

Synthetic $^{[4]}\text{B}$ -bearing dumortierite and natural $^{[4]}\text{B}$ -free magnesiodumortierite from the Dora-Maira Massif: differences in boron coordination in response to ultrahigh pressure

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Abstract: Dumortierite was synthesized in piston-cylinder experiments at 2.5–4.0 GPa, 650–700 °C in the $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$ (ABSH) system. Electron-microprobe (EMP) analyses reveal significant boron-excess (up to 0.26 $^{[4]}\text{B}$ per formula unit, pfu) and silicon-deficiency relative to the ideal anhydrous dumortierite stoichiometry $\text{Al}_7\text{BSi}_3\text{O}_{18}$. The EMP data in conjunction with results from single-crystal Raman spectroscopy and powder X-ray diffraction provide evidence that silicon at the tetrahedral site is replaced by excess boron via the substitution $^{[4]}\text{Si} \leftrightarrow ^{[4]}\text{B} + \text{H}$.

The Raman spectrum of synthetic dumortierite in the frequency region 2000–4000 cm^{-1} comprises eight bands, of which six are located at frequencies below 3400 cm^{-1} . This points to strong hydrogen bonding, most likely O2--H...O7 and O7--H...O2 , arising from a high number of octahedral vacancies at the Al1 site and substitution of trivalent Al^{3+} and B^{3+} for Si^{4+} at Si1 and Si2 sites, causing decreasing acceptor–donor distances and lower incident valence at the acceptor oxygen.

Contrary to the synthetic high-pressure ABSH-dumortierite, magnesiodumortierite from the Dora-Maira Massif, which is assumed to have formed at similar conditions (2.5–3.0 GPa, 700 °C), does not show any B-excess. Tourmaline shows an analogous behaviour in that magnesium-rich (e.g., dravitic) tourmaline formed at high pressure shows no or only minor amounts of tetrahedral boron, whereas natural aluminum-rich tourmaline and synthetic olenitic tourmaline formed at high pressures can incorporate significant amounts of tetrahedral boron. Two mechanisms might account for this discrepancy: (i) Structural avoidance of $^{[6]}\text{Mg--O--}^{[4]}\text{R}^{3+}$ configurations in magnesiodumortierite due to charge deficiency at the oxygens O2 and O7 and strong local distortion of M1 due to decreased O2–O7 bond length, and/or (ii) decreasing fluid mobility of boron in Al-rich systems at high pressures.

Key-words: dumortierite; magnesiodumortierite; Dora-Maira; ultrahigh-pressure (UHP); ABSH-system; synthesis; tetrahedral boron; Raman spectroscopy.

1. Introduction

According to Grew (1996), the Al-rich mineral dumortierite “is second only to dravite-schorl tourmaline as the most abundant borosilicate in aluminous metamorphic and metasomatic rocks”. Beside the most abundant components Al_2O_3 , B_2O_3 , SiO_2 , H_2O , dumortierite is known to incorporate many other elements as main constituents (e.g., Mg, Fe, Ti, Zr, Nb, Ta in the single chain of face-sharing octahedra; P, As, Sb, Bi at tetrahedral sites). Pieczka *et al.* (2013) suggested thirteen

different end-members in the dumortierite group to account for these major constituents and vacancies at octahedral sites.

The composition of dumortierite has long been considered as anhydrous with the structural formula $^{[6]}\text{Al}_7^{[3]}\text{B}^{[4]}\text{Si}_3\text{O}_{18}$. Moore & Araki (1978) were the first to take water (and octahedral vacancy) into account and proposed the formula $(\text{Al}_{6.75}\square_{0.25})\text{BSi}_3\text{O}_{17.25}(\text{OH})_{0.75}$. Werding & Schreyer (1990) synthesized dumortierite in the system $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$ (ABSH) between 0.3 to 2.0 GPa, 650 to 800 °C. Their analytical and

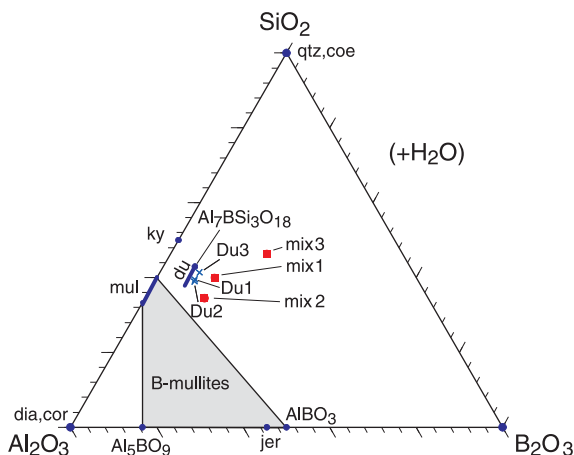


Fig. 1. Selected crystalline phases of the system $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2$ projected from H_2O . Also shown are solid starting compositions mix 1, mix 2, mix 3 of the experiments, and the compositions of the synthetic dumortierite Du1, Du2, Du3. Mix 3 also contained Li_2O (see Kutzschbach *et al.*, 2017b). Du represents the solid-solution range of dumortierites as determined by Werding & Schreyer (1990). Abbreviations: du, dumortierite; jer, jeremejevite; dia, diaspore; cor, corundum; mul, mullite; ky, kyanite; qtz, quartz; coe, coesite.

spectroscopic studies proved that dumortierite contains OH-groups according to two substitutions (1) $^{[4]}\text{Si} \leftrightarrow ^{[4]}\text{Al} + \text{H}$, mainly operative at low pressures, and (2) $^{[6]}\text{Al} \leftrightarrow 3\text{H} + ^{[6]}\square$ at high pressures. Considering both substitutions a general dumortierite formula can be given as: $^{[6]}\text{Al}_{7-x}^{[3]}(\text{BO}_3)^{[4]}(\text{Al}_y\text{Si}_{3-y}\text{O}_{18-3x-y})(\text{OH})_{3x+y}$, with $x > 0.1$ and $y < 0.5$. The solid-solution range of ABSH-dumortierite as determined by Werding & Schreyer (1990) is shown in Fig. 1, together with the end-member formula $\text{Al}_7\text{BSi}_3\text{O}_{18}$ for dumortierite (Pieczka *et al.*, 2013).

There is one threefold-coordinated site in dumortierite that is fully occupied by boron. Ono (1981) assumed that excess boron might also occupy the octahedral positions in dumortierite. This assumption has not been validated yet and seems to be rather unlikely due to the small ionic size of B^{3+} , whereas incorporation of boron at tetrahedral positions of dumortierite seems to be much more realistic. For example, taking tourmaline for comparison, boron is exclusively threefold-coordinated in most tourmaline formed at low pressure, whereas tourmaline containing significant amounts of $^{[4]}\text{B}$ is mostly known from environments exceeding pressure conditions of the lower crust and in Al-rich tourmaline like elbaite and olenite (e.g., Ertl *et al.*, 1997; Schreyer *et al.*, 2000; Lussier *et al.*, 2008). Investigations on B-coordination in natural low-pressure dumortierite using magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy (Evans *et al.*, 2012), X-ray absorption near-edge structure (XANES) at the boron *K*-edge (Fleet & Muthupari, 2000), and electron energy-loss spectroscopy (EELS) by Garvie *et al.* (1995), do not give any evidence for tetrahedrally coordinated boron. However, neither these methods nor B analysis by electron microprobe (EMP) has been applied to synthetic and natural dumortierite-group minerals that formed at high pressures.

This study is aimed to test the possibility of $^{[4]}\text{B}$ in synthetic high-pressure ABSH-dumortierite and natural magnesiodumortierite from the Dora-Maira Massif formed at ultra-high pressures (UHP). The incentive was a high-pressure synthesis of Li-bearing tourmaline at 4.0 GPa, 700 °C (Kutzschbach *et al.*, 2017b), in which the dumortierite by-product had a significantly smaller cell-volume than any of the ABSH-dumortierite obtained at lower pressures (Werding & Schreyer, 1990). For clarification, we performed EMP-analyses of dumortierite from this 4.0-GPa experiment and from new synthesis experiments in the ABSH system at 2.5 GPa, 650 °C – the latter *P-T* conditions are close to those suggested for magnesiodumortierite formation in the Dora-Maira Massif (2.5–3.0 GPa, 700 °C; Chopin *et al.*, 1995). All synthetic dumortierites show a significant boron-excess and silicon-deficiency relative to the $\text{Al}_7\text{BSi}_3\text{O}_{18}$ structural formula, suggesting silicon replacement at the tetrahedral site by excess boron via the substitution (3) $^{[4]}\text{Si} \leftrightarrow ^{[4]}\text{B} + \text{H}$. These results are then compared with and discussed in the light of new EMP analyses (including boron) of magnesiodumortierite from several localities in the UHP unit of the Dora-Maira Massif.

