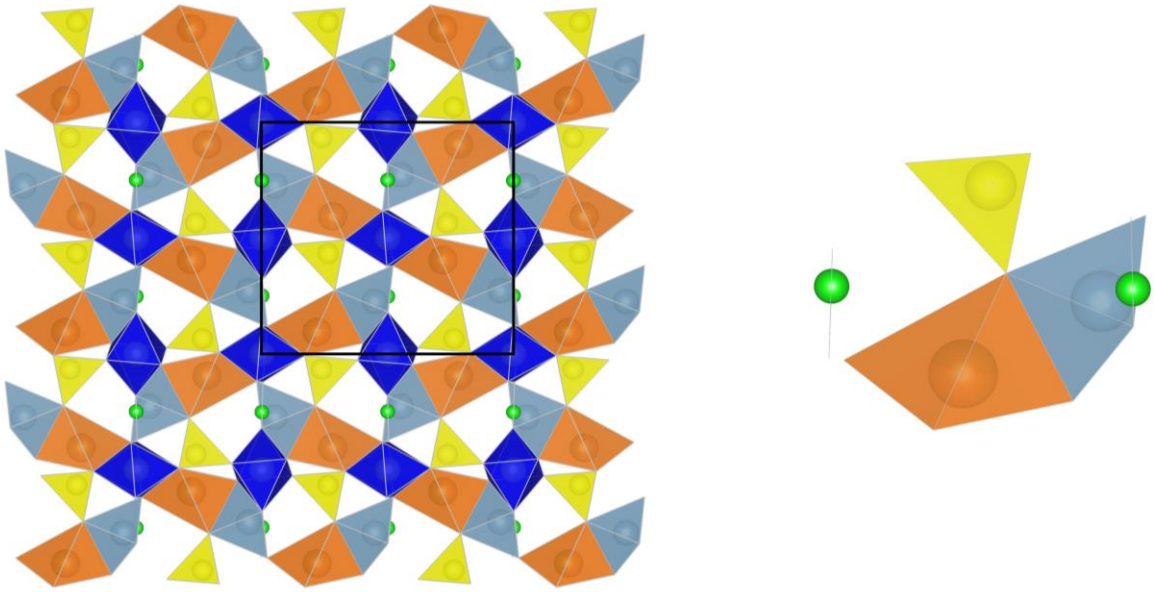
3.2. Vránaite – new anhydrous borosilicate with mullite-type structure

The new mineral vránaite (Cempírek et al. 2016 – [Paper 8]), ideally $Al_{16}B_4Si_4O_{38}$, is a borosilicate with a mullite-type structure, related to boralsilite (ideally $Al_{16}B_6Si_2O_{37}$) and boromullite (ideally $Al_9BSi_2O_{19}$), and other mullite-type structure borosilicates and alumosilicates (Figs. 3.2, 3.3).

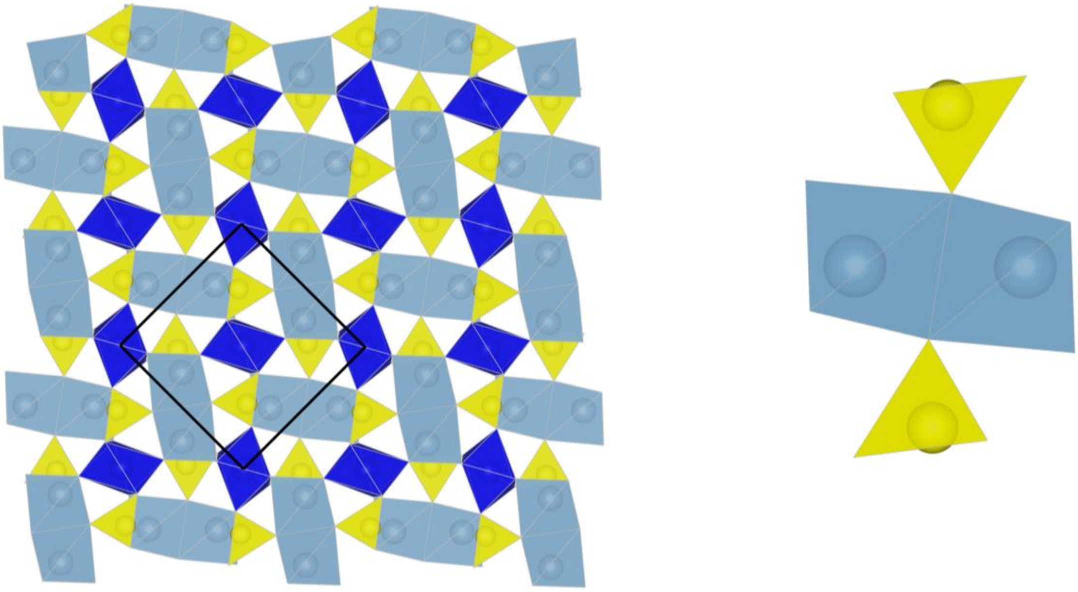
Mullite-type structures are formed by chains of AlO_6 octahedra that run parallel to [010] which are cross-linked by *interchain units* (Peacor et al. 1999). A single type of interchain unit is present, for example, in **grandidierite** – **ominelite** [cluster of one BO_3, one SiO_4, one AlO_5, and one $(Fe,Mg)O_5$ polyhedra], **andalusite** (cluster of two AlO_5 and two SiO_4 polyhedra), **sillimanite** (dimer of AlO_4 and SiO_4 tetrahedra), and **mullite** [occupancy-disordered cluster of two $(Al,Si,\square)O_5$ and two $(\square,Si)O_4$ polyhedra] (Fig. 3.2).

