

Using estimated thermodynamic properties to model accessory phases: the case of tourmaline

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ABSTRACT Accessory phases and minor components in minerals are commonly ignored in thermodynamic modelling. Such an approach seems unwarranted, as accessory phases can represent a significant element reservoir and minor components can substantially change their host mineral's stability field. However, a lack of thermodynamic data prohibits assessment of these effects. In this contribution, the polyhedron method is used to estimate the thermodynamic properties of tourmaline, a common and widespread accessory phase, stable over a range of P – T – X conditions. The polyhedron method allows ΔH , S , V , C_P and $V_m(T, P)$ properties to be estimated from a linear stoichiometric summation over the fractional properties of its polyhedron constituents. To allow for estimates of tourmaline, fractional thermodynamic properties for B^{III} and B^{IV} polyhedra were derived. Mixing contributions to molar volume were evaluated and symmetrical mixing parameters derived for Al–Mg, Al–Fe and Al–Li interaction on tourmaline's Y-site and T-site Al–Si interaction. Evaluation of the estimated properties using experimental and natural equilibria between tourmaline and melts, minerals and hydrothermal fluids, shows that reliable semi-quantitative results are obtained. The boron contents in fluids coexisting with tourmaline are calculated to within an order of magnitude of measured content, and where anchor-points are available, agreement improves to within a factor of 2. Including tourmaline in petrogenetic modelling of metamorphic rocks indicates that its presence leads to disappearance of staurolite and garnet, among others, and modifies the X_{Mg} of coexisting phases, in line with observations on natural rocks.

Key words: accessory phases; petrogenetic modelling; polyhedron method; thermodynamic properties; tourmaline.

INTRODUCTION

Thermodynamic modelling of minerals, melts and fluids is an increasingly important tool in petrology, geochemistry and other disciplines of the earth sciences for modelling and constraining the physical and chemical conditions of equilibrium in a variety of environments. Thermodynamic properties are now well constrained for the majority of common rock-forming minerals (e.g. Berman & Aranovich, 1996; Holland & Powell, 1998), as well as for the majority of fluid species, both at atmospheric conditions and in supercritical fluids (e.g. SupCrt98; Johnson *et al.*, 1992). There have also been recent advances in describing melts in terms of their thermodynamic properties with the models of Ghiorso *et al.* (2002) and White *et al.* (2001). More extensive and accurate mixing models for mineral solid solutions have accompanied the increase and optimization of thermodynamic properties, allowing for modelling of more subtle dif-

ferences in P – T – X at a higher resolution. This resolution increase has some side effects; factors that previously lacked significance can now have a strong impact on modelling results. For example, the presence of zoned minerals with low diffusion rates can modify the effective bulk composition in reactions, shifting equilibria and compositional isopleths in pseudo-section calculations (Evans, 2004). Furthermore, minor mineral components and accessory phases that were previously ignored might have a significant impact in terms of reaction positions and compositional isopleths. Improving thermodynamic modelling of natural systems by incorporating these factors is thus highly desirable. Although the impact of changing bulk-rock compositions during progressive mineral growth has recently been considered (e.g. Evans, 2004), the effects of accessory phases and sequestration of minor constituents into minerals are more difficult to evaluate because of the lack of data.

Direct measurement of thermodynamic properties for accessory minerals and substitution of minor elements into phases are practically and technically challenging. Because of these difficulties, methods have been devised to estimate the thermodynamic properties

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of minerals and use these estimates to assess the impact of minor constituents on mineral stability, and the effects of accessory phases on phase relations. The most versatile and extensive estimation scheme currently available is based on a linear stoichiometric summation of the fractional thermodynamic properties of elements in a specific coordination configuration (i.e. for the entropy of forsterite: $S_{\text{Mg}_2\text{SiO}_4} = S_{\text{Si}}^{\text{tet}} + 2S_{\text{Mg}}^{\text{oct}}$; Robinson & Haas, 1983; Chermak & Rimstidt, 1989; Holland, 1989). We recently extended and updated these models, exploiting new and better data on mineral properties, which allow modelling of a wider range of mineral compositions (van Hinsberg *et al.*, 2005a,b). A new treatment of (partially) OH-coordinated sites further improves the polyhedron method.

This study extends our original model to encompass boron, to estimate the thermodynamic properties of end-members of the tourmaline mineral group. Tourmaline is a common accessory phase in rocks of widely varying bulk-rock composition, geotectonic setting and P – T – X (Morgan & London, 1989; Henry & Dutrow, 1996; Werding & Schreyer, 1996; Kawakami, 2001). Because of its widespread occurrence and extensive compositional range, tourmaline has been proposed to be an ideal indicator mineral for the P – T – X conditions in its host environment (Henry & Guidotti, 1985; Henry & Dutrow, 1996). The sensitivity of tourmaline to changes in P – T – X also makes it a desirable mineral to include in thermodynamic modelling, because, not only will it influence mineral parageneses and reactions because of the uptake of elements and exchange with co-existing phases, but matching modelled and measured tourmaline composition will also yield information on the conditions prevailing in its host environment.

APPROACH

The method applied here follows the same essential approach as that used by Garofalo *et al.* (2000), in determining the fractional properties for boron polyhedra from a set of published thermodynamic properties for boron silicates. Tourmaline end-members are subsequently reconstituted from the partial properties of B and other cations. Garofalo *et al.* (2000) used the data sets of Robinson & Haas (1983), Chermak & Rimstidt (1989) and Holland (1989) for constituents other than B. Here the polyhedron model of van Hinsberg *et al.* (2005a,b) is employed, which is an extended and improved version of these original polyhedron data sets and benefits from a modified treatment of the OH groups. Using this model allows a wider range of data to be included in deriving partial properties for boron polyhedra as well as a more accurate consideration of OH in the tourmaline crystal structure.

Fractional properties for B^{III} and B^{IV} were derived from a multiple linear regression analysis on the residual thermodynamic properties remaining from

subtracting stoichiometric contributions for the other cations. Thermodynamic data for boron silicates are limited, with the exception of data for molar volume, which are available as unit-cell volumes derived from the Rietveld structure refinement on tourmaline grains. However, Rietveld refinement-derived unit-cell volumes are sensitive to the choice of elements modelled at each site and this varies among the different data sources, given that site occupancy, element site preferences and substitutions in tourmaline are still a matter of debate (Hawthorne *et al.*, 1993; Pieczka, 1999; Hughes *et al.*, 2000; Hawthorne, 2002). Redistribution of elements over sites is not a possibility, because this would result in a different molar volume from the refinement. To minimize element distribution effects, data sources were selected that use similar element site assignments and it is further assumed that the fractional molar volume of the boron polyhedra are significantly larger than any effects from varying refinement settings.