2. Sample material

2.1. Synthetic dumortierite of the ABSH-system

Dumortierite was synthesized in the ABSH-system in a piston-cylinder apparatus at 2.5 GPa, 650 °C in experiments lasting 28 days at the GFZ Potsdam. Two mixtures were prepared from the solid starting materials SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and H_3BO_3 , their compositions are plotted in Fig. 1. Mix 1 was weighed to correspond to the atomic ratio of the anhydrous dumortierite composition $\text{Al}_7\text{BSi}_3\text{O}_{18}$ and mix 2 had 30 mol% excess of Al relative to the $\text{Al}_7\text{BSi}_3\text{O}_{18}$ composition; both mixtures had 100 mol% excess of B. About 10 mg of the starting materials were loaded and welded shut in two gold capsules with dimensions 10 mm × 3 mm and 0.25 mm wall thickness together with 2 mg of distilled water. The two capsules were placed in a high-pressure cell of 1.27 cm diameter, consisting of a steel furnace and rock salt as pressure medium. Pressure was calibrated according the quartz $\leftrightarrow$ coesite transition (Mirwald & Massonne, 1980) and its uncertainty is ± 50 MPa. Temperature was monitored with a Ni–CrNi thermocouple placed close to the centre of the two capsules and the error is estimated to be ± 10 °C. At the end of the experiment, the sample was quenched isobarically to below 200 °C in less than 15 s prior to slow release of pressure. The capsules were cleaned and reweighed to check for leakage. Finally, the capsules were opened, the products were washed under doubly distilled water to remove any remaining boric acid or soluble quench phases, dried, and prepared for analysis by optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), EMP analysis, and Raman spectroscopy. In the following, dumortierite produced from mix 1 is referred to as Du1 and that from mix 2 as Du2.

Table 1. Summary of experiments, experimental products, and cell-dimensions of dumortierite.

No.	$P(\text{GPa})/T(^{\circ}\text{C})/t(\text{d})$	Start-mat.	Solid experimental products	$a(\text{\AA}), b(\text{\AA}), c(\text{\AA}), V(\text{\AA}^3)$
1	2.5/650/28	mix 1	Du1(96), Qtz(4)	11.761(2), 20.242(4), 4.6840(7), 1115.1(4)
2	2.5/650/28	mix 2	Du2(99), Cor(<1)	11.766(2), 20.235(4), 4.6843(6), 1115.2(4)
3	4.0/700/12	mix 3	Tur(68), Du3(28), Spd(3), Coe(1)	11.780(2), 20.190(4), 4.6842(6), 1114.1(3)

Du1, Du2, Du3 represent dumortierite from the three experiments, respectively. Abbreviations: Tur, tourmaline; Spd, spodumene; Coe, coesite; Qtz, quartz; Cor, corundum. Amount of experimental products (wt%) determined from Rietveld refinements. 2σ -uncertainties for lattice parameters are Rietveld-determined uncertainties multiplied by six.

In a recent study aimed at synthesizing Li-bearing tourmaline (Kutzschbach *et al.*, 2017b), dumortierite (here referred to as Du3) formed as a by-product in an experiment at 4.0 GPa, 700 °C, for 12 days in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, along with rossmanitic tourmaline and traces of spodumene and coesite (Table 1). Projected from Li_2O , the starting composition for this experiment (mix 3) is plotted in Fig. 1. For further experimental details we refer to Kutzschbach *et al.* (2017b). We present here new results of EMP-analysis and structural data from powder XRD of dumortierite Du3, which were not published in Kutzschbach *et al.* (2017b).

2.2. Natural high-pressure dumortierite-group material: magnesiodumortierite

Magnesiodumortierite is a member of the dumortierite group, which is only known definitely from the UHP-rocks of the Dora-Maira Massif, Italian Western Alps (Chopin, 1987; Schertl *et al.*, 1991; Chopin *et al.*, 1995; Ferraris *et al.*, 1995). Additionally, Mg-rich dumortierite (<0.5 Mg pfu) is described from the Bamble Sector, Norway, formed under medium-pressure conditions (Visser & Senior, 1991). The stability of magnesiodumortierite at upper-mantle conditions is in accordance with the experimental study of Werding & Schreyer (1996), who showed that dumortierite of the ABSH-system exhibits a huge pressure (P) – temperature (T) stability field extending from low P and T to at least 4.5 GPa at about 950 °C.

In magnesiodumortierite the single chain of face-sharing AlI octahedra is mainly occupied by Mg instead of Al, with an increased OH content compared to dumortierite (Ferraris *et al.*, 1995), possibly due to the substitution $[\text{Al}] \leftrightarrow [\text{Mg} + \text{H}]$ (Visser & Senior, 1991). Magnesiodumortierite occurs as an accessory mineral in the “pyrope quartzite” or “pyrope whiteschist” (*e.g.*, Chopin, 1984; Schertl *et al.*, 1991; Schertl & Schreyer, 2008; Grevel *et al.*, 2009) from which metamorphic coesite was first recorded. It occurs as rare inclusions in pyrope megablasts, in which it may coexist with ellenbergerite (Fig. 2), kyanite, rutile, clinocllore, talc and zircon. Magnesiodumortierite mostly forms anhedral crystals (up to 100 μm); a few euhedral crystals (up to 500 μm) are also observed. It is pleochroic, from pink to orange or brownish-red along c , colourless perpendicular to c . The coexisting ellenbergerite is also pleochroic, deep violet to colourless (Fig. 2). The intense colour of both phases is caused by $\text{Fe}^{2+}-\text{Ti}^{4+}$ charge transfer along the octahedral single chain common

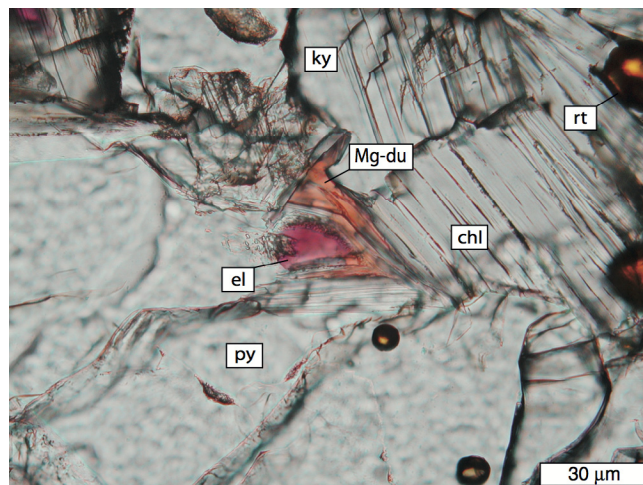


Fig. 2. Photomicrograph (plane-polarized light) of coexisting magnesiodumortierite (Mg-du) and ellenbergerite (el) inclusions in pyrope (py) from the Dora-Maira Massif, Western Alps, Italy (sample DM-du II). Further abbreviation: rt = rutile; ky = kyanite; chl = chlorite.

to both structures (Alexander *et al.*, 1986; Chopin & Langer, 1988; Platonov *et al.*, 2000). Magnesiodumortierite is known from at least four localities in the Dora-Maira UHP unit: Parigi (or Case Ramello), Tapina and Taiant (locality numbers 1, 5 and 7 in Schertl & Schreyer, 2008; their Fig. 2 and Table 1) as well as Pratoluogo (PL in Simon & Chopin, 2001). Two samples were reanalyzed here: DM-du I is sample 84DM04b = PL1 of Simon & Chopin (2001), from Pratoluogo; DM-du II (Fig. 2) is a new thin section of sample 15605b of Schertl *et al.* (1991, their Table 3b) which provided crystals VI and VIII in Chopin *et al.* (1995) from Parigi. The pyrope host in the latter sample is about 5 cm in size and is characterized by an unusually high amount (~2 vol%) of rutile inclusions.