Vránaite has two different interchain units; the Unit 1 is formed by Si_2O_7 disilicate group and BO_3 triangles, and partially occupied BO_4 and AlO_5 polyhedra (shown as balls on Fig. 3.3), and the Unit 2 formed by cluster of AlO_4 and AlO_5 polyhedra. Similar arrangement is present in **werdingite**, where the Unit 1 is formed by Si_2O_7 disilicate group and BO_3 triangles, and partially occupied AlO_4, and FeO_5 polyhedra (shown as balls on Fig. 3.3), and the Unit 2 is formed by cluster of AlO_4, AlO_5, and FeO_5 polyhedra. On the other hand, **boralsilite** has four interchain units, Unit 1 formed by two AlO_5 and two BO_4 polyhedra, Unit 3 formed by dimer of SiO_4 tetrahedra, and Units 2 and 4 formed by clusters of two AlO_5, one BO_3, and one AlO_4 polyhedra. **Boromullite** average structure has two interchain units with disordered occupancies (Fig. 3.3), but it actually is a 1:1 polysome between sillimanite and Al_5BO_9 structures with yet unknown superstructure periodicity (Buick et al. 2008).

In vránaite Unit 2, two Al positions with fivefold coordination, Al4 and Al5, are too close to one another to be occupied simultaneously; their refined site-occupancy factors are 54% and 20% occupancy, respectively. Bond valence calculations for the Al4 site suggest Li is likely to be sited here, whereas Be is most probably at the Al5 site. One of the nine O sites is only 20% occupied; this O9 site completes the coordination of the Al5 site and is located at the 4th corner of a partially occupied BO_4 tetrahedron, in which case the B site is shifted out of the plane of the BO_3 triangle. If all sites were filled (Al4 and Al5 to 50%), the formula becomes $Al_{16}B_4Si_4O_{38}$, close to $Li_{1.08}Be_{0.47}Fe_{0.02}Al_{14.65}B_{3.89}Si_{3.88}O_{36.62}$ calculated from the analyses assuming cations sum to 24. The simplified formula, assuming fully occupied B, Si, Al1, Al2, and Al3 sites and half-occupied Al4 and Al5 sites is $Al_{16}B_4Si_4O_{38}$ (Cempírek et al. 2016 – [Paper 8]).

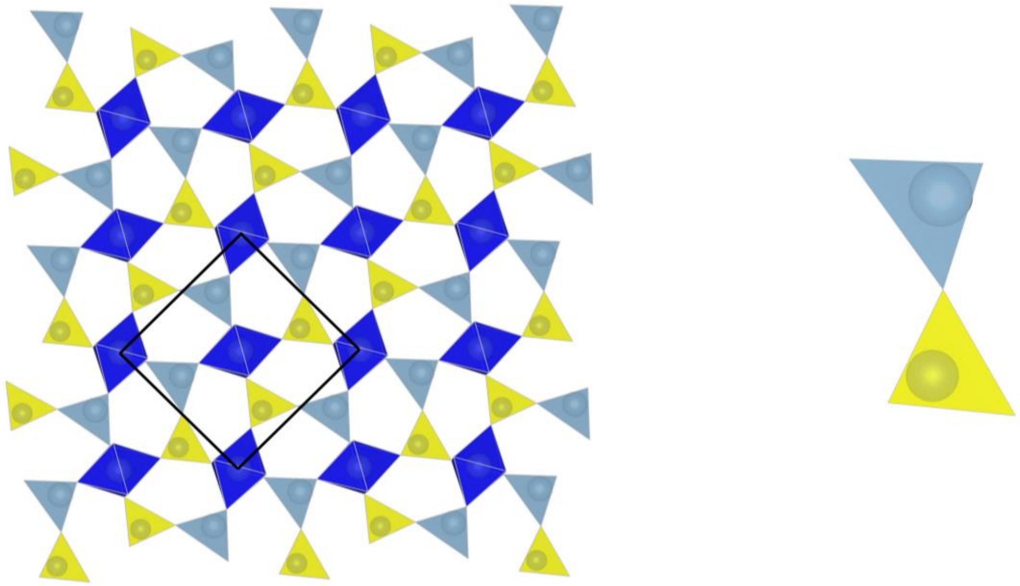


grandidierite – ominelite (structure after Dzikowski et al. 2007)