Molar volume

A database of 96 published tourmaline molar volumes was assembled, for which site occupancies are available (Table S1), supplemented with molar volume estimates for other B-bearing silicate minerals; grandierite and werdingite minerals for trigonal B, and a variety of minerals for tetrahedral B (Table S2). Including these minerals is especially beneficial because their B^{IV} content is substantially higher than in tourmaline, thus enhancing estimates of the fractional molar volume of tetrahedral B. Although volume data for dumortierite are available in the literature, the presence of partially OH-coordinated Si (Moore & Araki, 1978) is incompatible with the choice of polyhedra in van Hinsberg *et al.* (2005a) and this mineral was therefore excluded. B-bearing minerals containing Cl, S or C were similarly discarded, as was axinite, which contains Ca that is partially coordinated by OH.

The V and W anion sites of the tourmaline in the database (using the general tourmaline formula $\text{XY}_3\text{Z}_6\text{T}_6\text{O}_{18}(\text{BO}_3)_3\text{V}_3\text{W}$; Hawthorne & Henry, 1999) are not completely filled by OH, indicating that some of the elements at the Y and Z sites would, strictly speaking, be in a complete O coordination, rather than being partially OH-coordinated (i.e. the OHO component of van Hinsberg *et al.*, 2005a). However, this is only the case if O^{V} and O^{W} are localized and their ordered presence sufficiently disturbs the structure to change the fractional properties of the elements in the Y and Z sites. We rather suspect O on the V and W sites to be disordered, so that the Y and Z sites can be regarded as OHO-coordinated throughout, except when O contents are high. Because all tourmaline in the data set has more than 2.9 cpdf OH + F at the V + W sites, and sites are still OHO-coordinated even when the W site is fully occupied by O, excess O content is not a problem

here. The only exception is Ti^{4+} , which is assumed to be coordinated fully by O to accommodate the additional positive charge at sites normally occupied by divalent and trivalent cations.

Dividing the minerals in the data set into their respective polyhedra leaves five unknown components for tourmaline (V^{OHO} , Zn^{OHO} , Cr^{OHO} , B^{III} and B^{IV}) and a further seven for the other B-bearing silicates (Al^{V} , Mg^{V} , Fe^{V} , Mn^{V} , Ba^{VI} , Pb^{VI} and Sr-multi, which represents Sr in a more than six-coordinated configuration). These latter components as well as Zn^{OHO} and V^{OHO} were independently constrained using the FACTSAGE 5.1 computer package (Bale *et al.*, 2002), or estimated in the case of five-coordinated Mg, Fe and Mn (Table 1). Because of the large number of Cr^{OHO} estimators in the database, this component was regressed along with B^{III} and B^{IV} . Regression analyses were performed using multiple linear weighted regression, where weight factors were derived from the error on the calculated molar volume plus the propagated error from the fractional properties taken from van Hinsberg *et al.* (2005a).

Because the minerals used here are not end-member compositions, a non-ideal mixing contribution to their respective molar volume can be expected. To assess the importance of this contribution, mixing terms were calculated for the X, Y, Z and T sites, assuming symmetrical interactions among elements on these sites. Running an iterative exclusion routine during regression on the data, following a multivariate variable pre-selection, identified statistically significant mixing terms. The initial pre-selection step was implemented to identify the mixing contributions with the strongest impact on improving the goodness of fit of the regression, and avoids artefacts in the subsequent iterative exclusion routine because of inclusion of overly numerous non-significant variables. Significant mixing variables were included during regression of Cr^{OHO} , B^{III} and B^{IV} components, so that fractional molar volumes and mixing contributions were regressed together in the final run.

Enthalpy, entropy, heat capacity and $V_m(T,P)$

The data sources available to constrain boron polyhedra in terms of fractional enthalpy, entropy, heat capacity and thermal expansion are limited. For trigonal B there are only two ΔH and S measurements that can be used, albeit both of tourmaline (Kuyunko *et al.*, 1984; Ogorodova *et al.*, 2004). Heat capacity data are available for these tourmalines and have been supplemented with data from Hemingway *et al.* (1996). Data for reedmergnerite and danburite (the B equivalent of albite and anorthite respectively), as reported by Anovitz & Hemingway (1996), were used to constrain the fractional properties of B^{IV} . In contrast to the method of Garofalo *et al.* (2000), data for dumortierite (Hemingway *et al.*, 1996) cannot be included given the presence of H in the Si-ring. The incompatibility of these data is clear when ignoring this H content, because partial properties of B are distinctly different. Magnetic terms were removed from the measured properties to derive the pure vibrational contribution. A disorder correction was further applied to entropy to account for non-end-member composition, assuming full disorder at all sites (c.f. Hawthorne, 2002 for the Y and Z sites). To correct for the presence of Zn in the Hemingway *et al.* (1996) tourmaline, fractional properties of Zn^{OHO} were estimated from the properties of Zn^{VI} and the average difference between octahedral and OHO components for Mg, Fe and Mn. Although such an estimate has a higher associated uncertainty, it is to be preferred to ignoring Zn altogether. The presence of F was accounted for by calculating a F-free equivalent from exchange with phlogopite, assuming $\Delta H_{\text{reaction}} = 0$ and $\Delta S_{\text{reaction}} = 0$ (c.f. van Hinsberg *et al.*, 2005a). Thermal expansion data were taken from Hemingway *et al.* (1996) and Anovitz & Hemingway (1996). No data are available for estimates of the fractional compressibility of B polyhedra as the composition of minerals for which compressibility data are given is not reported (e.g. Anovitz & Hemingway, 1996).

Table 1. Constraining minerals for extra polyhedra components in molar volume regression, and their fractional properties as well as 1-sigma uncertainty.

