

LETTERS

Tetrahedral boron in naturally occurring tourmaline

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ABSTRACT

Evidence for boron in both trigonal and tetrahedral coordination has been found in ¹¹B magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectra of natural, inclusion-free specimens of aluminum-rich lithian tourmaline from granitic pegmatites.

INTRODUCTION

Minerals of the tourmaline group are by far the most widespread borosilicate phases and the dominant carriers of boron in crustal metamorphic and igneous rocks. The amount of boron and its crystallographic position in tourmaline are of interest not only to mineralogists, but also to geochemists studying the behavior of boron and its isotopes in natural systems. Previous studies of boron contents in tourmaline have yielded variable results. From recent X-ray diffraction studies, boron in tourmaline group minerals occurs exclusively at a single site, coordinated to three O atoms and fully occupying this site, so three boron ions are present in the formula based on 31 anions (Burns et al. 1994; MacDonald and Hawthorne 1995; Hawthorne 1996; Bloodaxe et al. 1999). Only two tourmaline analyses by XANES have been reported, and neither sample showed tetrahedral boron (M. Fleet, personal communication, 1999). Finally, wet chemical analyses of 85 schorl-dravite gave $B = 2.992 \pm 0.052$ atoms per formula unit (apfu) and $B = 3.011 \pm 0.029$ apfu for 21 elbaite (Povondra 1981; Povondra et al. 1985); although the average B contents are close to stoichiometric, individual samples show significant deviations from $B = 3$.

Compositions containing excess boron have been reported (Barton 1969; Dyar et al. 1994), and Novozhilov et al. (1969) have obtained electron paramagnetic resonance (EPR) evidence for the substitution of silicon by boron at the tetrahedral site in elbaite (0.01% of Si or 0.0006 B apfu). Serdyuchenko (1980) proposed that excess boron is accommodated not only at the tetrahedral Si site, but also a trigonal site that he inferred substituted for hydroxyl groups. Ertl et al. (1997) refined the crystal structure of an olenite with 4.225 B and 4.871 Si pfu, and their reported average Si-O bond lengths of 1.61 Å are consis-

tent with some substitution of silicon by boron (Hawthorne 1996). Wodara and Schreyer (1997; 1998) synthesized olenites with an even greater amount of excess boron and boron substitution for silicon, and cited ¹¹B magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) evidence for the presence of both trigonal and tetrahedral boron. In summary, the coordination and partitioning of boron in tourmaline have not yet been definitively characterized. In part, this results from insufficient sensitivity of the most commonly used methods for analyzing for trigonal and tetrahedral cations; tourmaline is refractory and dissolves with difficulty, and Si analyses by electron microprobe have large errors (typically $\sigma = 0.6$ wt% SiO₂, or about 0.1 Si pfu). Single crystal X-ray diffraction may not be able to detect 0.1–0.2 B at the Si tetrahedral sites, i.e., 1.7–3.3% replacement of Si by B, yet 3.1–3.2 B is a significant excess and has been reported in SIMS analyses of tourmaline (Guidotti et al. 1997; Dyar et al. 1998).

In experiments on borosilicates and borates, Bray et al. (1961) and Turner et al. (1986) demonstrated that boron nuclei in trigonal coordination environments can be differentiated from those occupying tetrahedral sites on the basis of ¹¹B quadrupolar coupling parameters and isotropic chemical shift values, as measured by ¹¹B MAS NMR spectroscopy. This approach should therefore ascertain whether excess boron in tourmalines can be incorporated in tetrahedral sites. In the few prior ¹¹B NMR investigations of tourmaline group minerals, no evidence of tetrahedral boron was detected (Turner et al. 1986; Tsang and Ghose 1973). To determine if the occupancy of tetrahedral sites is a possibility for boron in tourmalines, we selected specimens with a range of boron-rich, low-iron compositions for examination by ¹¹B MAS NMR spectroscopy. Our expectation was that Si-deficient (<six Si atoms pfu) and B-excess (>three atoms pfu) compositions would favor the formation of tetrahedral boron sites, and low concentrations of transition elements would be desirable for optimal NMR resolution. The analysis of the ¹¹B MAS NMR spectra of these speci-

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mens, described below, supports the hypothesis that fourfold-coordinate boron nuclei are present in these specimens, and illustrates the utility and sensitivity of this approach in differentiating threefold- and fourfold-coordinate boron species in specimens of natural origin.