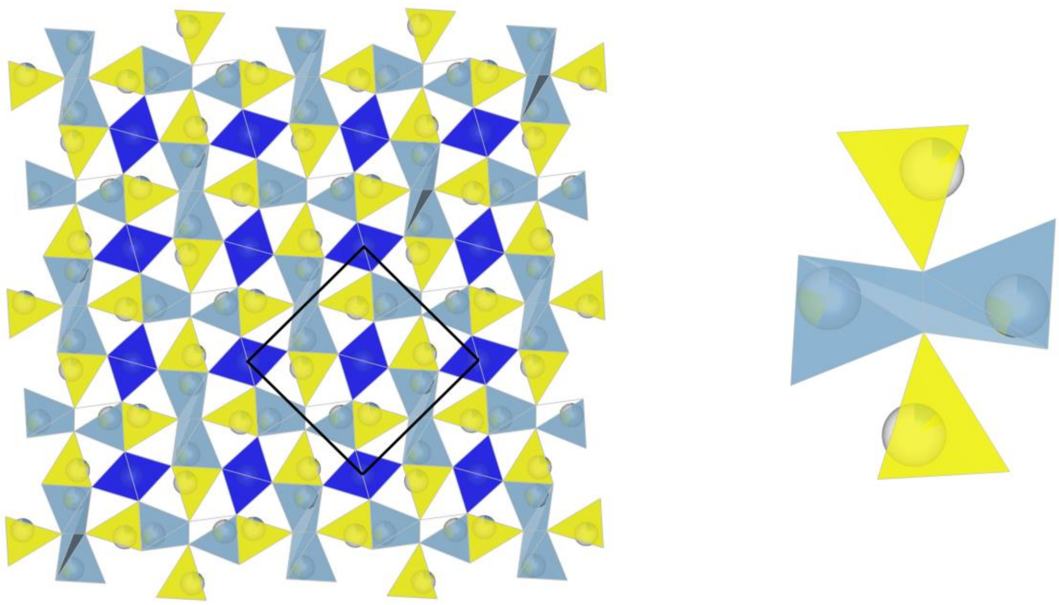


andalusite (structure after Winter and Ghose 1979)

Figure 3.2: Structures of mullite-type structure minerals with a single type of interchain unit (left) and detailed views of their interchain units (right). The structure view is parallel to the chains of AlO_6 octahedra (dark blue); the view is rotated for easier comparison of structures with different space group settings and unit cells.

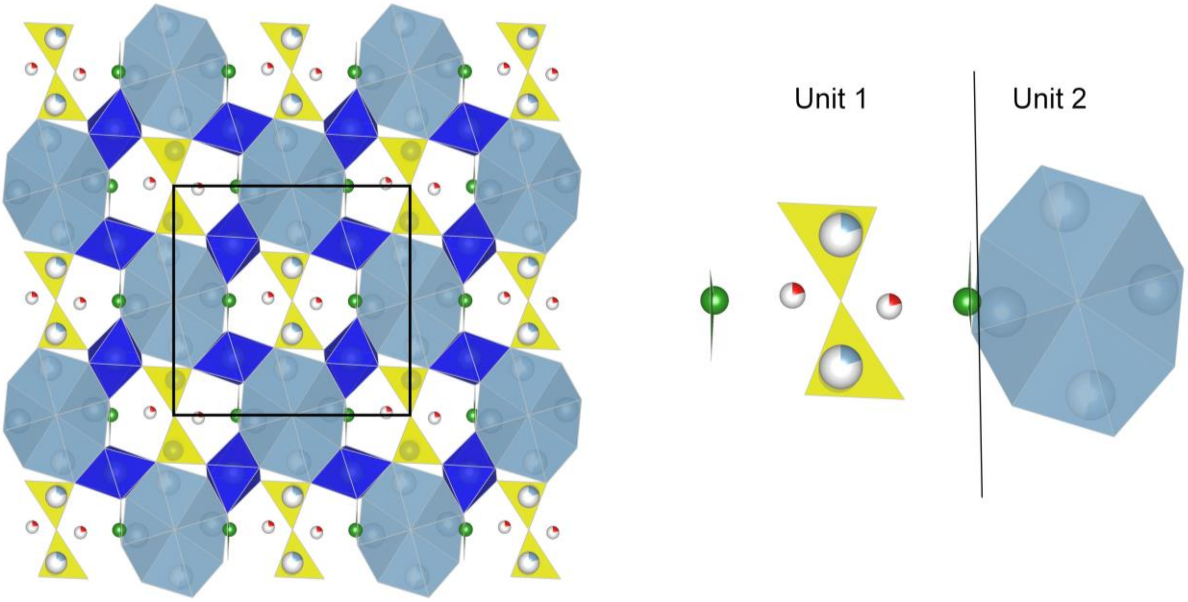


sillimanite (structure after Winter and Ghose 1979)