Mineral	Formula	Poly.	V_f (J bar ⁻¹)	Error
Uvarovite	$\text{Ca}_3^{\text{multi}}\text{Cr}_2^{\text{VI}}\text{Si}_3^{\text{IV}}\text{O}_{12}$	Cr^{VI}	0.95	0.39
Kosmochlor	$\text{Na}^{\text{multi}}\text{Cr}^{\text{VI}}\text{Si}_2^{\text{IV}}\text{O}_6$	Cr^{VI}		
Krinovite	$\text{Na}^{\text{multi}}\text{Mg}_2^{\text{VI}}\text{Cr}^{\text{VI}}\text{Si}_3^{\text{IV}}\text{O}_{10}$	Cr^{VI}		
Zincsilite	$\text{Zn}^{\text{OHO}}\text{Si}_3^{\text{IV}}\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O}$	Zn^{OHO}	1.97	0.18
Tivanite	$\text{V}^{\text{OHO}}\text{Ti}^{\text{VI}}\text{O}_3(\text{OH})$	V^{OHO}	2.51	0.33
V-carpholite	$\text{Mn}^{\text{OHO}}\text{V}^{\text{OHO}}\text{Al}^{\text{OHO}}\text{Si}_2^{\text{IV}}\text{O}_6(\text{OH})_4$	V^{OHO}		
Mukhinite	$\text{Ca}^{\text{multi}}\text{Al}_2^{\text{VI}}\text{V}^{\text{OHO}}\text{Si}_3^{\text{IV}}\text{O}_{12}(\text{OH})$	V^{OHO}		
Andalusite	$\text{Al}^{\text{V}}\text{Al}^{\text{VI}}\text{Si}^{\text{IV}}\text{O}_5$	Al^{V}	1.95	0.12
Sr-Ti-oxide	$\text{Sr}_2^{\text{multi}}\text{Ti}^{\text{VI}}\text{O}_4$	Sr^{multi}	0.42	0.14
Sr-Ti-oxide	$\text{Sr}_2^{\text{multi}}\text{Ti}^{\text{VI}}\text{O}_3$	Sr^{multi}		
Ba-silicate	$\text{Ba}_2^{\text{VI}}\text{Si}^{\text{IV}}\text{O}_4$	Ba^{VI}	2.12	0.05
Margarosanite	$\text{Pb}^{\text{VI}}\text{Ca}_2^{\text{VI}}\text{Si}_3^{\text{IV}}\text{O}_9$	Pb^{VI}	1.99	0.13
Estimated from	$\text{Mg}^{\text{IV}}\text{-Mg}^{\text{VI}}$	Mg^{V}	2.20	0.29
Estimated from	$\text{Fe}^{\text{IV}}\text{-Fe}^{\text{VI}}$	Fe^{V}	2.63	0.42
Estimated from	$\text{Mn}^{\text{IV}}\text{-Mn}^{\text{VI}}$	Mn^{V}	2.82	0.42

EVALUATION OF MOLAR VOLUME REGRESSION ANALYSIS

A comparison among calculated fractional molar volumes of Cr^{OHO} , B^{III} and B^{IV} for different regression scenarios, shows limited variation. The B^{III} and B^{IV} values calculated from tourmaline only are 1.57 ± 0.04 and $1.39 \pm 0.33 \text{ J mol}^{-1} \text{ bar}^{-1}$; whereas, the values, calculated from all minerals excluding tourmaline are 1.66 ± 0.74 and $1.46 \pm 0.83 \text{ J mol}^{-1} \text{ bar}^{-1}$ respectively. Calculated from the full data set, values 1.55 ± 0.03 , 1.25 ± 0.08 and $1.79 \pm 0.10 \text{ J mol}^{-1} \text{ bar}^{-1}$ for B^{III} , B^{IV} and Cr^{OHO} respectively are obtained. Excluding minerals with elements in fivefold coordination does not result in a significant change in regressed parameters, which suggests that the values for five-coordinated elements are reasonable estimates. The good agreement between regressed values from analyses on varying data sets, indicates that the data are robust and further do not depend disproportionately on individual data points.

The multivariate variable selection routine revealed a sharp increase in goodness of fit for an initial set of 24 mixing parameters. In order to further constrain the number of variables, only components of major elements were taken into account, ensuring a sufficient number of estimators per component. This procedure indicates that only four mixing variables contribute significantly to the molar volume: Al-Mg, Al-Li and Al- Fe^{2+} at the Y-site, and Al-Si at the T-site. Given that these element pairs are also important substitutions in the tourmaline structure lends credence to this result, because mixing contributions for molar volume will be crystallography-controlled (i.e. these substitutions have an effect on lattice site size and morphology, thereby influencing the occupancy of adjacent sites). Interestingly, Fe-Mg mixing was not significant in the regression and completely lacks any correlation with molar volume residuals.

Re-running the regression analysis with all minerals included and the four mixing parameters listed above results in the final properties given in Table 2. The increase in the R^2 -value between the regression without and with mixing parameters is small (i.e. 0.971 to 0.978), indicating that the mixing contribution is

limited. All components are significant in this final run, and, although the gain in goodness of fit is small, the residuals are more evenly distributed. Checking the various assumptions made in the regression analysis (e.g. Montgomery & Peck, 1982) shows no violations of these assumptions, with residuals normally distributed, no bias or systematic behaviour in residuals and variance inflation factors of < 1.5 .

ΔH , S , C_p AND $V_M(T)$ DATA

Calculation of fractional properties for the other thermodynamic properties is more straightforward because of the limited data set. Calculated values of enthalpy and entropy for B^{III} are highly similar for the two tourmaline minerals, especially when the differences in composition between these are taken into account, which is promising. The value for the fractional entropy is negative as a result of a strong disorder contribution, which also explains why it deviates from estimates by Garofalo *et al.* (2000). Although mathematically this negative value is not a problem in the polyhedron method, it is counterintuitive, and may indicate non-ideal mixing contributions to entropy or (partial) ordering on the sites. Full disorder will thus need to be assumed when reconstituting tourmaline minerals from these data, and this assumption may affect the applicability of the trigonal B data to other B-silicates. Fractional properties for B^{IV} are in good agreement for the various data of danburite and reedmergnerite (Table 3). Heat capacity values for the fractional properties are similar up to about 900 K; at higher temperatures they start to deviate between estimators (Fig. 1a). This divergence probably results from calculations at temperatures exceeding those for which C_p coefficients were originally fit. Overall, trigonal B contributions to heat capacity are small. Thermal expansion curves show good agreement among the various minerals, both in values and in slope (Fig. 1b).