3. Analytical methods

3.1. Powder X-ray diffraction

Powder XRD analyses were performed with a Stoe StadiP P diffractometer at the GFZ-Potsdam, operated at 40 kV and 40 mA, using $\text{CuK}\alpha_1$ radiation and a germanium (1 1 1) primary monochromator. The spectra were recorded in the 2θ range 5 to 125° with a detector step size of 0.1°, a 2θ resolution of 0.01°, and counting times of up to 20 s per step. Rietveld refinement was done using the GSAS

software package (Larson & Von Dreele, 1987). The initial structure parameters for dumortierite were taken from Alexander *et al.* (1986), using the average site-occupancies derived from the EMP-data (18 O basis, H₂O by difference, see Section 4.2.1). The initial structural parameters for the other identified phases were taken from the Inorganic Structure Database (ICSD, FIZ Karlsruhe).

3.2. Electron-microprobe analyses

The composition of the synthetic dumortierites was determined by EMP analysis using a JEOL Hyperprobe JXA-8500F equipped with a thermal field-emission cathode and five wavelength-dispersive spectrometers at GFZ-Potsdam. The operating conditions were 10 kV accelerating voltage, 5 nA beam current, 5 µm beam diameter. Counting times on the peaks/background were 20/10 s for Si, 30/15 s for Al and 80/40 s for B. A liquid-nitrogen cold trap was used to reduce effects of hydrocarbon contamination. The standards were natural schorl (B, Al) and natural orthoclase (Si). Data reduction was done with the a $\phi(\rho Z)$ correction scheme (CITZAF; Armstrong, 1995). Relative analytical errors (1σ) are ~1% for Si and Al and ~5% for B.

The composition of natural magnesiodumortierite from the Dora-Maira Massif was determined using the same microprobe with a beam diameter of 10 µm, 10 kV accelerating voltage, and 20 nA beam current. As standards we used natural schorl (B, Al), olivine (Si), diopside (Mg), rutile (Ti) and hematite (Fe). The acquisition times were 20 s for Ti, Al, Mg, 30 s for B, Fe, and 40 s for Si. Half of the peak acquisition time was used to collect the background level on both sides of the corresponding peak.

3.3. Polarized single-crystal Raman spectroscopy

Room-temperature spectra of synthetic dumortierite Du1 and Du2 were recorded at GFZ-Potsdam using a HORIBA Jobin Yvon LabRAM HR800 UV-VIS spectrometer with a grating of 1800 grooves/mm. The 488 nm line of a coherent Ar⁺ laser model Innova 70-3 with a power of 220 mW was used for excitation, which corresponds to about 30 mW on the sample. By using an Olympus objective (100×) with a numerical aperture of 0.8, the spot sizes were 3–5 µm. The inherent polarization of the excitation laser light is coincident with the y direction of the microscope stage (N–S direction), which allowed orientation-dependent measurements with the electric field vector, **E**, of the light parallel (**E** || *c*) and perpendicular (**E** ⊥ *c*) to the crystallographic *c* axis. Energy of the scattered photons was determined with a Peltier-cooled CCD detector at a resolution of about 1 cm⁻¹. Acquisition time for each spectrum was 30 s and 30 accumulations were performed for noise reduction. The region of the OH-stretching vibration was monitored between 2000 and 4000 cm⁻¹. Five spectral windows were required resulting in a total time of 75 min per measurement. To avoid

spectral contributions from the supporting medium, we placed the dumortierite crystals onto a KBr pellet. Blank measurements on the KBr pellet before and after the acquisition of the spectra proved that spectral contribution of remaining surface water was below the detection limit. After subtraction of background using a cubic spline function, the spectra were fitted with the program PeakFit by Jandel Scientific. Band shapes were approximated with pseudo-Voigt functions and the criterion for the maximum number of functions included in the fit was $\Delta I \leq I \cdot 0.5$, where *I* is the integrated intensity of a particular band in counts and ΔI its uncertainty. Fitting the spectra gave standard deviations (1 SD) for band position, integrated intensity (*I*) and full width at half maximum (FWHM). Error for the relative integrated intensity (*I*_{rel}) was calculated by error propagation. The *r*² value (goodness) of the individual fit for Du2 spectra is 0.9977 (**E** || *c*) and 0.9956 (**E** ⊥ *c*).

To further confirm the formation of dumortierite and absence of OH-bearing sassolite (H₃BO₃), we recorded additional Raman spectra in the frequency region 180–1200 cm⁻¹ using the same single crystals as for the spectra in the frequency region 2000–4000 cm⁻¹ and **E** || *c*.

4. Results

4.1. Powder XRD

As summarized in Table 1, the quantitative phase analysis of the two experiments at 2.5 GPa, 650 °C resulted in nearly single-phase dumortierite; additional phases were either quartz (4 wt%) formed from starting material mix 1, or traces of corundum (<1 wt%) from the Al-rich starting material mix 2. In the experiment performed at 4.0 GPa, 700 °C, dumortierite Du3 (28 wt%) was the second most abundant phase after tourmaline (68 wt%); small amounts of spodumene (3 wt%) and coesite (1 wt%) were also recognized (Table 1, see also Kutzschbach *et al.*, 2017b).

The orthorhombic cell-dimensions (space group *Pmcn*) of the synthetic dumortierite from this study are given in Table 1. The *b*₀/*a*₀-ratio deviates in all three samples from $\sqrt{3}$, which would indicate hexagonal lattice geometry (Moore & Araki, 1978). Generally, the cell-dimensions of the three high-pressure synthetic dumortierites are significantly smaller than those given for natural dumortierite and than those presented in Werdning & Schreyer (1990) for synthetic ABSH-dumortierite formed at lower pressures. For illustrating the latter point, the unit-cell volumes of synthetic low-pressure ABSH-dumortierite (Werdning & Schreyer, 1990) and from our study are plotted *versus* their EMP-determined Al/Si-ratios (data from Table 2) in Fig. 3. Obviously, the equation ($V_o = 2.6866 \cdot (\text{Al/Si}) + 1113.4$) given by Werdning & Schreyer (1990) for the positive correlation between *V*_o and Al/Si-ratio of dumortierite does not hold for the synthetic high-pressure dumortierite of this study, indicating that the difference must be sought in an additional compositional variable.

Table 2. Composition of natural magnesiodumortierite and synthetic dumortierite as derived from EMP analysis.

	Magnesiodumortierite from Dora-Maira				Dumortierite synthesized at 2.5–4 GPa and 650–700 °C					
	<i>n</i> = 8		<i>n</i> = 7		<i>n</i> = 20		<i>n</i> = 20		<i>n</i> = 2	
wt%	DM-du I		DM-du II		Du1		Du2		Du3	
B ₂ O ₃	5.97(35)		5.86(34)		7.93(48)		8.02(52)		7.91(45)	
MgO	7.53(37)		8.15(11)		–		–		–	
TiO ₂	3.27(30)		3.69(9)		–		–		–	
FeO	0.04(6)		0.17(5)		–		–		–	
Al ₂ O ₃	48.31(65)		45.58(25)		60.27(5)		60.40(48)		58.19(5)	
SiO ₂	31.58(50)		31.84(14)		26.90(79)		26.26(33)		28.37(71)	
H ₂ O	3.32(71) ^a		4.61(69) ^a		4.90(94) ^a		5.32(72) ^a		5.54(21) ^a	
Norm	18 O ^a	OH = 2	18 O ^a	OH = 2	18 O ^a	OH = 2	18 O ^a	OH = 2	18 O ^a	OH = 2
[4]										
B	0.00	0.00	0.00	0.00	0.25(8)	0.29(7)	0.26(8)	0.31(8)	0.24(7)	0.29(7)
Si	2.97(6)	2.98(3)	2.97(2)	3.05(2)	2.46(8)	2.53(7)	2.39(4)	2.48(4)	2.57(7)	2.68(6)
Al	0.00	0.00	0.00	0.00	0.29(10)	0.18(5)	0.35(8)	0.21(5)	0.19(1)	0.03(1)
[6]										
Al	5.36(8)	5.37(7)	5.01(5)	5.14(3)	6.19(8)	6.50(6)	6.15(8)	6.51(4)	6.03(1)	6.44(1)
Mg	1.06(5)	1.06(5)	1.13(2)	1.16(1)	–	–	–	–	–	–
Ti	0.23(2)	0.23(2)	0.26(1)	0.27(1)	–	–	–	–	–	–
Fe	0.00(0)	0.00(0)	0.01(1)	0.01(1)	–	–	–	–	–	–
Σ	6.65(8)	6.67(6)	6.42(7)	6.59(3)	6.19(8)	6.50(6)	6.15(8)	6.51(4)	6.03(1)	6.44(1)
□	0.35(8)	0.33(6)	0.58(7)	0.41(3)	0.81(8)	0.50(6)	0.85(8)	0.49(4)	0.97(1)	0.56(1)
Al _{tot}	5.36(8)	5.37(7)	5.01(5)	5.14(3)	6.48(8)	6.68(6)	6.48(8)	6.72(4)	6.22(1)	6.47(1)
B _{tot}	0.97(6)	0.97(5)	0.96(6)	0.98(5)	1.25(8)	1.29(7)	1.26(8)	1.31(8)	1.24(7)	1.29(7)
Si _{tot} + B _{tot}	3.94(9)	3.95(5)	3.93(8)	4.03(3)	3.71(10)	3.81(5)	3.65(8)	3.79(5)	3.81(0)	3.97(1)
H	2.08(44)	2.00	2.87(42)	2.00	2.98(55)	2.00	3.23(43)	2.00	3.35(12)	2.00