EXPERIMENTAL DETAILS

Sample selection and analysis

Tourmaline samples for this study (Table 1) were selected and analyzed according to methods discussed by Dyar et al. (1998). B and Li were quantified by secondary mass spectrometry, Fe³⁺ by Mössbauer spectroscopy, H by uranium extraction, and all other constituents by electron microprobe analysis. All samples were obtained as whole, museum quality single crystals, and powders were made from grains that were individually inspected and screened for lack of zoning. Grains with visible fractures or inclusions of any kind were avoided. X-ray diffraction analysis revealed no sign of secondary phases.

These samples contain no other ¹⁴B-bearing phases. ¹⁴B-bearing minerals reported from granite pegmatites overall include the axinite and kornepupine groups, behierite, boralsilite, boromuscovite, datolite, danburite, diomignite, hellandite-(Y), manandonite and rhodizite (e.g., London et al. 1987; Foord et

al. 1991; Anovitz and Grew 1996; Grew 1996; Grew et al. 1998). As far as we are aware, none of these minerals has been reported from pegmatites in Maine (King and Foord 1994) or Colorado (Eckel 1961); boromuscovite was discovered in the Little Three pegmatite, which is similar to the Himalaya pegmatite, both located in San Diego County. Except for boromuscovite, we would not expect any of these minerals to be in the studied pegmatites. Either they require relatively high temperatures (kornepupine group, boralsilite) or a distinctive geochemical environment (axinite group in most cases, danburite, datolite); behierite, diomignite, and manandonite have been found at only one or two localities. Boromuscovite might be associated with elbaite in the studied pegmatites; however, no impurity was observed in the studied samples, and thus we rule out the possibility of contamination from this phase.

¹¹B NMR

Boron-11 NMR spectra were collected with Chemagnetics Infinity spectrometers operating at field strengths of 11.74 T and 7.05 T. The $\pi/2$ pulse length of a 0.25 M aqueous boric acid solution was found to be around 6 μ s. Single pulse excitation with pulse widths of between 2.6 and 2.9 μ s were used for solid-state experiments. The spectra are averages of between 500 and 2200 scans, with 40 s delays between acquisitions.

TABLE 1. Compositions (wt%) and formulae of tourmaline samples

	SS4	SS13	SS15	SS16	86276	MM-I	86321
SiO ₂	37.15	37.25	37.49	37.57	37.95	37.94	37.38
TiO ₂	0	0	0.01	0	0.02	0.08	0.03
B ₂ O ₃	11.89	11.81	12.52	12.74	11.59	11.60	11.04
Al ₂ O ₃	42.45	43.11	44.14	42.21	41.8	43.38	30.56
Cr ₂ O ₃	—	—	—	—	—	0.01	0.01
Fe ₂ O ₃	0.01	0.00	0.01	0.06	0.70	0.00	0.07
FeO	0.00	0.00	0.00	0.00	0.00	0.00	0
MnO	0.17	0.74	0.12	0.18	0.45	0.23	0
MgO	0	0.01	0	0	0	0.02	13.92
ZnO	—	—	—	—	—	0.01	—
Li ₂ O	2.47	2.22	2.56	2.88	1.5	2.54	0
CaO	0.62	0.26	0.61	0.78	0.95	0.48	2.99
Na ₂ O	1.76	1.88	1.76	1.78	1.78	1.77	1.21
K ₂ O	0.02	0.02	0.02	0.02	0.01	0.01	0.03
H ₂ O	2.86	2.86	2.86	2.86	2.86	3.27	2.94
F	0.94	0.86	1.04	1	0.59	1.35	1.22
Sum	100.34	101.02	103.14	102.08	100.20	102.69	101.40
-F=O	-0.40	-0.36	-0.44	-0.42	-0.25	-0.57	-0.51
Sum	99.94	100.66	102.70	101.66	99.95	102.12	100.89
Formulae per 31 O							
Si	5.797	5.791	5.690	5.753	5.964	5.784	5.961
Ti	0.000	0.000	0.001	0.000	0.002	0.009	0.004
B	3.202	3.169	3.280	3.367	3.144	3.052	3.039
Al	7.807	7.899	7.895	7.617	7.743	7.794	5.744
Cr	—	—	—	—	—	0.001	0.001
Li	1.550	1.388	1.562	1.773	0.948	1.557	0.000
Fe ³⁺	0.001	0.000	0.001	0.007	0.083	0.000	0.008
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.022	0.097	0.015	0.023	0.060	0.030	0.000
Mg	0.000	0.002	0.000	0.000	0.000	0.005	3.309
Zn	—	—	—	—	—	0.001	—
Ca	0.104	0.043	0.099	0.128	0.160	0.078	0.511
Na	0.532	0.567	0.518	0.528	0.542	0.523	0.374
K	0.004	0.004	0.004	0.004	0.002	0.002	0.006
Sum	19.020	18.960	19.066	19.202	18.649	18.836	18.958
H	2.977	2.966	2.895	2.921	2.998	3.325	3.127
F	0.464	0.423	0.499	0.484	0.293	0.651	0.615