CALCULATION OF TOURMALINE PROPERTIES

Using the final fractional properties for trigonal and tetrahedral B (Table 3), along with polyhedra properties derived earlier allows calculation of the thermodynamic properties of tourmaline end-members. This has been done for the dominant end-members as listed by Hawthorne & Henry (1999) and the results are given in Table 4. Reported values are corrected for magnetic contributions as well as mixing for molar volume and entropy. ΔG_f^0 values were calculated from estimated enthalpy and entropy, after being corrected for the entropy of the elements. The reported uncertainties are pure propagated error. Only the OH and O end-members have been calculated, although their F-equivalents can be calculated by exchange with, for example, phlogopite (see above). Heat capacity values were fitted to $C_p = a + bT + cT^{-2} + dT^{-0.5}$, and

Table 2. Fractional molar volumes for the B^{III} , B^{IV} and Cr^{OHO} polyhedra, and symmetrical mixing contributions to molar volume. Errors reported are the 1-sigma error propagated uncertainty.

Fractional	V (J bar^{-1})	Error
B^{III}	1.47	0.05
B^{IV}	1.27	0.07
Cr^{OHO}	1.89	0.10
Mixing contributions on V		
Al ^Y -Mg ^Y	5.05	2.33
Al ^Y -Fe ^Y	3.73	1.57
Al ^Y -Li ^Y	5.77	1.61
Si ^T -Al ^T	-12.33	4.22

Table 3. Fractional thermodynamic properties for the trigonal and tetrahedral B polyhedra and their associated 1-sigma uncertainty.

Fractional	B ^{III}	Error	B ^{IV}	Error
ΔH	-376 319	64 241	-662 240	21 139
S	-3.24	11.94	16.82	2.46
V	1.47	0.05	1.27	0.07
C_p at T (K)				
300	3.4	9.5	25.0	2.3
350	4.0	9.1	29.7	2.2
400	4.0	9.1	34.2	2.2
450	4.1	9.1	38.4	2.2
500	4.5	9.1	42.5	2.2
550	5.2	9.1	46.4	2.2
600	6.1	9.0	50.0	2.2
650	7.2	8.9	53.5	2.2
700	8.3	8.8	56.7	2.2
750	9.5	8.6	59.7	2.1
800	10.7	8.5	62.5	2.1
850	11.7	8.4	65.1	2.1
900	12.6	8.4	67.5	2.1
950	13.3	8.4	69.6	2.1
1000	13.8	8.3	71.6	2.1
1050	14.1	8.4	73.4	2.1
1100	14.1	8.4	74.9	2.1
1150	13.8	8.5	76.3	2.1
1200	13.2	8.7	77.5	2.2
V_T at T (K)				
150	1.57	0.21	1.02	0.09
200	1.57	0.22	1.02	0.09
250	1.57	0.22	1.02	0.09
300	1.56	0.22	1.02	0.09
350	1.56	0.22	1.02	0.09
400	1.55	0.22	1.02	0.09
450	1.55	0.22	1.02	0.09
500	1.54	0.22	1.02	0.09
550	1.53	0.22	1.03	0.09
600	1.52	0.22	1.03	0.09
650	1.50	0.22	1.03	0.09
700	1.49	0.23	1.03	0.09
750	1.48	0.23	1.03	0.09
800	1.46	0.23	1.03	0.09
850	1.45	0.23	1.03	0.09
900	1.43	0.23	1.03	0.09
950	1.41	0.23	1.03	0.10
1000	1.39	0.24	1.03	0.10
1050	1.37	0.24	1.03	0.10
1100	1.35	0.24	1.03	0.10
1150	1.33	0.24	1.03	0.10
1200	1.30	0.24	1.03	0.10

thermal expansion to $V_T = V_0[1 + v_1(T - T_0) + v_2(T^2 - T_0^2)]$.

TESTING THE TOURMALINE PROPERTIES

Although the uncertainty on estimated tourmaline properties is generally <5%, this can still lead to significant deviations in calculation results, given that the uncertainty on enthalpy is commonly of the same order of magnitude as $\Delta G_{\text{reaction}}$. This effect is not limited to estimated properties, but also affects measured enthalpy values, necessitating optimisation to create internally consistent databases (c.f. Sverjenski *et al.*, 1991; Chatterjee *et al.*, 1998). However, these deviations are expressed as shifts in reaction position, with reaction trends constrained much more accurately (c.f. van Hinsberg *et al.*, 2005b). A number of tests were

used to assess the quality of the estimated tourmaline properties and their suitability for calculations of equilibria between tourmaline and coexisting fluids, melts and minerals.

Relative differences among tourmaline end-members

The relative differences between the thermodynamic properties of tourmaline end-members control its element preference in exchange with other phases. For exchange with biotite and garnet, tourmaline is predicted to be richer in Mg, but poorer in Mn, in agreement with compositions of natural coexisting tourmaline and biotite/garnet (e.g. Henry & Guidotti, 1985; Bucher *et al.*, 2005; our own data). The K content of tourmaline has further been proposed as an indicator of pressure, as the K content in tourmaline from ultrahigh-pressure (UHP) rocks of the Kokchetav massif and Erzgebirge is unusually high (H.R. Marschall, pers. comm.; Shimizu & Ogasawara, 2005). Because the molar volume of K-dravite is larger than that of Na-dravite (Table 4), this cannot be a property of tourmaline itself, but has to result from competition with coexisting phengite and feldspar in these rocks. For both minerals, the formation of K-dravite does indeed lower the overall volume of the assemblage, indicating that at higher pressures, K will partition more strongly into tourmaline.

Unfortunately, this approach cannot readily be extended to heterovalent substitutions, given that the tourmaline crystallography allows exchange to be achieved in a variety of substitutions. For example, Ca-Na exchange can not only be achieved by $\text{Ca}^{\text{X}}\text{Mg}^{\text{Y}} = \text{Na}^{\text{X}}\text{Al}^{\text{Y}}$, but also by deprotonation; $\text{Ca}^{\text{X}}\text{O}^{\text{W}} = \text{Na}^{\text{X}}\text{OH}^{\text{W}}$, or incorporation of trivalent cations at the tetrahedral site; $\text{Ca}^{\text{X}}(\text{Al},\text{B})^{\text{T}} = \text{Na}^{\text{X}}\text{Si}^{\text{T}}$ (c.f. Von Goerne & Franz, 2000). Still, calculations using estimated end-member properties can be used to validate or discredit specific substitutions. Calculations using Al-uvite and dravite data show, for example, that observed trends in Ca-Na partitioning between plagioclase and tourmaline (Henry & Guidotti, 1985; own data) are not controlled by the $\text{Ca}^{\text{X}}\text{Al}^{\text{T}} = \text{Na}^{\text{X}}\text{Si}^{\text{T}}$ vector, indicating that another phase has to take part in this exchange.