Numbers in brackets = standard deviation (1SD). Mean and standard deviation were calculated by averaging *n* individual analyses and cation assignments. Cations given in atoms per formula unit (pfu). Assignment is described in the Methods section.

^a water content calculated as difference to 100 wt%, valid for normalization to 18 O. P₂O₅, not analysed for magnesiodumortierite in this study, is about 0.02–0.31 wt% (Chopin *et al.*, 1995), *i.e.*, 0.00–0.03 P⁵⁺ pfu at the tetrahedral sites.

4.2. EMP analyses

4.2.1. Normalization scheme

Given the variable H₂O content and amount of vacancies, the calculation of a dumortierite formula in the absence of H₂O measurements is not possible, even when B content is measured. Therefore, Chopin *et al.* (1995) suggested to normalize on the basis of 18 O, a fully occupied B site and a fixed OH number of 2 pfu, resulting in 31 positive charges or BO₁₆(OH)₂ for the anionic part. To account for excess, tetrahedral B, we adapted this scheme by normalizing to 34 positive charges, *i.e.*, O₁₆(OH)₂ for the anionic part, yielding roughly constant H₂O contents of 3.13–3.19 wt% or 3.18–3.25 wt% if the oxide components are renormalized to a sum of 100 wt%. However, constant H₂O contents are unlikely because H₂O-free totals of the synthetic dumortierite (94.46–95.10 wt%) are lower than for the natural (magnesio)dumortierite (95.39–96.68 wt %), which are themselves low compared to most natural dumortierite. The small amount of P in magnesiodumortierite, not included in our EMP-analyses (0.02–0.31 wt% P₂O₅; Chopin *et al.*, 1995), would further increase the difference. Since H₂O is the only main component that has not been analyzed for, it is reasonable to assume that the

lower totals are due to higher water contents in the synthetic compared to the natural magnesiodumortierite. Therefore, we decided to use the difference of the analytical total to 100% as a measure of the H₂O content and 18 O as the calculation basis for the microprobe analysis, as it best reflects relative changes in H₂O contents. We acknowledge that this procedure could overestimate absolute H₂O contents; this is why the former calculation on the basis of O₁₆(OH)₂ pfu is also presented in parallel to the latter in Table 2. The alternative normalization scheme Si + B = 4 has not been tested as it does not allow for the possibility of tetrahedral Al.

After normalization the structural (magnesio)dumortierite formulae were obtained by assigning B to the trigonal B site. In case B_{tot} > 1.0 pfu, excess B was assigned to the tetrahedral site together with Si_{tot} and the remainder to 4 was filled with Al. The remaining Al and Ti, Fe and Mg were allocated to the octahedral sites; subtraction from 7 gives the amount of octahedral vacancies. In contrast to Ono (1981), we exclude the possibility of octahedral boron. The results of the two normalization schemes are compiled in Table 2, but due to the reasons pointed out above, we will only refer to the formulae resulting from the 18 O (H₂O by difference) scheme.

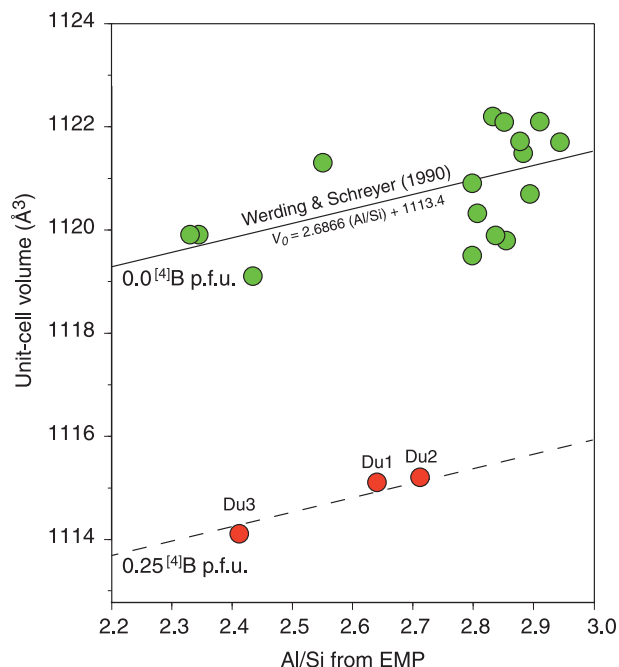


Fig. 3. Unit-cell volume versus Al/Si-ratio (EMP-determined) for dumortierite synthesized in the P - T -ranges 0.3–2.0 GPa, 650–880 °C (in green after Werdinger & Schreyer, 1990) and 2.5–4.0 GPa, 650–700 °C (in red, this study). The difference in the volumes (ΔV) corresponds to about 0.5%. The solid line is a least-squares fit (Werdinger & Schreyer, 1990), the dashed line is drawn parallel to the solid line to pass as close as possible to the three data points of Du1–Du3.

4.2.2. EMP-analyses of synthetic dumortierite

Dumortierite Du1 and Du2 generally form polysynthetically twinned crystals, which are commonly arranged as acicular, radial aggregates (Fig. 4). The texture strongly resembles that of synthetic tourmaline (e.g., Berryman *et al.*, 2015b) and thus might indicate a similar growth mechanism as described for the synthesis of olenitic tourmaline (Kutzbach *et al.*, 2017a; Schreyer *et al.*, 2000). The crystals are up to 40 μm in length parallel to the c -axis and generally 1–5 μm wide (Fig. 4); a few crystals up to a width of 10 μm were also observed, from which 20 reliable dumortierite EMP-analyses were taken from each sample. Backscattered-electron images indicate that the dumortierite crystals do not show any porosity or zonation. The Du3 dumortierite commonly forms inclusions in tourmaline and is generally less wide, not exceeding 5 μm (see Fig. 1 in Kutzbach *et al.*, 2017b). Therefore, for the fine-grained Du3 only two reliable EMP-analyses were obtained (Table 2).

The structural formula for the synthetic dumortierites are:

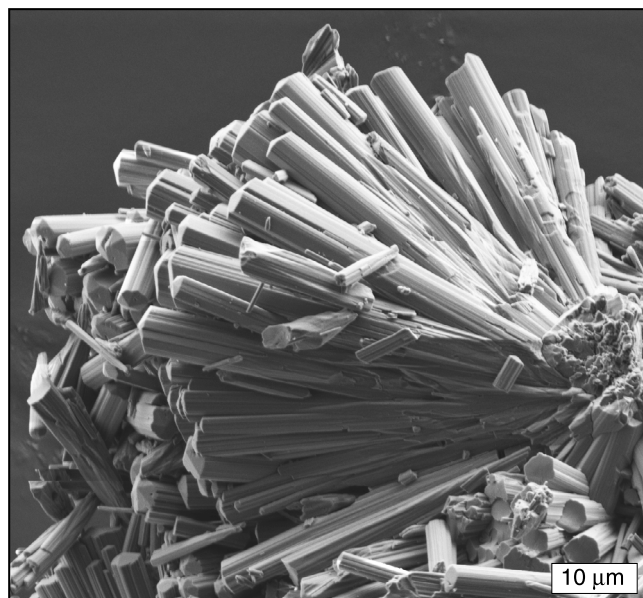
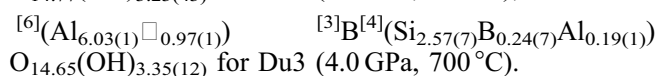
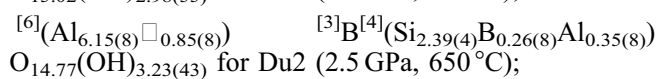
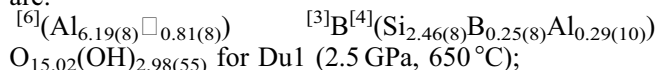


Fig. 4. Scanning electron microscope image of synthetic dumortierite (Du1). Note the polysynthetic twinning of the crystals along the c -axis resulting in pseudo-hexagonal cross-sections.