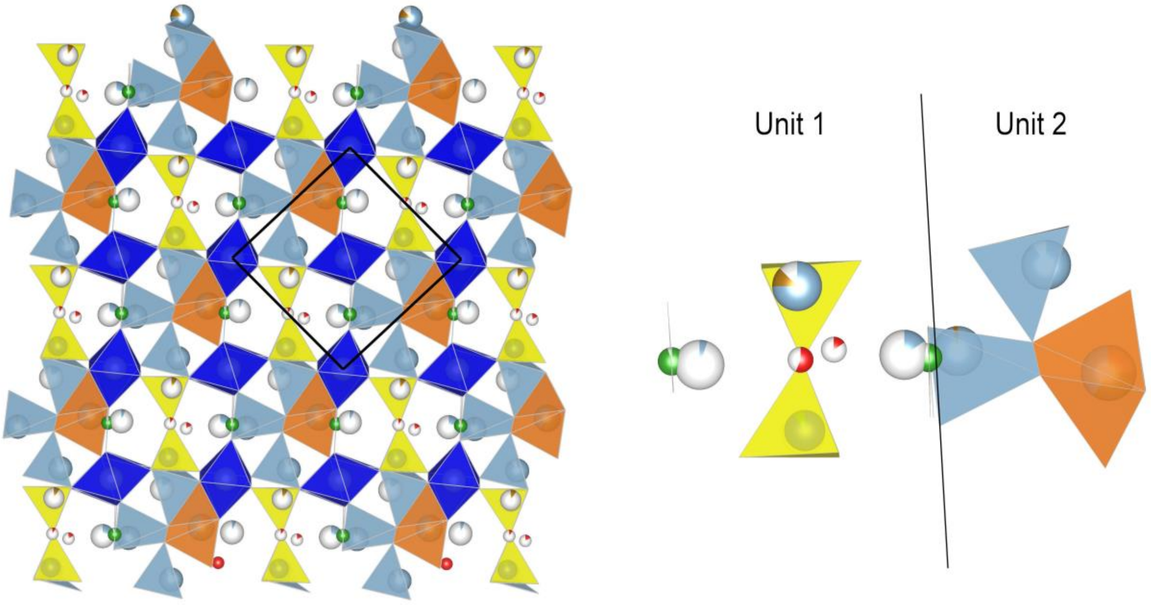


mullite (structure after Angel and Prewitt 1986)

Figure 3.2 (continued): Structures of mullite-type structure minerals with a single type of interchain unit (left) and detailed views of their interchain units (right). The structure view is parallel to the chains of AlO_6 octahedra (dark blue); the view is rotated for easier comparison of structures with different space group settings and unit cells.

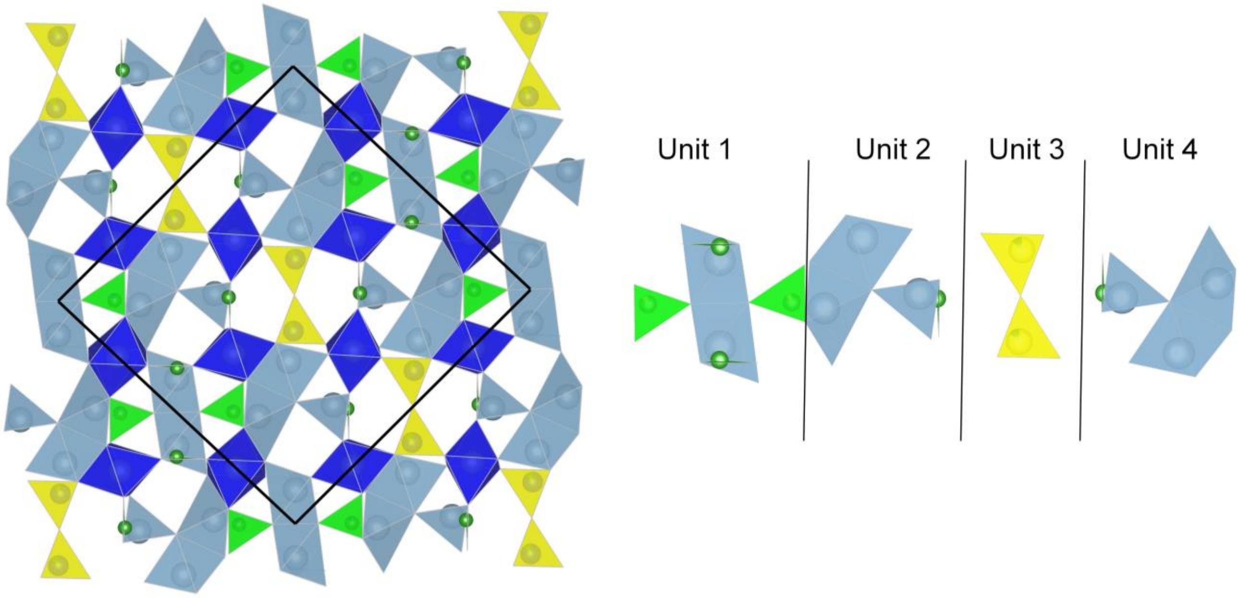


vránaite (structure after Cempírek et al. 2016 – [Paper 8])