Quantifying element partitioning between tourmaline and coexisting phases allows the effects of uncertainty on enthalpy to be evaluated. Comparing actual D -values is not meaningful in this respect, because these are highly sensitive to small variations in ΔG_r . Instead, the residual ΔG_r have been calculated for a range of tourmaline equilibria with minerals and melts (Fig. 2). Results show that deviations are limited (<1% of enthalpy). The stronger discrepancy for tourmaline-melt equilibria may in part be due to inconsistency between tourmaline data and the melt model used, and an increasing deviation for compositions further from the end-members also suggests a contribution from non-ideal mixing. Overall, results

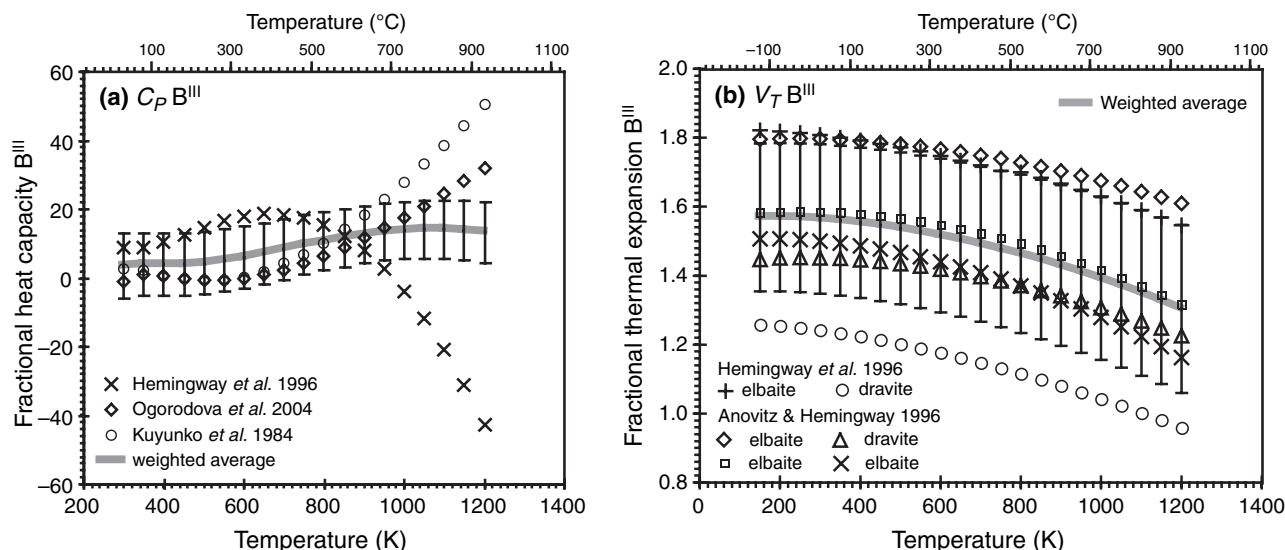


Fig. 1. Comparisons between fractional heat capacity (a) and thermal expansion (b) for trigonal B estimated from different tourmaline analyses, and the weighted average of these with its associated 1-sigma uncertainty.

show that actual *D*-values are beyond the capabilities of the model, but trends can be obtained.

Tourmaline-forming reactions

The B-content of fluids in equilibrium with tourmaline provides an additional test of thermodynamic properties, given that tourmaline can commonly be assumed to be the dominant B-exchanging phase. Calculations of equilibrium B-content have been performed for the experiments reported in Von Goerne *et al.* (1999, 2001) and Von Goerne & Franz (2002), using the HCH computer package (Shvarov, 1999) with thermodynamic properties for the minerals taken from the 2002 update of the Holland & Powell (1998) data set. Intermediate tourmaline compositions were calculated from the partial properties, adding an ideal mixing contribution to entropy. Agreement between calculated and measured B-content is good (Fig. 3a), with all values within an order of magnitude of measured B content. The strongest deviations are observed for samples containing chlorite. Given that chlorite composition was not reported, a composition of $Mg_{4.5}Al_3Si_{2.5}O_{10}(OH)_8$ was assumed here, which may not be appropriate for all samples and can account for part of the discrepancy. Similarly, cordierite was not a stable phase in any of our calculations, which will affect fluid composition and can explain why these samples also deviate strongly in B-content. To stabilize cordierite would require a shift in the tourmaline free energy of 150–350 kJ mol⁻¹ (depending on temperature and tourmaline composition). Such a shift greatly improves the calculated B-content.

The experiments shown in Fig. 3a were modelled in a closed system to account for mass balance effects on

B-content. However, the experiments reported by Von Goerne *et al.* (1999) are more appropriately modelled as an open system, with boron content controlled by equilibrium with the phase assemblage. A 250 kJ mol⁻¹ correction to the free energy of tourmaline was applied following the findings for cordierite-bearing samples described above. Results show good agreement between calculated and measured boron content (Fig. 3b). In fact, the maximum boron content in the experiments is capped at 8.08 wt% B₂O₃ by the complete breakdown of tourmaline, so values at 850 °C cannot be compared. The calculations also correctly predict growth or dissolution of tourmaline, thereby showing that the upper stability of tourmaline is reached between 750 and 800 °C, in line with experimental results.

Garofalo *et al.* (2000) provided a similar opportunity to evaluate the tourmaline properties for the Fe-bearing system. They reported the fluid composition of a natural fluid inclusion in equilibrium with the assemblage tourmaline-quartz-albite-feldspar-muscovite. Using an approach identical to that of Garofalo *et al.* results in a boron content that is a factor 3 to 6 lower than the measured value (Fig. 3a), indicating that tourmaline stability is overestimated. Changing the enthalpy data for schorl by +125 kJ mol⁻¹ remedies this discrepancy, which is within the uncertainty of the estimated properties. The schorl data of Garofalo *et al.* (2000) do not require a correction for this equilibrium. However, using estimates based on their fractional properties for the range of chemical systems and mineral parageneses discussed above, shows that their data are also subject to deviations resulting from uncertainty on enthalpy. Differences between tourmaline end-members are less well reproduced and

Table 4. Thermodynamic properties for tourmaline end-members and their associated 1-sigma uncertainty. Fe end-members contain Fe^{2+} unless otherwise stated. Heat capacity values have been fitted to $C_p = a + bT + cT^{-2} + dT^{-0.5}$ and thermal expansion to $V_T = V_0\{1 + v_1(T - T_0) + v_2(T^2 - T_0^2)\}$.