*Localities: Himalaya Mine, California (SS4); Black Mountain, Maine (SS13); Brown Derby pegmatite, Colorado (SS15, SS16); Mount Mica, Maine (86276, MM-I); DeKalb, New York (86321). Analysis of 86321 is from Dyar et al. (1998).

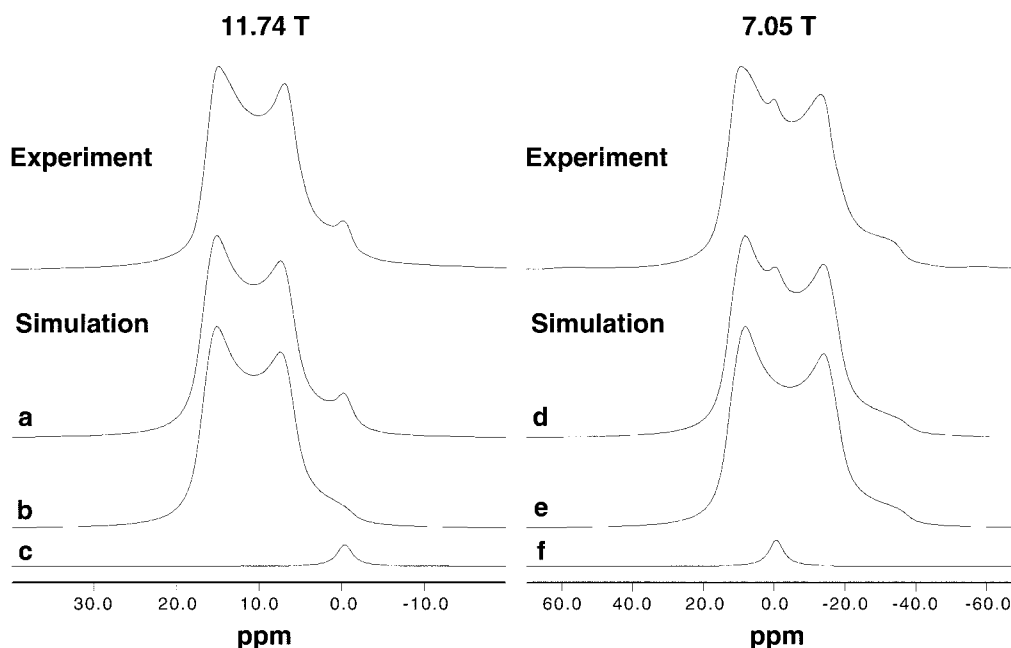


FIGURE 1. Experimental and simulated ^{11}B MAS NMR spectra of tourmaline SS15 for two magnetic field values. (a) Superposition of simulated spectra of a single threefold-coordinate site (b) and a single fourfold-coordinate site (c). (d) Sum of a single threefold-coordinate site (e) and a single fourfold-coordinate site (f). Chemical shifts are referenced to the ^{11}B resonance of danburite.