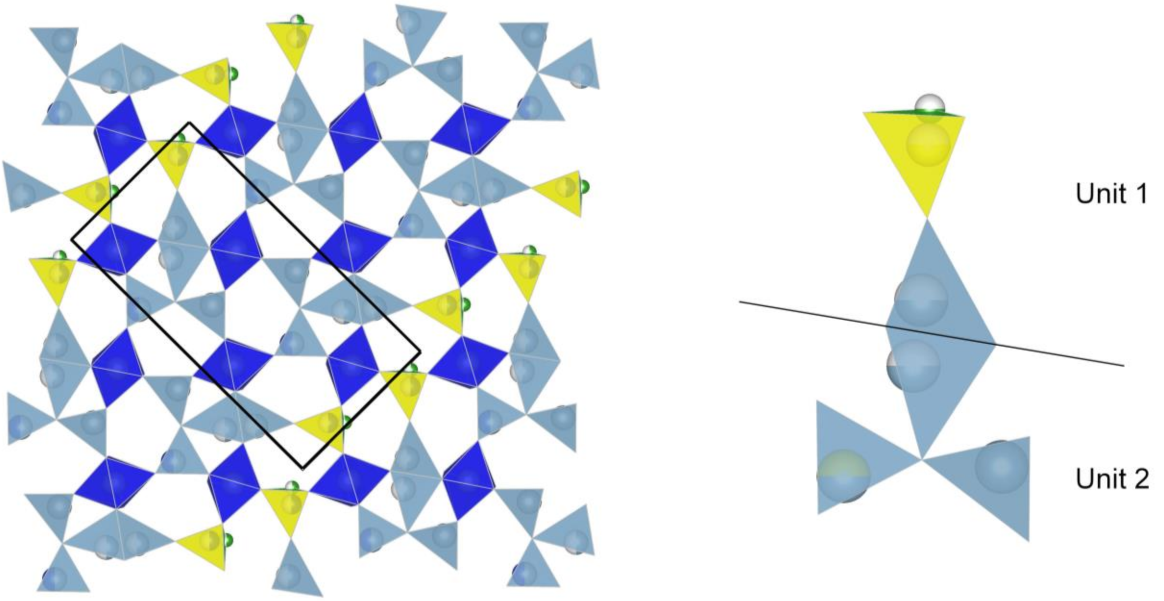


werdingite (structure after Grew et al. 2011)

Figure 3.3: Structures of mullite-type structure minerals with multiple types of interchain units (left) and detailed views of their interchain units (right). The structure view is parallel to the chains of AlO_6 octahedra (dark blue); the view is rotated for easier comparison of structures with different space group settings and unit cells.



boralsilite (structure after Grew et al. 2008)



boromullite (structure after Buick et al. 2008)

Figure 3.3 (continued): Structures of mullite-type structure minerals with multiple types of interchain units (left) and detailed views of their interchain units (right). The structure view is parallel to the chains of AlO_6 octahedra (dark blue); the view is rotated for easier comparison of structures with different space group settings and unit cells.

4. Dumortierite-supergroup minerals

Dumortierite supergroup (Pieczka et al. 2013a,b) currently comprises two mineral groups and six minerals that differ in their composition and stoichiometry (Table 4.1). All minerals are isostructural with dumortierite (ideally $Al_7BSi_3O_{18}$, orthorhombic, space group *Pnma*).

The dumortierite structure (Fig. 4.1) is characterized by presence of chains of face-sharing octahedra (the Al1 sites) with circumjacent ‘‘pinwheels’’ of six SiO_4 tetrahedra, two Si1 and four Si2 sites. The tetrahedra are connected to $[Al_4O_{11}]$ sheets (edge-sharing Al2 and Al3 sites) oriented parallel to (001), and to $[Al_4O_{12}]$ double-chains parallel to the [100] direction containing face- and edge-sharing Al4 octahedra; the sheets and double-chains of octahedra are also joined by BO_3 triangles (Fig. 4.1; Pieczka et al. 2013a). Substitutions and vacancies in the face-sharing Al1 sites and adjacent tetrahedral sites are responsible for the major part of compositional variation in the dumortierite supergroup.