End-member	Formula	ΔG (J mol ⁻¹)	Error	ΔH (J mol ⁻¹)	Error	S (J mol ⁻¹ K ⁻¹)	Error	V (J mol ⁻¹ bar ⁻¹)	Error	$C_p: a$	b	c	d	$V_T: v_1$	v_2
Dravite	$\text{NaMg}_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-14,600,677	331,689	-15,579,476	331,689	607.9	19.2	32.92	1.47	2198	-0.0645	9,335,269	-25,559	2,53E-05	-4,42E-09
Schorl	$\text{NaFe}_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-13,494,461	347,165	-14,443,029	347,165	692.6	20.9	33.07	1.58	2215	-0.0427	10,834,734	-25,790	2,55E-05	-4,10E-09
Elbaite	$\text{NaLi}_{1.5}\text{Al}_{1.5}\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-14,396,406	436,173	-15,370,560	436,173	611.5	23.5	32.50	2.69	2213	-0.1408	4,796,916	-24,646	2,49E-05	5,58E-09
Olenite	$\text{NaAl}_3\text{Al}_3\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-14,312,223	314,566	-15,255,702	314,566	517.2	17.9	28.79	1.31	2071	-0.1100	8,669,737	-24,349	2,88E-05	-1,38E-08
OH-buergerite	$\text{NaFe}_3^{3+}\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-12,832,406	603,147	-13,752,283	603,147	592.8	26.8	28.26	4.20	2519	-0.2761	29,792,617	-35,211	2,16E-05	-8,03E-09
Oxy-dravite	$\text{NaMg}_2\text{Al}_2\text{MgAl}_4\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4\text{O}$	-14,919,706	333,658	-15,865,383	333,658	649.3	19.2	34.05	2.01	2285	-0.0663	11,314,036	-27,214	2,41E-05	-2,15E-09
Oxy-schorl	$\text{NaFeAl}_2\text{FeAl}_4\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4\text{O}$	-14,182,229	343,975	-15,107,751	343,975	705.7	20.3	33.86	1.91	2297	-0.0519	12,313,679	-27,368	2,42E+00	-1,94E-09
Oxy-elbaite	$\text{NaLiAl}_2\text{Al}_4\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4\text{O}$	-14,772,480	403,314	-15,725,199	403,314	617.7	22.1	32.97	2.39	2296	-0.1172	8,288,472	-26,605	2,38E-05	4,47E-09
Povondraite	$\text{NaFe}_2^{3+}\text{Mg}_2\text{Fe}_2^{3+}\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4\text{O}$	-11,464,655	1,007,013	-12,357,230	1,007,013	818.9	39.8	31.70	8.25	3331	-0.4539	60,600,709	-52,557	8,99E-06	1,04E-08
Mn-dravite	$\text{NaMn}_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-13,868,306	348,705	-14,813,740	348,705	717.8	22.2	33.06	1.66	2278	-0.0965	12,299,211	-26,927	2,15E-05	-1,01E-09
Ti-dravite	$\text{NaMg}_2\text{TiAl}_4\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4\text{O}_2$	-14,439,505	355,858	-15,378,117	355,858	610.1	32.1	32.08	1.50	2049	-0.0709	6,481,878	-22,916	2,70E-05	-1,23E-08
Ti-schorl	$\text{NaFe}_2\text{TiAl}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4\text{O}_2$	-13,702,027	366,175	-14,620,485	366,175	666.5	33.3	32.18	1.58	2061	-0.0564	7,481,521	-23,070	2,71E-05	-1,21E-08
OH-uvite	$\text{CaMg}_2\text{MgAl}_4\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-14,697,555	319,345	-15,669,153	319,345	627.9	16.1	33.42	1.39	2073	-0.0477	4,744,100	-22,700	2,34E-05	-5,33E-09
OH-feruvite	$\text{CaFe}_3\text{MgAl}_4\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-13,591,339	334,821	-14,532,706	334,821	712.5	17.8	33.57	1.50	2091	-0.0260	6,243,565	-22,932	2,36E-05	-5,02E-09
OH-hiddicoite	$\text{CaLi}_2\text{Al}_4\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-14,415,561	458,657	-15,389,808	458,657	603.1	21.8	32.22	2.83	2094	-0.1494	-1,307,043	-21,483	2,28E-05	7,97E-09
B-uvite	$\text{CaMg}_2\text{Al}_4\text{BSi}_4\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-14,722,431	340,759	-15,694,793	340,759	607.9	28.1	32.25	1.43	2228	-0.0514	10,186,207	-26,516	2,40E-05	-4,08E-09
B-feruvite	$\text{CaFe}_3\text{Al}_6\text{BSi}_4\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-13,616,215	356,235	-14,558,345	356,235	692.6	29.7	32.40	1.54	2245	-0.0297	11,685,731	-26,747	2,42E-05	-3,76E-09
Al-uvite	$\text{CaMg}_2\text{Al}_6\text{AlSi}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-14,876,564	321,962	-15,848,640	321,962	631.4	17.2	31.44	2.00	2125	-0.0428	6,392,895	-23,844	2,16E-05	-3,09E-09
Al-feruvite	$\text{CaFe}_3\text{Al}_6\text{AlSi}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-13,770,348	337,438	-14,712,192	337,438	716.0	18.9	31.59	2.11	2143	-0.0210	7,892,360	-24,076	2,19E-05	-2,78E-09
Mg-foitite	$[\text{Mg}_2\text{AlAl}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4]$	-14,564,858	313,226	-15,532,803	313,226	588.5	14.4	33.20	1.86	2174	-0.0461	8,760,279	-25,459	2,12E-05	-3,50E-09
Fe-foitite	$[\text{Fe}_2\text{AlAl}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4]$	-13,827,380	323,543	-14,775,171	323,543	644.9	15.5	33.01	1.76	2186	-0.0317	9,759,922	-25,613	2,14E-05	-3,29E-09
Rossmannite	$[\text{LiAl}_2\text{Al}_4\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4]$	-14,424,933	382,882	-15,393,218	382,882	579.4	17.3	32.12	2.24	2185	-0.0970	5,734,722	-24,850	2,08E-05	3,25E-09
K-dravite	$\text{KMg}_2\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3\text{OH}_4$	-14,624,646	333,497	-15,602,108	333,497	625.6	24.2	33.37	1.51	2207	-0.0757	8,031,320	-25,335	2,74E-05	-5,57E-09