MAS speeds were between 10.5 and 11.0 kHz. ^{11}B chemical shifts were referenced to the resonance of danburite, $\text{CaB}_2\text{Si}_2\text{O}_8$, which has a chemical shift of -0.7 ppm (Turner et al. 1986) relative to boron trifluoride diethyl etherate (BF_3OEt_2 , $\delta = 0$ ppm). For confirmation, we periodically measured the ^{11}B shift of a 0.25 M boric acid solution and found it to be within 1 ppm of the value measured previously, 19.6 ppm (Salentine 1983; Dewar and Jones 1967).

The experimental ^{11}B MAS NMR lineshapes were simulated following the method of Alderman et al. (1986), with the expression for the frequency of the second-order quadrupole interaction as derived by Goldman et al. (1992) in the fast sample spinning speed limit. In these calculations, it was assumed that the observed resonances corresponded to $+1/2 \leftrightarrow -1/2$ ^{11}B NMR transitions, with no contributions to the lineshape

from satellite transitions. Chemical shift anisotropy and homonuclear and heteronuclear dipolar couplings were neglected; comparisons of spectra acquired at slower spinning speeds confirm that the effect of these terms can be ignored.

RESULTS AND DISCUSSION

Experimental and simulated ^{11}B MAS NMR spectra of one of the Brown Derby pegmatites (SS15) are shown in Figure 1. Assuming there are two populations of boron nuclei, one corresponding to boron nuclei in trigonal sites and one corresponding to boron nuclei in tetrahedral sites, the ^{11}B spectra are specified by seven parameters: two quadrupolar coupling constants e^2Qq/h , two quadrupolar asymmetry parameters η ($0 < \eta < 1$), two isotropic chemical shifts δ_{cs} , and the ratio of the two integrated resonance intensities. The simulated spectra (Fig. 1)

TABLE 2. ^{11}B MAS NMR parameters for tourmaline samples

Sample	BO_3				BO_4			
	δ_{cs} ppm	e^2Qq/h MHz	η^*	$I(\text{BO}_3)^\dagger$	δ_{cs} ppm	e^2Qq/h MHz	η^\ddagger	$I(\text{BO}_4)^\dagger$
SS15	19.4	2.9	0.14	0.97	0.0	0.1	0.8	0.03
SS4	19.6	2.9	0.16	0.97	0.1	0.2	0.8	0.03
SS16	19.9	2.9	0.14	0.97	0.0	0.1	0.7	0.03
MMI	20.0	2.9	0.15	0.94	0.0	0.1	0.7	0.06
86321	20.1	2.9	0.16	1.00	—	—	—	—
Typical§	16–18	2.3–3.0	0.0–0.1	—	1–2	0.0–0.8	0.5–0.8	—

Notes: Isotropic chemical shifts, quadrupolar constants, and asymmetry parameters are averages of values obtained from fits of spectra acquired at 11.74 T and 7.05 T. Estimated errors are ± 1 ppm, ± 0.1 MHz, or as shown.

* Uncertainty is ± 0.05 .

† Relative integrated ^{11}B resonance intensity (normalized).

‡ Uncertainty is ± 0.02 .

§ Data on borates from Bray et al. (1961) and Turner et al. (1986).

were computed by searching the quadrupolar and chemical shift variables within the known ranges of these parameters for trigonal and tetrahedral borates, as measured in previous studies (Bray et al. 1961; Turner et al. 1986; Sen et al. 1994).

As seen in the calculated spectra of trigonal sites, there are features in the experimental spectra that cannot be simulated unless a population of tetrahedral boron sites is included. In particular, the narrow, symmetric feature at ~ 0 ppm is absent from simulated lineshapes of the trigonal site alone.

The validity of this two-population model was tested by comparing the fit values extracted from the 11.74 T measurements for consistency with the independently calculated fit values of the 7.05 T spectra. For the five specimens with well-resolved ^{11}B spectra, the NMR parameters (Table 2) extracted from the fit of the 11.74 T spectra matched the values derived from the independent fit of the 7.05 T spectra to within the experimental uncertainty. Systematic deviations between simulated and experimental spectra can be attributed to the idealized assumption that the tetrahedral and trigonal sites are specified by single sets of quadrupolar and chemical shift parameters. For non-ideal samples that are not completely crystalline, have more than one type of trigonal or tetrahedral environment, or contain trace amounts of paramagnetic material, it will be more accurate to represent the lineshape parameters by distribution functions rather than well-defined, discrete values. The potential deviations are greatest for tetrahedral boron sites due to the lack of visible features in the NMR spectra and low concentrations relative to trigonal boron.