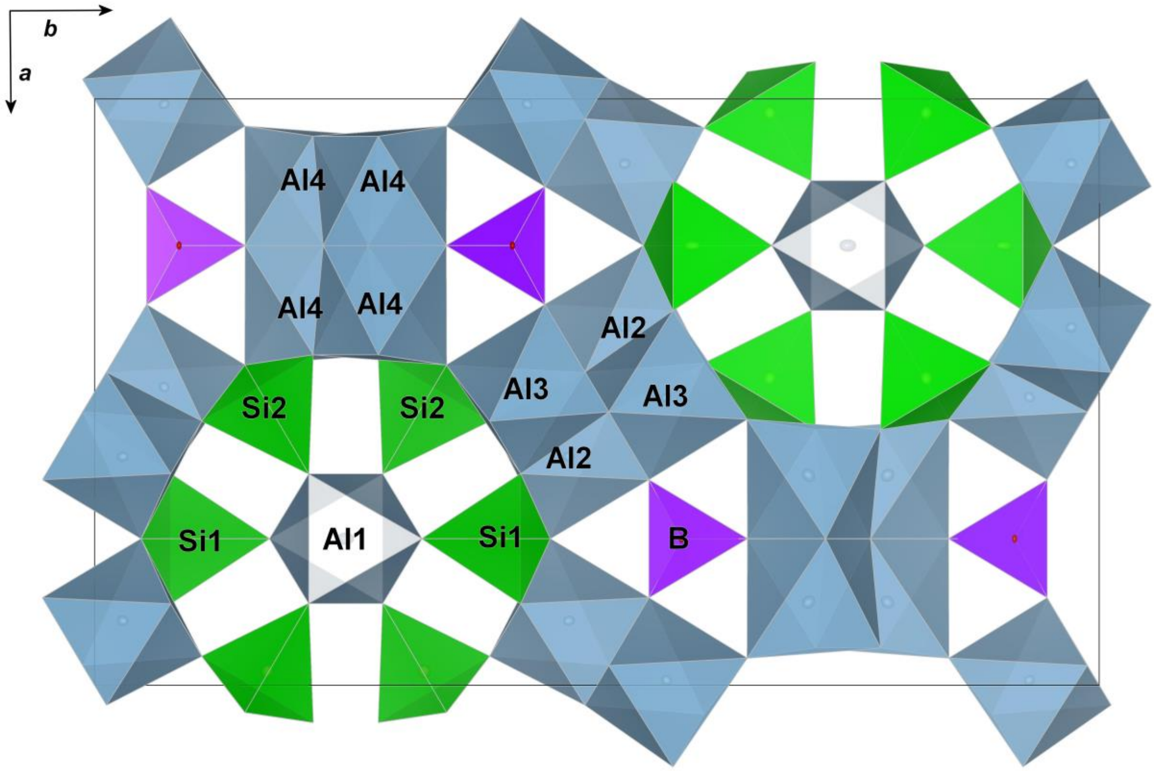


Figure 4.1: Structure of dumortierite (after Alexander et al. 1986).

Table 4.1: Groups and minerals of the dumortierite supergroup

Group	*Mineral*	*Ideal formula*
dumortierite group		
	dumortierite	$AlAl_6BSi_3O_{18}$
	magnesiodumortierite	$MgAl_6BSi_3O_{17}(OH)$
holtite group		
	holtite	$(Ta_{0.6}\square_{0.4})Al_6BSi_3O_{18}$
	nioboholtite	$(Nb_{0.6}\square_{0.4})Al_6BSi_3O_{18}$
	titanoholtite	$(Ti_{0.75}\square_{0.25})Al_6BSi_3O_{18}$
szklaryite group		
	szklaryite	$\square Al_6BAs^{3+}_3O_{15}$

Despite the high number of ions with variable charge (ranging from +3 to +5) that can enter its structure, the far most common of the dumortierite-supergroup minerals is (typically almost pure) dumortierite. For example, during studies of dumortierite-supergroup minerals from multiple localities in the Bohemian Massif (Losert 1956, Cempírek 2003, Cempírek and Novák 2004, 2005, 2006, Fuchs et al. 2005, Loun and Cempírek 2010), dumortierite and its varieties with low amounts of Fe, Mg, and Ti were encountered only; dumortierite nanofibers were reported to be the cause of pink coloration in rose quartz (Goreva et al. 2001, Ma et al. 2002). Magnesiodumortierite was reported from a single locality in ultrahigh-pressure rocks at Dora Maira (Ferraris et al. 1995, Chopin et al. 1995).

Holtite-group mineral occurrences are generally restricted to highly fractionated pegmatites (Groat et al. 2009) such as Greenbushes, Australia (Pryce 1971, Hoskins et al. 1989), Voron'i Tundry, Kola Peninsula, Russia (Voloshin et al. 1977, 1987), Virorco, Argentina (Galliski et al. 2012 - [Paper 9]), or Szklary, Poland (Pieczka et al. 2011, 2013b). Except the occurrence at Szklary where titanoholtite, nioboholtite, and Sb,As-rich holtite are present, holtite is present at all localities.

Elevated contents of Ti, As, and Sb were rarely reported from various geological environments, ranging from fractionated pegmatites (e.g., Groat et al. 2001, 2009, 2012), quartzites (Borghi et al. 2004, Vaggelli et al. 2004), to primitive pegmatites (Vrána 1979, Cempírek and Novák 2004, Cempírek et al. 2010 – [Paper 6]). However, the only locality where the contents of As attain values sufficient for szklaryite is the unique rare-element pegmatite in Szklary, Poland (Pieczka 2010, Pieczka et al. 2011, 2013b).

4.1. Dumortierite and holtite from pegmatites at Virorco, San Luis, Argentina

Cempírek (2003) noticed the unusual occurrence of green dumortierite reported by Gay and Galliski (1978) from Virorco, Argentina, texturally similar to those in the Kutná Hora region (e.g., Fiala 1954; Losert 1956, Cempírek and Novák 2006, Cempírek et al. 2006); subsequent cooperation with Dr. M.Á. Galliski resulted in the revisiting of the locality and collection of more research material. Revision of the Virorco pegmatite mineral assemblages (Galliski et al. 2012 – [Paper 9]) showed that the locality actually contains a unique assemblage of Li-rich tourmaline, Ta-bearing dumortierite, holtite, As-bearing holtite, and As-rich dumortierite.