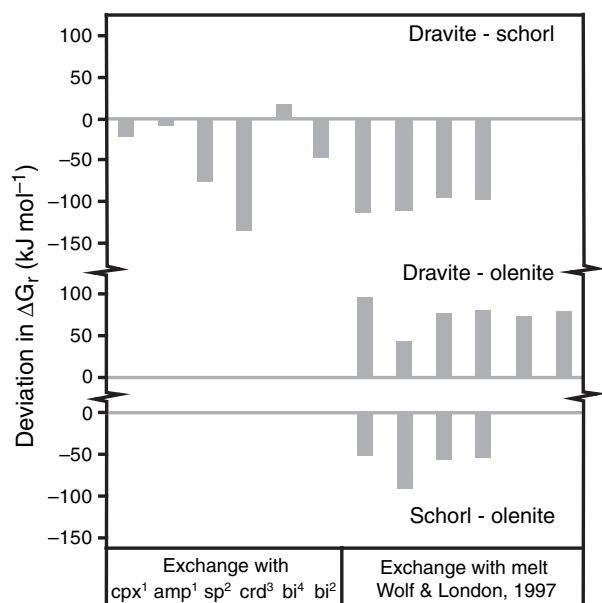


Fig. 2. Residual ΔG_r for exchange equilibria between tourmaline and a set of minerals and melts, showing the effect of uncertainty on estimated enthalpy in modelling. Data sources: Morgan & London, 1989 (1); own data (2); Wolf & London, 1997 (3); and Henry & Guidotti, 1985 (4).

deviations in the Mg-system exceed those of the current data set.

Overall, these tests show that reaction trends are reproduced well, but reaction positions are affected by the uncertainty on estimated enthalpy. Still, results are not meaningless as shown for calculated B-content,

and where independent anchor points are available such issues can be avoided (c.f. Fig. 3b). Ultimately, the deviations show that the estimated properties derived here need to be made consistent with mineral and fluid species databases.

APPLICATION

The appearance of tourmaline in a rock will result in a change in the bulk-rock composition available to other minerals, because it will selectively sequester part of the composition. This change in effective bulk-rock composition will shift mineral assemblage stability fields in closed-system calculations (e.g. pseudo-section calculations; Evans, 2004). Furthermore, the composition of coexisting minerals can be expected to shift, because of selective uptake of elements by tourmaline (e.g. a preference for Mg over Fe). To evaluate these effects, tourmaline growth was simulated for a tourmaline-rich sample from the French Massif Central (MCVH30; a metapelitic sample with ~30 vol.% tourmaline, 48 wt% SiO_2 and 15 wt% $\text{MgO} + \text{FeO}$). Modelling was performed along a P - T gradient with the bulk-rock composition of the sample varying between B-free and a renormalized composition including 5.6 wt% B_2O_3 (corresponding to a final tourmaline volume mode of 50%). Stable-phase parageneses, modes and mineral chemistry in this P - T - X space were calculated using PERPLEX (Connolly, 2005) in the MnTiCNKFMASHB chemical system, with the 2002 update of the Holland & Powell (1998) thermodynamic mineral database. Tourmaline data were added to this database, together with B as a system component, and

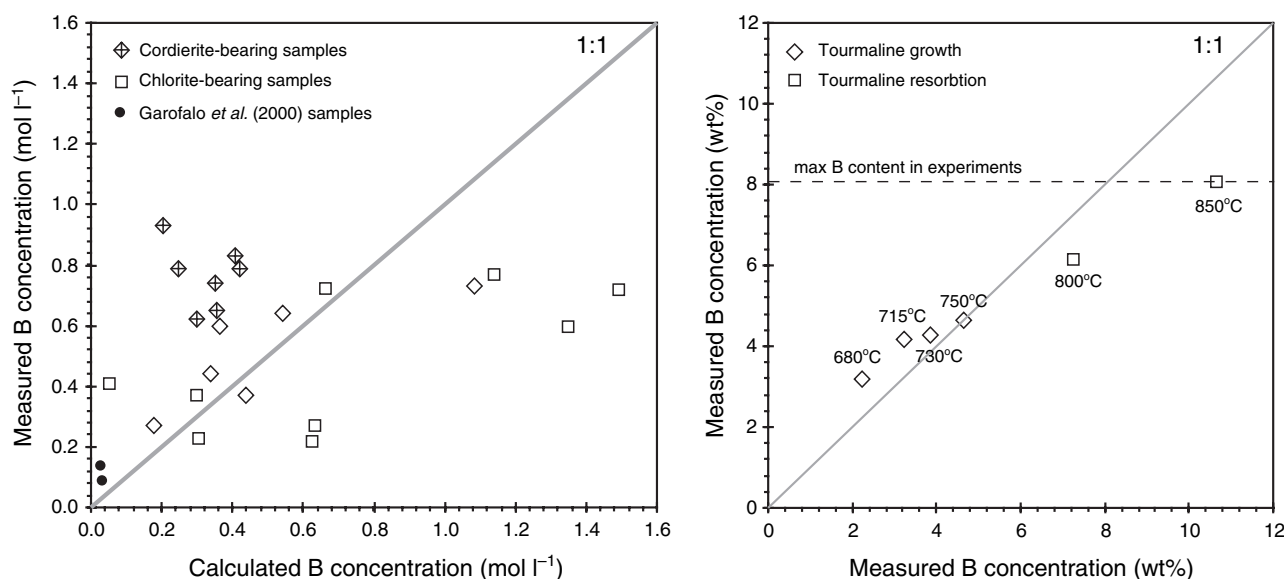


Fig. 3. Comparison between measured and calculated B-content for tourmaline synthesis experiments of Von Goerne *et al.* (1999, 2001) and Von Goerne & Franz (2000). Data for natural samples reported by Garofalo *et al.* (2000) are also shown. Results show reasonable agreement with all values reproduced within an order of magnitude. Equilibria in (b) were modelled in an open system, resulting in the modelled concentration exceeding the maximum B-content possible in the experiments.