The suggestion of more than one trigonal site is consistent with earlier proposals. Lowenstein (1956) suggested that B in the tourmaline structure might be shifted out of the plane of the BO_3 triangle toward the O4 site. Bray et al. (1961) noted that an oxygen atom bound to silicon could displace the boron atom out of strictly trigonal coordination, and Serdyuchenko (1980) proposed a model with BO_3 triangles in the hydroxyl (W) site in addition to B occupancy in Si tetrahedra. All of the tourmalines studied here are deficient in Si (Table 1), and substitution by B or Al might cause the proposed shift in B toward O4. Furthermore, all of our samples (and, indeed, almost all the analyzed samples in the literature) have vacancies in the W site ranging from 0.024 to 0.708 atoms per 31 O formula unit

that could accommodate BO_3^{3-} ; the resulting distortion might also favor distortion of adjacent BO_3 . Single crystal X-ray diffraction studies of our samples are in progress to evaluate these possibilities.

The width and position of the feature near 0 ppm appearing in the experimental spectra of six of the specimens showed little dependence on magnetic field strength. This behavior supports the assignment of this line to tetrahedral boron sites, which are characterized by a near-zero chemical shift and a second order quadrupolar interaction that is substantially smaller than for trigonal sites. On the other hand, chemical shifts and quadrupolar interactions for trigonal sites are large compared to those of tetrahedral sites, and thus the width and position of the ^{11}B resonance for these sites will be strongly affected by the magnetic field strength of the measurement. This field dependence is reflected in the substantial differences observed between the 11.74 T and 7.05 T line shapes, and is consistent with the assignment of the resonance excluding the 0 ppm feature to a normal trigonal site.

No tetrahedral boron signal was detected in samples taken from the 86276 specimen. The 0 ppm spike in the spectrum of SS13 (Fig. 2), also seen at 7.05 T, indicates fourfold-coordinate borons are present, but no fitting was attempted due to the lack of structure in the trigonal resonance. The SS13 spectrum illustrates that the signal of the tetrahedral sites is clearly separable from the trigonal sites even in the presence of factors that reduce resolution, such as structural disorder or paramagnetic ions. In connection with the latter explanation, elemental analyses indicate that the combined Fe and Mn concentrations of the 86276 and SS13 tourmalines were a factor of three or more greater than for the other specimens.

The relative populations of the trigonal and tetrahedral sites cannot be straightforwardly extracted from the integrated intensities of the $+1/2 \leftrightarrow -1/2$ resonances of odd-half-integer quadrupolar nuclei like ^{11}B without further measurements or comparisons with suitable standards. The results of experiments with different ^{11}B excitation pulse widths are in accordance with the expectation that B nuclei in tetrahedral sites represent a small fraction of the total boron population in these specimens. Nonetheless, MAS NMR evidence for tetrahedral boron and SIMS evidence for excess boron (Guidotti et al. 1997; Dyar et al. 1998) show that the conventional stoichiometry in elbaite and other tourmaline species cannot be automatically presumed. Evidently, there are geochemical environments such as granitic pegmatites that are conducive to incorporation of extra boron in fourfold-coordinate sites in tourmaline, as exemplified by the specimens considered here.

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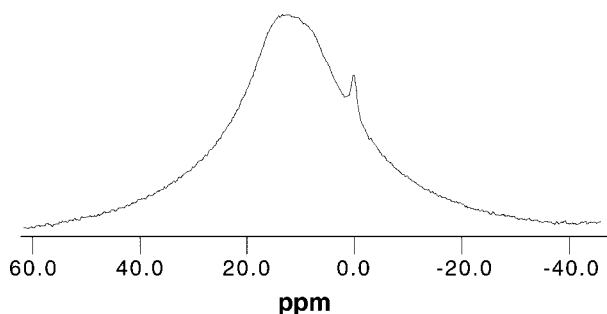


FIGURE 2. Experimental ^{11}B MAS NMR spectrum of tourmaline SS13 acquired at 11.74 T.

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