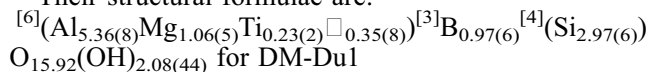
Compared to the theoretical water-free dumortierite composition $\text{Al}_7\text{BSi}_3\text{O}_{18}$, the synthetic dumortierites are depleted in SiO_2 and Al_2O_3 and have a significant excess of B_2O_3 (Fig. 1, Table 2).

Within the range of analytical errors, the compositions of Du1 and Du2 are nearly identical, whereas Du3, which was synthesized at higher pressures, has lower $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$ compared to Du1 and Du2. These results are consistent with the decreasing importance of substitution (1) $^{[4]}\text{Si} \leftrightarrow ^{[4]}\text{Al} + \text{H}$ and increasing importance of octahedral vacancies and of substitution (2) $^{[6]}\text{Al} \leftrightarrow 3\text{H} + ^{[6]}\square$ with increasing pressure (Werdinger & Schreyer, 1990). The unit-cell volumes (Table 1) of the three dumortierites ($\sim 1115 \text{ \AA}^3$ for Du1 and Du2; $\sim 1114 \text{ \AA}^3$ for Du3) reflect this chemical variation. Additionally, in all three dumortierite samples the amount of excess boron is nearly the same, about 0.25 B pfu. Considering the Si deficiency and the ionic radii, we assume that this excess boron is incorporated into the structure of synthetic ABSH-dumortierite at the tetrahedral site according to the new substitution (3) $^{[4]}\text{Si} \leftrightarrow ^{[4]}\text{B} + \text{H}$. The water contents of the synthetic dumortierite (2.98–3.35 H pfu or 4.90–5.54 wt% H_2O) in this study exceed the water contents reported in Werdinger & Schreyer (1990), who found 0.85 to 1.47 H pfu, corresponding to 1.32–2.30 wt% H_2O and are also higher than the water-content of natural dumortierite, which is generally below 2 wt% (Alexander *et al.*, 1986).

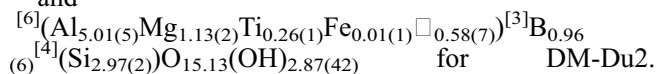
4.3. EMP-analyses of natural magnesiodumortierite

The magnesiodumortierite crystals from the two Dora-Maira localities have similar compositions. Within errors their B_2O_3 and SiO_2 contents are identical; DM-du II has slightly higher MgO , TiO_2 and FeO contents, whereas Al_2O_3 is higher in DM-du-I (Table 2).

Their structural formulae are:



and



Neither magnesiodumortierite sample contains excess boron or shows a deficiency in silicon. The analyses perfectly reproduce the main compositional range found in previous studies that used a combination of single-crystal XRD, EMP, and SIMS analyses (Ferraris *et al.*, 1995; Schertl *et al.*, 1991; Chopin *et al.*, 1995) with the exception of the Al content in DM-du II (45.58 wt%, 5.01 Al pfu), which is lower compared to the Al-poorest dumortierite analyses presented in Schertl *et al.* (1991) and Chopin *et al.* (1995) with 46.2 wt% (5.18 Al pfu) and 46.5 wt% (5.20 Al pfu) Al_2O_3 , respectively.

The single-crystal structure analysis of magnesiodumortierite (Ferraris *et al.*, 1995) showed a deficit of electrons at the tetrahedral T(2) site, which could be indicative of either tetrahedral R^{3+} -cations or partial vacancy. Our new EMP-analyses exclude any tetrahedral Al or B; additionally, if taking tetrahedral P^{5+} into account (not analysed in this study, Table 2), tetrahedral vacancies are not evident within the range of analytical uncertainties.

4.4. Polarized single-crystal Raman spectroscopy

For both frequency regions studied, the Raman spectra of Du1 and Du2 were identical within errors with respect to band positions and relative integrated intensities. Hence in the following, only the Raman spectra of Du2 are presented. The spectra of Du 1 are deposited as Appendix A1 (supplementary material linked to this article at <https://pubs.geoscienceworld.org/eurjmin/>).

Frequency region 180–1200 cm^{-1} . The band positions in the Raman spectra of the synthetic dumortierite (Du2) in this frequency region are in good agreement with those in the spectrum of a natural Mg-free and H_2O -free dumortierite from Minas Gerais, Brazil (Fig. 5), which was taken from the RRUFF database (Entry-Nr.: R050628). The most distinct difference is the pronounced intensity of two bands at $\sim 560 \text{ cm}^{-1}$ and $\sim 611 \text{ cm}^{-1}$, which are either very weak or absent in the natural dumortierite. The spectrum of natural sassolite (H_3BO_3) from Tuscany, Italy (RRUFF, Entry-Nr.: R060224), shows a very intense band at $\sim 880 \text{ cm}^{-1}$, which has not been detected in the spectrum of Du2 (Fig. 5).

Frequency region 2000–4000 cm^{-1} . The Raman spectrum with $\text{E} \parallel c$ comprises eight bands $\nu 1$ to $\nu 8$ in the order of increasing wavenumber (Fig. 6). Band positions, band widths, absolute and relative intensities are compiled in Table 3. The spectrum is marked by three intense bands (23.4–30.4% I_{rel}), located at 2926 cm^{-1} ($\nu 4$), 3319 cm^{-1} ($\nu 6$) and 3504 cm^{-1} ($\nu 7$) and five bands ($\nu 1$ at 2390 cm^{-1} , $\nu 2$ at 2513 cm^{-1} , $\nu 3$ at 2695 cm^{-1} , $\nu 5$ at 2926 cm^{-1} and $\nu 8$ at 3614 cm^{-1}) with significantly lower intensities (1.9–

6.9% I_{rel}). Whereas the highest frequency bands $\nu 7$ and $\nu 8$ are sharp (69 and 24 cm^{-1} FWHM), the bands below 3500 cm^{-1} appear rather broad ($130\text{--}260 \text{ cm}^{-1}$ FWHM).

The band position of the most intense band $\nu 7$ (at 3504 cm^{-1}) is consistent with a strong absorption band found in FTIR spectra of various natural dumortierite ($3493\text{--}3495 \text{ cm}^{-1}$; Fuchs *et al.*, 2005; Choo & Kim, 2003; Horn *et al.*, 2014). Similarly, the band $\nu 8$ at 3614 cm^{-1} has also been observed in FTIR spectra of natural dumortierite (Fuchs *et al.*, 2005; Horn *et al.*, 2014). However, in contrast, our Raman spectrum comprises six bands at frequencies below 3400 cm^{-1} , which have not been reported so far in any of the available FTIR studies of dumortierite.

If the orientation of E is chosen perpendicular to the c axis, all bands show a significant loss of absolute intensity, which varies from $\sim 40\%$ ($\nu 1$) to complete disappearance ($\nu 5$). The other bands show an intensity loss of $\sim 70\%$ to $\sim 90\%$.