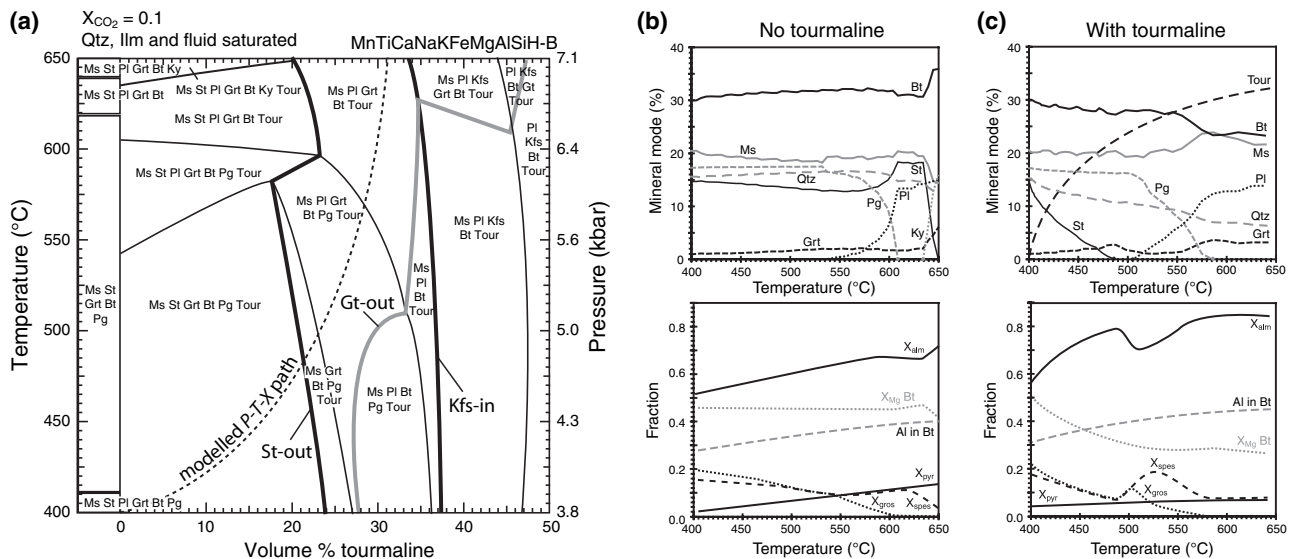


Fig. 4. Phase stability diagram and changing mineral modes and chemistry along a tourmaline-bearing and -free P - T - X path calculated using PERPLEX (Connolly, 2005) for a French Massif Central schist composition with varying added B content. Compared with a tourmaline-free scenario, tourmaline changes the effective bulk composition, thereby shifting mineral parageneses in P - T space, and changing mineral modes and chemistry, resulting in disappearance of Ky and St in the peak assemblage. Tourmaline's preference for Mg further reduces the X_{Mg} of coexisting garnet and biotite. Thermodynamic data were taken from the 2002 update of the Holland & Powell (1998) data set, supplemented with estimated tourmaline properties. Mixing models used are TiBio(HP), Pheng(HP), Gt(HP), St(HP), IlGkPy, feldspar and Tour(V) – see <http://www.perplex.ethz.ch> for information on these models. Bulk composition was determined by XRF on glass beads fused with Li-borate flux from agate-milled rock powder at the Department of Earth Sciences, Utrecht University, giving a composition by weight of SiO_2 – 48.0%, TiO_2 – 1.3%, Al_2O_3 – 28.5%, MgO – 4.1%, MnO – 0.2%, FeO – 11.1%, CaO – 0.1%, Na_2O – 1.5% and K_2O – 5.2% (1 σ relative standard deviation < 1.5%).

an ideal mixing solution added to the solution database. In these calculations tourmaline mode is controlled by B-content, given that tourmaline is the only B-bearing phase, but tourmaline composition can vary.

The resulting phase stability diagram for this P - T - X space shows that the presence of tourmaline does indeed lead to changes in mineral parageneses and shifts in their P - T stability (Fig. 4a). These changes are especially evident at high modal tourmaline content of greater than 20%, with influx of B leading to progressive disappearance of staurolite, paragonite and garnet, and eventual appearance of K-feldspar (thick lines in Fig. 4a). Although this sample has an unusually high tourmaline mode, similar changes are observed at much lower tourmaline content for samples with psammitic and granitic compositions (i.e. lower in Mg plus Fe). For example, the staurolite-out curve is intersected at 5.5% tourmaline for a psammitic schist from the Massif Central (sample MCVH04; 61 wt% SiO_2 , 4.5 wt% MgO + FeO), whereas an orthogneiss sample from the same region (Pinols orthogneiss; 69 wt% SiO_2 , 3.5 wt% MgO + FeO) would lose its garnet at a tourmaline mode of just 3.5%. Such tourmaline modes are readily reached in this area and the predicted mineralogical changes are indeed observed.

To determine the changes in mineral composition and mode, a P - T - X path within this space was calculated (dashed line in Fig. 4a). The P - T - X path represents continuous growth of tourmaline during

prograde metamorphism up to peak conditions of 650 °C and 7 kbar, with tourmaline growth concentrated at low- T prograde conditions, following our findings from tourmaline intersector thermometry (van Hinsberg & Schumacher, 2007). For comparison, a P - T - X path was also modelled for a zero-tourmaline scenario (i.e. along the 0 vol.% line in Fig. 4a). Progressive growth of tourmaline results in a decrease in the amount of biotite, paragonite and staurolite and an increase in muscovite and plagioclase (Fig. 4b). Kyanite does not form when tourmaline is present. Mineral compositions also change. Both garnet and biotite shift to lower X_{Mg} as a result of the preferential uptake of Mg by tourmaline. These modelled differences are in good agreement with observed variations in schists from the Massif Central, with tourmaline-rich schists generally devoid of staurolite and aluminosilicates. Tourmaline-rich samples are commonly also devoid of garnet, and where garnet is found, its presence is confined to inclusions in the cores of tourmaline. This suggests that these rocks moved out of the garnet stability field during their prograde evolution. Although the garnet-out isograd is not reached in this calculation, it is a distinct feature of the introduction of tourmaline.

The application of the data discussed above indicates that the estimated thermodynamic properties of tourmaline give meaningful results in calculations, at the least semi-quantitatively. More constraints, or,

preferably, more measured tourmaline thermodynamic properties are obviously needed to improve the estimates and allow for more accurate modelling. These constraints would seem a worthwhile pursuit, because of the widespread occurrence of tourmaline, its distinct effects on phase parageneses and compositional sensitivity to changes in P – T – X make it a promising indicator mineral in petrogenetic modelling of rocks, melts and ore deposits.

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SUPPLEMENTARY MATERIAL

The authors have provided the following supplementary material, which is available alongside the article at <http://www.blackwell-synergy.com>.

Table S1. Tourmaline minerals used in the molar volume regression analysis. Site occupancies as given in the original references with molar volume and error calculated from the lattice constants and their associated uncertainty.

Table S2. Non-tourmaline minerals used in the regression analysis to constrain the fractional properties of trigonal and tetrahedral B. Element coordination taken from the respective references, with molar volume calculated from the lattice constants. Uncertainties given are 1 standard deviation.