## NOTES

# Boron-11 Nuclear Magnetic Resonance Spectroscopic Study of Borate and Borosilicate Minerals and a Borosilicate Glass<sup>1</sup>

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Borates and borosilicates form a wide class of technologically and geochemically important systems (1-3), many of which have been characterized quite thoroughly by means of wide-line NMR spectroscopy in pioneering studies by Bray and co-workers (3). More recently, "magic-angle" and "variable-angle" sample-spinning Fourier transform NMR methods have been applied to the investigation of the structures of such materials (4-6) in an attempt to supplement existing nuclear quadrupole coupling constant  $(e^2 q O/h)$  data with chemical-shift information for both tetrahedral (BO<sub>4</sub>) and trigonal  $(BO_3)$  sites. In this Note, we report the results of a study aimed at determining the optimum conditions for obtaining well-resolved boron-11 MASS NMR spectra of a wide range of borates and borosilicates. We show that rapid ( $\geq 6$  kHz) sample spinning, together with high-power proton decoupling, is generally desirable for rapid acquisition of boron-11 NMR spectra of borates and borosilicates, from which accurate trigonal/tetrahedral ratios may be determined. In addition, we demonstrate for the systems we have studied that the  $BO_3/BO_4$  solid-state chemical-shift ranges occur in well-defined, nonoverlapping regions (although overlap may of course occur as more systems are investigated). Taken together, our results indicate that high-field boron-11 MASS NMR should be a useful, rapid method for quantitatively estimating trigonal/ tetrahedral ratios in many natural and synthetic boron-containing materials, such as glasses, minerals, and some zeolites.

NMR spectra were obtained on a home-built 11.7 T spectrometer (corresponding to a boron-11 NMR frequency of 160.4 MHz) basically as described previously (4, 6). All spectra were recorded using 2  $\mu$ s pulse excitation. The solution 90° pulse width for boron trifluoride etherate (BF<sub>3</sub> · Et<sub>2</sub>O) was 9  $\mu$ s. Chemical shifts are reported in parts per million (ppm) from an external sample of BF<sub>3</sub> · Et<sub>2</sub>O and positive values correspond to low-field, high-frequency, paramagnetic, or deshielded shifts.

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Model compounds (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O (borax), K<sub>2</sub>B<sub>10</sub>O<sub>16</sub> · 8H<sub>2</sub>O, BPO<sub>4</sub>) were of the highest purity commercially available, and their sources are given in Table 1. They were all used without further purification. The natural minerals were from the University of Illinois' Mineralogical Collection, and their structures were confirmed by powder X-ray diffractometry in our laboratories. Their original localities are given in Table 1. Spectral simulations were used to determine quadrupole coupling constants  $(e^2qQ/h)$ , asymmetry parameters ( $\eta$ ) and isotropic chemical shifts ( $\delta_i$ ), corrected for the effect of second-order quadrupolar shifts, using methods described previously ( $\delta$ ).

We show in Fig. 1A the static boron-11 NMR spectra of three common borates: kernite  $(Na_2B_4O_6(OH)_2 \cdot 3H_2O)$ , inderite  $(MgB_3O_3(OH)_5 \cdot (H_2O)_4 \cdot H_2O)$ , and borax  $(Na_2B_4O_7 \cdot 10H_2O)$ . Kernite and borax are among the most common naturally occurring borate minerals. Kernite contains complex chains of composition  $[B_4O_6(OH)_2]^{2-}$ , consisting of BO<sub>4</sub> tetrahedra joined at the vertices, with remaining vertices connected to BO<sub>3</sub> triangles. Borax contains isolated  $[B_4O_5(OH)_4]^{2-}$  groups consisting of two BO<sub>4</sub> and two BO<sub>3</sub> units. Inderite consists of isolated  $[B_3O_3(OH)_5]^{2-1}$ polyanions, where each boron has two oxygens which bridge to the other two borons, forming a six-member ring. The results of Fig. 1A indicate that even at high magnetic field strengths, where the second-order quadrupole interaction is greatly diminished, well-resolved static boron-11 NMR spectra of minerals are not obtained, due, we believe, to the presence of boron-boron and boron-hydrogen dipole-dipole interactions. On application of an intense <sup>1</sup>H-decoupling field, the  ${}^{11}B-{}^{1}H$  dipolar interaction is eliminated, and slightly narrower spectra are obtained for all species, as shown in Fig. 1B. However, upon MASS at an intermediate rate ( $\sim$ 3.5-4 kHz), there is a noticeable decrease in linewidth of all three species (Fig. 1C), and this effect is very pronounced in the presence of proton decoupling (Fig. 1D). The effect of decoupling is largest for inderite and borax, since they have an H/B (hydrogen-to-boron) ratio of 5, while the H/B ratio for kernite is only 2. However, even in the presence of mediumspeed MASS and <sup>1</sup>H decoupling, there is still considerable intensity in the spinning sidebands (Fig. 1D). Rapid ( $\geq 6$  kHz) "magic-angle" sample-spinning effectively removes this sideband intensity (Fig. 1E), and rapid spinning combined with proton decoupling yields well-resolved spectra (Fig. 1F) from which we can determine the  $BO_3/BO_4$  ratios by spectral simulation.