5. Discussion

The frequency region of the OH-stretching vibration has proven to yield valuable crystal structure information especially in complex hydrous silicates such as amphiboles (e.g., Andrut *et al.*, 2000; Chen *et al.*, 2004; Leissner *et al.*, 2015; Hawthorne, 2016) and tourmalines (e.g., Watenphul *et al.*, 2016; Kutzschbach *et al.*, 2016; 2017b; Berryman *et al.*, 2015a; Fantini *et al.*, 2014). This is because the relative integrated intensity of a particular Raman band directly correlates with the probability of the cation configuration around the corresponding OH group (e.g., Fantini *et al.*, 2014; Berryman *et al.*, 2015a; Kutzschbach *et al.*, 2016; 2017b). Because the synthesis experiments used H_3BO_3 as starting material, an interpretation could be complicated due to the formation of OH-bearing sassolite. However, as evident from the comparison of Raman spectra of the frequency region $180\text{--}1200 \text{ cm}^{-1}$ (Fig. 5), it is reasonable to assume the absence of sassolite and, therefore, Raman bands observed in the frequency region $2000\text{--}4000 \text{ cm}^{-1}$ are assigned to dumortierite only.

In general, the position of Raman OH-stretching bands can be influenced directly by the charge of the cations coordinating the OH group (Gonzalez-Carreño *et al.*, 1988; Fuchs *et al.*, 2005) or indirectly by the formation of $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds (Bosi *et al.*, 2012; Skogby *et al.*, 2012; Kutzschbach *et al.*, 2016; 2017b). Previous studies on the dumortierite structure have concluded that O10, O2 and O7 are the most suitable sites for forming hydroxyl groups (Moore & Araki, 1978; Alexander *et al.*, 1986; Werding & Schreyer, 1990; Ferraris *et al.*, 1995; Cempírek & Novák, 2005; Fuchs *et al.*, 2005; Evans *et al.*, 2012; Evans & Groat, 2012). All other anion sites are most likely O^{2-} only (Evans & Groat, 2012).

The O10 site is coordinated by four Al4 and incorporation of OH at O10 requires the substitution of divalent cations for Al^{3+} for charge balance (Ferraris *et al.*, 1995; Evans & Groat, 2012). Due to the absence of divalent ions in the

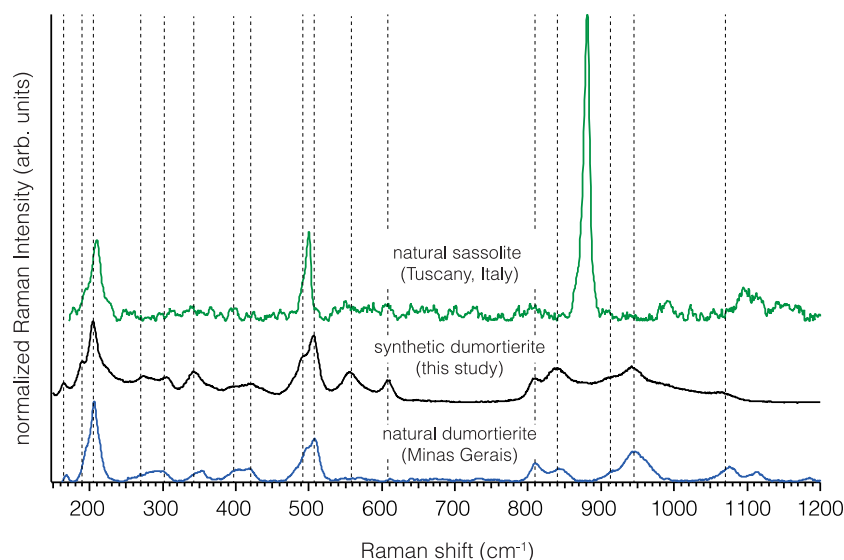


Fig. 5. Single-crystal Raman spectra of synthetic dumortierite Du2 recorded with the electric field vector $\mathbf{E}$ parallel ($\mathbf{E} \parallel c$) to the c axis of dumortierite in the frequency region of the lattice vibrations. Spectra of natural dumortierite (R050628) and sassolite (R060496) are taken from the RRUFF database (www.ruff.info). Raman intensities were normalized to the height of the band at $\sim 210 \text{ cm}^{-1}$. Dotted lines indicate band positions in the Du2 spectrum and serve as a guide to the eye.

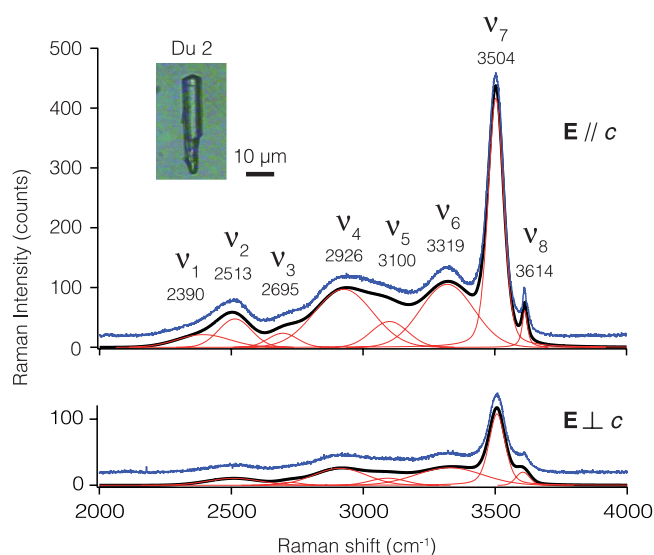


Fig. 6. Single-crystal Raman spectra of synthetic dumortierite Du2 recorded with the electric field vector $\mathbf{E}$ parallel ($\mathbf{E} \parallel c$) and perpendicular ($\mathbf{E} \perp c$) to the c axis of dumortierite in the frequency region of the OH-stretching vibrations. See Table 3 for the fitting parameters of the bands $\nu 1$ to $\nu 8$.

synthetic dumortierite of our study, we exclude the possibility that OH occupies O10. Remaining sites for OH are O2 and O7, which are both coordinated by two Al1 sites and either Si1 in case of O2 or Si2 in case of O7 (Fig. 7). Here, additional H serves as a charge balance for the substitutions $^{[6]}\text{Al} \leftrightarrow 3\text{H} + ^{[6]}\square$ and $^{[4]}\text{Si} \leftrightarrow \text{H} + ^{[4]}\text{R}^{3+}$. Octahedral vacancies in dumortierite are commonly restricted to the Al1 site (Evans & Groat, 2012). Because the Al1 octahedra are arranged parallel to the c -axis (Fig. 7), the

OH vector is expected to have a significant component parallel to the c -direction, which is in agreement with the pronounced loss of Raman intensity at $\mathbf{E} \perp c$ in our spectra (Fig. 6).

Assignment of bands $\nu 7$ and $\nu 8$ ($>3400 \text{ cm}^{-1}$). The location of bands $\nu 7$ at 3504 cm^{-1} and $\nu 8$ at 3614 cm^{-1} is consistent with absorption bands in infrared (IR) spectra of various natural dumortierites (Choo & Kim, 2003; Fuchs *et al.*, 2005; Horn *et al.*, 2014). Fuchs *et al.* (2005) assigned those bands on the basis of the sum of relative positive charges surrounding the O2 and O7 sites. A band at $\sim 3495 \text{ cm}^{-1}$ has been assigned by these authors to a nine-charge environment ($\text{Si}^{4+}\text{Al}^{3+}\text{R}^{2+}$; $\text{R}^{2+} = \text{Fe}^{2+}$, Mn^{2+} , Mg^{2+}). Due to the absence of R^{2+} cations in the synthetic dumortierite, a nine-charge environment could only be obtained by an $\text{Al}^{3+}\text{Al}^{3+}\text{R}^{3+}$ configuration. Given the occupancy of about $\square_{0.8}\text{Al}_{0.2}$ at the Al1 and $\text{Si}_{2.5}\text{R}^{3+}_{0.5}$ at the tetrahedral site (Table 2), the probability for a $\text{Al}^{3+}\text{Al}^{3+}\text{R}^{3+}$ configuration is only 0.67% (4% for $\text{Al}^{3+}\text{Al}^{3+}$ times 16.7% for R^{3+} at tetrahedral sites). Hence, this cation configuration is unlikely to account for the high relative integrated intensity (30.4%) of our band $\nu 7$. In contrast, the seven-charge cluster $\square\text{Al}^{3+}\text{Si}^{4+}$ has a comparable probability to occur (26.7%) and hence $\nu 7$ is assigned to this configuration. The same configuration had been assigned by Fuchs *et al.* (2005) to a band at $\sim 3675 \text{ cm}^{-1}$, which is absent in our Raman spectra (Fig. 6). Similarly, band $\nu 8$ is assigned to a $\square\text{Al}^{3+}\text{R}^{3+}$ configuration, whose low probability (5.3%) is compatible with the low relative integrated intensity of $\nu 8$ (1.9%).