The Virorco pegmatites form thin, steeply dipping dikes *ca.* 1–10 cm thick with variable lengths (a few dm to <2 m), emplaced in partially uralitized norite and gabbro. Despite their small volume, they contain *a highly fractionated mineral assemblage*, with Li-bearing tourmaline, dumortierite-holtite, muscovite, and kyanite as the major phases; the accessory and trace minerals include beryl, chrysoberyl, garnet, fluorapatite, columbite-tantalite, pollucite, gahnite, zircon, uraninite, and thorite. Lithium-rich amphibole holmquistite was found in the exocontact assemblage (Galliski et al. 2012 – [Paper 9]). To a certain extent, the geological position and mineral assemblage are similar to those of the Szklary pegmatite, Poland (Pieczka 2010; Pieczka et al. 2011) which is emplaced in a serpentinite and contains a mineral assemblage that includes tourmaline, chrysoberyl, columbite, stibiocolumbite-stibiotantalite, and holtite; however, no lithium-bearing minerals were found in the Szklary pegmatite. Pieczka et al. (2011) proposed anatectic origin of the pegmatite and suggested that contact metamorphism (desilication) with the host serpentinite caused an increase of Al_2O_3 content in the original melt.

Evolution of the Virorco pegmatite is rather distinct from that in Szklary. At Virorco, high content of Li in the melt is documented by exocontact holmquistite, and tourmaline-supergroup minerals ranging from dravite-rich compositions to rossmanite, passing through schorl and Mn-rich elbaite; presence of kyanite in the pegmatite core indicates high pressure of crystallization. The evolution of dumortierite-group minerals is analogous to Szklary, except the very high enrichment in Sb in Szklary; initial increase of Ta, Nb, and minor As is followed by an extensive enrichment in As (+ Sb + Bi) along with gradual decrease in Ta + Nb. The zoned texture and widespread enrichment in Sb in the Szklary pegmatite is similar to holtite occurrences from Greenbushes, Australia, Vorony'i Tundy, Russia (e.g., Groat et al. 2012) or dumortierite from Horní Bory (Cempírek et al. 2010 – [Paper 6]); on the other hand, the very high As in Ta-free dumortierite in Virorco is less frequent, and seems to be restricted to the latest stages of dumortierite or holtite crystallization (e.g., Cempírek and Novák 2004, Pieczka et al. 2011, 2013b).

Contrary to Szklary where magmatic crystallization of holtite together with columbite and stibiocolumbite was suggested (Pieczka et al. 2011), the variable assemblages and particularly the compositional trends of tourmaline, dumortierite–holtite, and columbite observed in Virorco pegmatites reflect several superimposed processes. The initial stage comprises the magmatic crystallization of a highly evolved and boron-rich peraluminous melt. The second stage was prograde medium-pressure metamorphism, with a fluid-phase-related episode of crystallization. The most likely source of the initial melt is an extraction of residual melt from an almost completely crystallized rare-element parental pegmatite. Therefore, besides the scientific importance of the mineralogically unique assemblage present at Virorco, the occurrence could also indicate presence of a highly fractionated pegmatite body in depth with contents of economic minerals such as Li-silicates and Ta,Nb-oxides (Galliski et al. 2012 – [Paper 9]).

5. Summary and outlook

Since the mid-1990's, we have witnessed a very dynamic growth of knowledge on tourmaline–supergroup minerals, including their crystal chemistry in various geological environments, crystal-structural constraints for their occurrence and composition, trace elements, isotope geochemistry, and experimental studies on their stability. Descriptions of new tourmaline end members or anomalous compositions that lead to new end members [Papers 1–5] allow systematic classification of this group with extreme compositional variability. Precise and unequivocal classification allows exact characterization of mineral properties and significance of their presence in specific rock types, and provides guidelines for targeted experimental work on element partitioning or stability of tourmalines with specific compositions or specific properties useful in technological applications. Studies of natural assemblages will always be essential parts of mineral research efforts as natural systems can show extreme chemical complexity over a large field of pressure-temperature conditions. In author's opinion, the current number of tourmaline-supergroup species may easily double in the next 20 years, as more and more natural systems are studied in much greater depth with more advanced analytical techniques than was ever possible before.

Despite the very significant progress in last 20 years, the crystal chemistry of minerals with the mullite-type structure [Papers 6–8] still represents a vastly underexplored field with large potential for results significant in petrology and mineral exploration. For example, systematic assessment of amounts and extent of boron substitutions in sillimanite would have significant importance for petrologists, and potentially also for tracing reactions with marine fluids in rock sequences that were subjected to high-grade (low and medium pressure, high temperature) metamorphic overprint. Although most of the minerals are still very rare in nature, future research may reveal that borosilicates with the mullite-type structure are present in many geological environments.

Dumortierite-supergroup [Paper 9] represents a challenging topic with regard to their frequently non-stoichiometric empirical formula, high amounts of structural vacancies, and contents of light elements (B, H) that are usually difficult to analyze. There are many opened questions in front of us, such as dumortierite ordering mechanisms and supersymmetry, stability of holtite- and szklaryite-group minerals, their distribution in natural (especially mineral deposit forming-) systems, applications in geothermobarometry, etc. Again, we may expect new discoveries in those areas in the near future.

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7. Supplements

Below is the list of supplemented publications, including the candidate's contributions to the publications.

Paper 1 **Cempírek, J.,** Novák, M., Ertl, A., Hughes, J.M., Rossman, G.R., Dyar, M.D. (2006): Fe-bearing olenite with tetrahedrally coordinated Al from an abyssal pegmatite at Kutná Hora, Czech Republic: structure, crystal chemistry, optical and XANES spectra. *The Canadian Mineralogist* **44**, 23–30.