Interestingly, Werding & Schreyer (1990) observed for both low- and high- P synthetic ($^{[4]}\text{B}$ -free) dumortierite only one IR absorption band at 3495 cm^{-1} in the OH-vibration range, which corresponds to $\nu 7$ in our spectra.

Table 3. Fitting parameters of the oriented single-crystal Raman spectra of Du2.

Band	Raman shift (cm ⁻¹)	SD ^a	FWHM (cm ⁻¹)	SD ^a	Intensity (counts)	SD ^a	<i>I</i> _{rel} (%)	± ^b
E c								
ν_1	2390	30	230	40	5000	2000	4.3	2.5
ν_2	2513	3	150	10	7000	3000	6.1	3.5
ν_3	2695	4	130	20	4000	2000	3.5	2.4
ν_4	2926	6	260	20	27000	4000	23.4	5.6
ν_5	3100	4	160	20	8000	3000	6.9	3.6
ν_6	3319	2	240	10	27000	2000	23.5	4.8
ν_7	3504	1	69	1	35000	400	30.4	5.2
ν_8	3614	1	24	1	2200	70	1.9	0.4
E ⊥ c								
ν_1	not detected							
ν_2	2510	3	240	10	2600	300	8.3	2.1
ν_3	2721	4	110	20	500	300	1.6	1.3
ν_4	2912	5	240	20	6000	1000	19.2	4.7
ν_5	3093	5	160	20	2000	1000	6.4	3.8
ν_6	3326	4	300	20	9000	1000	28.7	5.4
ν_7	3507	1	72	1	9900	300	31.6	4.9
ν_8	3604	1	61	1	1300	80	4.2	0.9

^a Standard deviation (1 SD) as derived from the fit.

^b Calculated by error propagation.

Again, due to the lack of R²⁺ cations in their experiments, this band may be assigned to the OH-stretching vibration of a □Al³⁺Si⁴⁺-configuration.

Assignment of bands < 3400 cm⁻¹. Due to their low frequency, the Raman bands ν_1 – ν_6 represent cation configurations enabling strong hydrogen bonding (Libowitzky, 1999). Evans *et al.* (2012) suggest that H at O2 and O7 form hydrogen bonds with adjacent under-bonded O2 and O7 acting as acceptors, respectively. The strength of the hydrogen bond increases with decreasing distance between acceptor and donor oxygen; given the correlations of Libowitzky (1999) for silicates only, for an OH band below 3400 cm⁻¹ the O2–O7 distance would have to decrease to 2.568–2.754 Å, compared to the O2–O7 distance of 2.793–2.800 Å as calculated by Alexander *et al.* (1986). Such a strong decrease in bond length would cause high local distortion around the Al1 site. Strong hydrogen bonding due to local distortion has been previously identified in other dumortierite-like minerals¹ based on the appearance of low-frequency infrared absorption bands, *e.g.*, at 2910 and 2500 cm⁻¹ in phosphoellenbergerite (Brunet & Schaller, 1996) or at 3046, 2186 and 2040 cm⁻¹ in magnesium hydrogen vanadate (Đorđević *et al.*, 2008). The location of the six Raman bands below 3400 cm⁻¹ in synthetic dumortierite might be similarly explained by local distortion caused by vacancies at the Al1 site. Distortion is expected to be highest in the proximity of (□□)-configurations, which appear with a probability of 64% (□_{0.8}Al_{0.2} at Al1). The sum of the relative integrated intensities of ν_1 – ν_6 (67.7%) is in good agreement with this value, which supports our hypothesis.

Hydrogen bonds are also strengthened by reducing the incident valence at the acceptor oxygen atoms. If Si⁴⁺ at Si1 or Si2 is substituted by a trivalent ion (Al³⁺ or B³⁺), the incident valence at the O2 or O7 decreases by 0.25 valence units (vu). Similar to dumortierite, tourmaline forms O3–H...O5 hydrogen bonds with O5 being attached to Si in the Si₆O₁₈ ring structure (Gatta *et al.*, 2014). Kutzschbach *et al.* (2016) have shown that substituting B³⁺ for Si⁴⁺ at the tetrahedral site in tourmaline causes a Raman shift of 130–160 cm⁻¹ at an O3–O5 distance of 3.0504 Å. Given a donor–acceptor distance in dumortierite of only 2.793–2.800 Å (Alexander *et al.*, 1986), the effect of tetrahedral B (or tetrahedral Al) in dumortierite is expected to be much greater. Due to the complexity of the dumortierite structure and the high number of Raman bands, an unambiguous assignment of bands ν_1 – ν_6 is not possible. Qualitatively however, the multitude of bands appearing below 3400 cm⁻¹ is probably related to strong hydrogen bonding due to local distortion at Al1 in combination with the substitution of Al³⁺ and B³⁺ for Si⁴⁺ at Si1 and Si2 sites.

Excess tetrahedral boron. The EMP analyses of the synthetic high-pressure dumortierite formed at 2.5–4.0 GPa, 650–700 °C in the ABSH-system show significant boron-excess and silicon-deficiency relative to the anhydrous Al₇BSi₃O₁₈ formula. Combined with the results from XRD- and Raman-analyses, we have strong indications for silicon replacement at the tetrahedral site by excess boron via the substitution ^[4]Si ↔ ^[4]B + H. Beside tourmaline, with the same exchange vector (Kutzschbach *et al.*, 2016) and kornrupine, whose *P*-stability significantly increases with the incorporation of boron via the substitution ^[4]Si + ^[6]Mg ↔ ^[4]B + ^[6]Al (Krosse, 1995), involving a change of the mineralogical terminology from kornrupine to prismatine for ≥0.5 B pfu (Grew, 1996), dumortierite is a further example for a

¹ A term defined by Evans & Groat (2012) for compounds isostructural to dumortierite or ellenbergerite

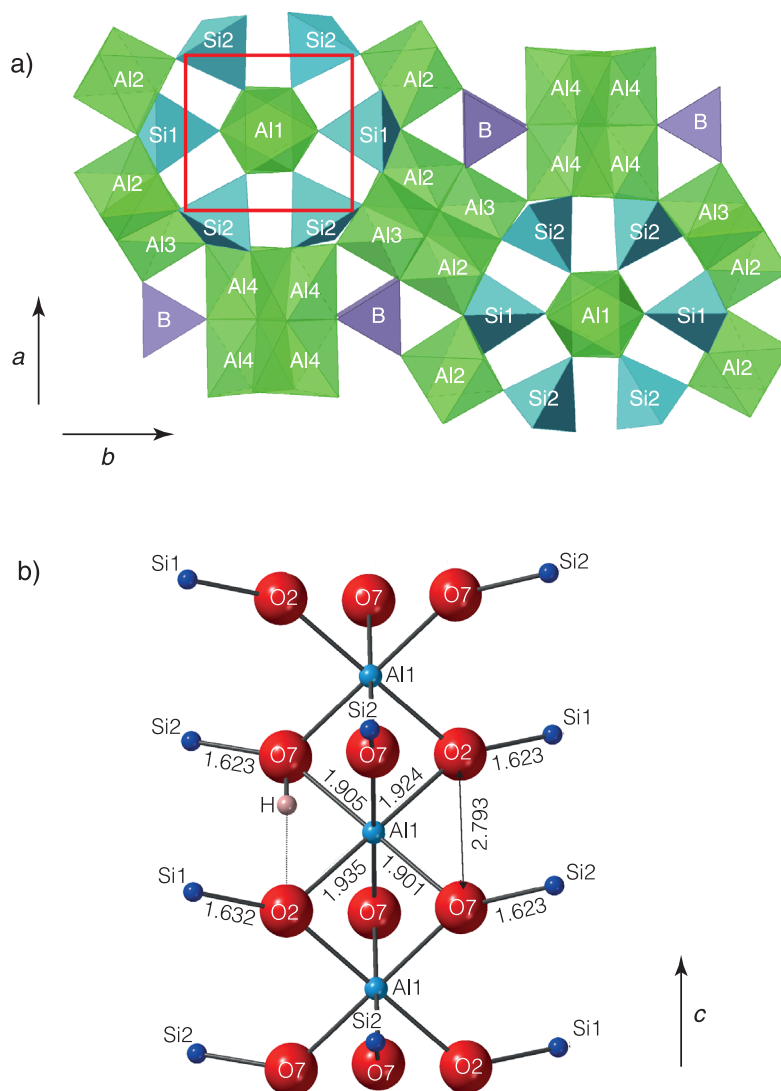


Fig. 7. a) Crystal structure of dumortierite viewed parallel to c . AlO_6 octahedra are arranged in single (Al1) and double chains parallel to the c -axis. b) Atomic arrangement around Al1 sites viewed perpendicular to the c -axis with H attached to O7. The region is also marked with a red square in a). O7 and O2 are the most likely sites for protonation (e.g., Evans & Groat, 2012), which is needed to charge balance vacancies at Al1 or trivalent cations that substitute for Si^{4+} at Si1 and Si2 sites. Adjacent O2/O7 act as acceptors for hydrogen bonds (dotted line). Distances are taken from the structure refinement of Alexander *et al.* (1986).