Candidate's contribution to the publication: *This paper was based on the candidate's Ph.D. study. The candidate was the primary author and contributed to the design of the research project, he acquired part of data, participated in all of the data interpretation, and drafted several parts of the paper. Estimated contribution of the candidate is ca. 40%.*

Paper 2 Bačík, P., **Cempírek, J.,** Uher, P., Novák, M., Ozdín, D., Filip, J., Škoda, R. (2013): Oxy–schorl, $Na(Fe_2^{2+}Al)Al_6Si_6O_{18}(BO_3)_3(OH)_3O$, a new mineral from Zlatá Idka, Slovak Republic and Přibyslavice, Czech Republic. *American Mineralogist* **98**, 485–492.

Candidate's contribution to the publication: *The candidate was the second author on this joint paper of two research teams; The candidate participated on the design of the research project, acquired structural and compositional data, participated in all data interpretation, and drafted significant parts of the paper. Estimated contribution of the candidate is ca. 40%.*

Paper 3 Bačík, P., Uher, P., **Cempírek, J.,** Vaculovič, T. (2012): Magnesian tourmalines from plagioclase–muscovite–scapolite metaevaporite layers in dolomite marble near Prosetín (Olešnice Unit, Moravicum, Czech Republic). *Journal of Geosciences* **57**, 143–153.

Candidate's contribution to the publication: *The candidate was invited to join the existing project for which he was the third author on the paper. He contributed to the data interpretation, and drafted some parts of the paper. Estimated contribution of the candidate is ca. 25%.*

Paper 4 **Cempírek, J.,** Houzar, S., Novák, M., Groat, L.A., Selway, J.B., Šrein, V. (2013): Crystal structure and compositional evolution of vanadium-rich oxy–dravite from graphite quartzite at Bítovánky, Czech Republic. *Journal of Geosciences* **58**, 149–162.

Candidate's contribution to the publication: *The candidate was the primary author and* *was responsible for a major part of design of the research project, data acquisition and interpretation, and drafting of the paper. Estimated contribution of the candidate is ca. 80%.*

Paper 5 Gadas, P., Novák, M., **Cempírek, J.,** Filip, J., Vašinová–Galiová, M., Groat, L.A., Všianský, D. (2014): Mineral assemblages, compositional variation, and crystal structure of feruvitic tourmaline from a contaminated anatectic pegmatite at Mirošov near Strážek, Moldanubian Zone, Czech Republic. *The Canadian Mineralogist* **52**, 285–301.

Candidate's contribution to the publication: *The candidate contributed to the design of the research project, acquired X–ray diffraction data, participated in all data interpretation, and drafted several parts of the paper. Estimated contribution of the candidate is ca. 25%.*

Paper 6 **Cempírek, J.,** Novák, M., Dolníček, Z., Kotková, J., Škoda, R. (2010): Crystal chemistry and origin of grandidierite, ominelite, boralsilite and werdingite from the Bory Granulite Massif, Czech Republic. *American Mineralogist* **95**, 1533–1547.

Candidate's contribution to the publication: *This paper was based on the candidate's Ph.D. study. The candidate was the primary author, and designed the research project, acquired a large part of the data, and significantly participated in data interpretation and paper drafting. Estimated contribution of the candidate is ca. 60%.*

Paper 7 Novák, M., **Cempírek, J.,** Gadas, P., Škoda, R., Vašinová–Galiová, M., Pezzotta, F., Groat, L.A. (2015): Boralsilite and Li,Be–bearing "boron mullite" $Al_8B_2Si_2O_{19}$, breakdown products of spodumene from the Manjaka pegmatite, Sahatany Valley, Madagascar. *The Canadian Mineralogist* **53**, 357–374.

Candidate's contribution to the publication: *The candidate participated in designing the research project and acquiring data; he significantly participated on data interpretation and drafting of the paper. Estimated contribution of the candidate is ca. 40%.*

Paper 8 **Cempírek, J.,** Grew, E.S, Kampf, A.R., Ma, C., Novák, M., Gadas, P., Škoda, R., Vašinová–Galiová, M., Pezzotta, F., Groat, L.A., Krivovichev, S.V. (2016) Vránaite, ideally $Al_{16}B_4Si_4O_{38}$, a new mineral related to boralsilite, $Al_{16}B_6Si_2O_{37}$, from the Manjaka pegmatite, Sahatany Valley, Madagascar. *American Mineralogist* **101**, 2108–2117.

Candidate's contribution to the publication: *The candidate was the primary author and participated in the design of the research project, data acquisition and interpretation and drafting of the paper. Estimated contribution of the candidate is ca. 20%.*

Paper 9 Galliski, M.Á., Márquez–Zavalía, M.F., Lira, R., **Cempírek, J.,** Škoda, R. (2012): Mineralogy and origin of the dumortierite-bearing pegmatites of Virorco, San Luis, Argentina. *The Canadian Mineralogist* **50**, 873–894.

Candidate's contribution to the publication: *The candidate was the fourth author, and was invited to join the existing project. The candidate acquired part of the data, and significantly participated in data interpretation and drafting of the paper. Estimated contribution of the candidate is ca. 30%.*

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End of Supplements