P -induced incorporation of tetrahedral boron. However, in contradiction to the rule of thumb that the coordination number generally increases with rising pressure (“pressure/coordination-rule”), for the four borosilicates kornepupine, prismaticine, dumortierite and tourmaline no P -induced phase transition occurs, and for the two latter phases the triangular $(\text{BO}_3)^{3-}$ -groups remain unchanged in both structures and only a small proportion of tetrahedral boron is added. Noteworthy is that, in analogy to prismaticine, the $^{[4]}\text{B}$ -bearing borosilicate reedmergnerite persists to much higher pressures than its chemical $^{[4]}\text{Al}$ -counterpart albite (Schreyer & Werding, 1997).

Boron isotopes strongly fractionate during geological processes and have the potential for modeling geochemical cycles (Marschall *et al.*, 2007; Konrad-Schmolke &

Halama, 2014). Atomistic calculations (e.g., Kowalski *et al.*, 2013) and experimental studies (e.g., Palmer *et al.*, 1992; Meyer *et al.*, 2008; Kutzschbach *et al.*, 2017c) have shown that the B isotope fractionation between solids and fluids not only depends on temperature but also on the B-coordination, whereby the lighter isotope (^{10}B) preferentially fractionates into the B-polyhedron of longer B–O bonds (i.e., the tetrahedral $(\text{BO}_4)^{5-}$ -group). Therefore, in high-pressure rocks that have dumortierite as the main B-bearing phase, boron at the tetrahedral site of dumortierite would have the effect to preferentially fractionate the heavy isotope ^{11}B into the coexisting fluid. It is unknown to what extent this effect is offset by an increased proportion of $^{[4]}\text{B}$ in the fluid as pressure increases (Kowalski *et al.*, 2013).

In contrast to the synthetic high- P ABSH-dumortierite reported here, magnesiodumortierite from the Dora-Maira Massif, which is assumed to be formed at similar high P - T -conditions (2.5–3.0 GPa, 700 °C; Chopin *et al.*, 1995), shows no B-excess. Again tourmaline shows a similar behaviour to dumortierite, in that magnesium-rich (e.g., dravitic) high- P tourmaline generally shows no (Krosse, 1995) or only minor amounts (Marschall *et al.*, 2004) of tetrahedral boron, whereas natural Al-rich tourmaline can incorporate up to 1.23 $^{[4]}\text{B}$ pfu (Ertl *et al.*, 1997) and synthetic olenitic tourmaline up to 2.53 $^{[4]}\text{B}$ pfu at high pressures of 4.0 GPa at 700 °C (Kutzschbach *et al.*, 2016). How to explain this discrepancy?

(1) Structural bond-valence constraints: In magnesiodumortierite Mg preferentially substitutes for Al at M1 (Ferraris *et al.*, 1995; Al1 site in Fig. 7a), which is bridged by O2 and O7 with tetrahedral positions T1 and T2 (Si1 and Si2 in Fig. 7b). A simultaneous occupation of Mg^{2+} at M1 and B^{3+} at T1 and/or T2 would lead to a strong local positive charge deficiency in the $^{[6]}\text{Mg-O-}^{[4]}\text{B}$ configuration, which might provoke an energetically unstable situation even if O is substituted by OH. The same structural restriction should hold for a $^{[6]}\text{Mg-O-}^{[4]}\text{Al}$ configuration, and indeed, no tetrahedral Al was determined in magnesiodumortierite (Scherl *et al.*, 1991; Chopin *et al.*, 1995; this study). Similar structural short-range considerations have been made for tourmaline (e.g., Ertl *et al.*, 2008) to explain the lack of tetrahedral boron in Al-poor tourmaline.

Magnesiodumortierite also contains significant amounts of TiO_2 (up to 3.69 wt% or 0.26 Ti^{4+} pfu, Table 2), which should also occupy the M1 position (Ferraris *et al.*, 1995). One could argue that the presence of highly charged Ti^{4+} in magnesiodumortierite counteracts the above given effect and would allow for $^{[6]}\text{Ti-O-}^{[4]}\text{R}^{3+}$ configurations. However, as Ti-incorporation should proceed via the coupled substitution $^{[6]}\text{Al} + ^{[6]}\text{Al} \leftrightarrow ^{[6]}\text{Mg} + ^{[6]}\text{Ti}$ (Chopin *et al.*, 1995), again unstable $^{[6]}\text{Mg-O-}^{[4]}\text{R}^{3+}$ configurations would be involved.

(2) Decreased fluid-mobility of boron in Al-rich systems at high P : In most chemical systems boron tends to strongly partition into fluid during fluid–rock interaction processes (e.g., Motti & Holland, 1978). However, experimental studies have shown (e.g., Stachowiak & Schreyer, 1998) that in Al-rich systems boron becomes decreasingly fluid-mobile with rising P and decreasing T . Thus the increasing compatibility of boron might trigger the incorporation of tetrahedral boron into the Al-rich phases dumortierite and olenite at high pressures and explain the lack of tetrahedral boron in magnesiodumortierite and dravite, despite their UHP origin. Experimental studies on solubilities and fluid B-speciation in chemically complex systems at high pressures are readily not available, however, strongly needed for verification of this tentative assumption.

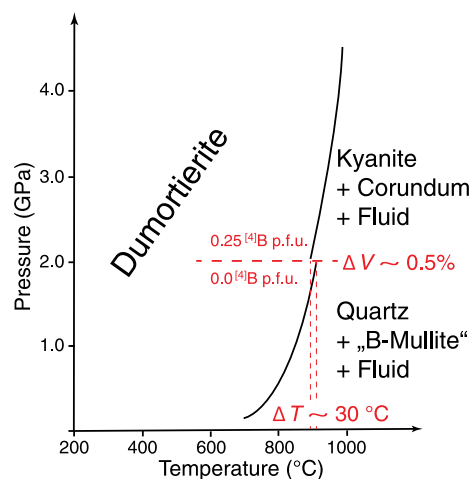


Fig. 8. P - T -stability field of dumortierite modified after Werding & Schreyer (1996). They observed a discontinuity in the equilibrium curve at ~ 2.0 GPa. At this pressure dumortierite changes composition from $^{[4]}\text{B}$ -free to a dumortierite with 0.25 $^{[4]}\text{B}$ pfu, which is accompanied with a V -decrease of about 0.5% (Fig. 3). For further discussion see text.

At a pressure of about 2.0 GPa the experimentally determined P - T -stability of dumortierite (Fig. 8) shows a shift in the equilibrium curve of about 30 °C. Werding & Schreyer (1996) argued that this anomaly stems from different water-activities in experiments performed with low and high $\text{B}_2\text{O}_3/\text{H}_2\text{O}$ ratios below and above 2.0 GPa, respectively. Interestingly, this discontinuity correlates with the first occurrence of tetrahedral boron in dumortierite associated with a unit-cell volume reduction of about 0.5% in dumortierite (Fig. 3). A changed composition of dumortierite has the effect of changing the reaction stoichiometry of the equilibrium dumortierite = kyanite + corundum + B-bearing fluid (Fig. 8). Unfortunately, Werding & Schreyer (1996) did not present chemical analyses nor cell-dimensions for dumortierite of their experimental study. The lack of thermodynamic data for ($^{[4]}\text{B}$ -bearing) dumortierite and the unknown composition of the fluid involved in this reaction require future experimental studies for clarification of the observed discontinuity.

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