These results are all consistent with the presence of a small <sup>11</sup>B–<sup>1</sup>H dipolar interaction in all three borates, the effect being larger with increasing H/B ratio. This dipolar interaction can be removed either by <sup>1</sup>H decoupling or by very rapid MASS (Fig. 1E), although in the case of inderite (H/B = 5.0) averaging of the <sup>1</sup>H dipolar interaction by spinning alone appears incomplete. Averaging of the <sup>11</sup>B–<sup>11</sup>B interaction requires MASS of  $\ge 1-2$  kHz only, since as expected this interaction is rather weak. Thus, the results of Fig. 1 indicate that the simplest, best resolved boron-11 NMR spectra of polycrystalline mineral phases will generally be obtained by use of the highest spinning speeds possible, preferably in the presence of <sup>1</sup>H dipolar decoupling.

Assignment of the various resonances observed in Fig. 1 is straightforward since previous solution NMR studies indicate that trigonal boron signals occur at around 19 ppm, while tetrahedral signals occur at around 2 ppm (7, 8). In addition, Bray and co-workers (9, 10) and Lal and Petch (11) have shown that  $e^2qQ/h$  for trigonal boron ranges from ~2.4 to 2.8 MHz, while for tetrahedral boron  $e^2qQ/h$  varies from ~0 to 0.8 MHz. Thus, the low-field doublets arise from BO<sub>3</sub> units, while the sharp, high-

	Boron-11 Nuclear Quadrupole Coupling (	Constant an	d Chemical	-Shift Data fo	or a Series of Bo	orates and B	orosilicates		
			Boron-11	NMR parame	sters	The	ory	Exper	iment
		Trig	onal	Tetr	ahedral				
Sample	Formula and source	QCCª	$\delta_i{}^b$	QCC"	$\delta_{i}{}^{b}$	#BO3	#BO4	#BO3°	#BO4 <sup>c</sup>
Boracite	Mg <sub>3</sub> B <sub>7</sub> O <sub>13</sub> Cl, Stramfurt, Germany	2.6	16.0	~0.3	1.0	-	6	1	6
Colemanite	CaB <sub>3</sub> O <sub>4</sub> (OH) <sub>3</sub> ·H <sub>2</sub> O, Turkey	2.4	17.0	~0.3	1.4	1	4.	Ţ	4.
Datolite	Cap2oi20s, MEXICO CaB(SiO <sub>4</sub> )(OH), W. Patterson,	qa	q a		~0./ 1.0				
Inderite	N.J. MgB3O3(OH) <sub>5</sub> · (H <sub>2</sub> O) <sub>4</sub> · H <sub>2</sub> O, K مت Co. Calif	2.4	18.1	$\sim 0.2$	1.0	1	7	-	7
Inyoite	CaB <sub>3</sub> O <sub>3</sub> (OH) <sub>5</sub> · 4H <sub>2</sub> O, Death Valley, Colif	2.3	17.4	~0.2	1.5	I	3	1	7
Kernite	Vaucy, Cau. Na <sub>3</sub> B <sub>4</sub> O <sub>6</sub> (OH) <sub>2</sub> · 3H <sub>2</sub> O, Kern Co., Calif	2.4	18.5	$\sim 0.2$	0.9	2	2	2	2
Tourmaline	(Na, Ca)(Li, Mg, A1)(A1, Fe, Mn) <sub>6</sub> (BO <sub>3</sub> ) <sub>3</sub> (Si <sub>6</sub> O <sub>18</sub> )(OH) <sub>4</sub> , Nauror, Masse	ð	12.75	q	đ	1	ļ	-	-
Ulexite	NaCaB <sub>5</sub> O <sub>6</sub> (OH) <sub>6</sub> · 5H <sub>2</sub> O, Uhknown	2.45	18.2	~0.3	1.2	2	3	2	3
Boron Phosphate	<b>BPO<sub>4</sub></b> , Alfa Products	þ	q	0	-3.3	I	1		1
Lithium Borate	Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , Noah Chemical	2.5	17.9	$\sim 0.2$	1.7	7	7	2	7
Potassium Pentabora	te K <sub>2</sub> B <sub>10</sub> O <sub>16</sub> · 8H <sub>2</sub> O, Alfa Products	2.5	18.9	~0.3	4.4	4 (	-	4 (	- 0
Pyrex (1)	1422401.101120, MCB Reagents	2.5 2.5	12.6	~0.5 ~0.5	2.U 1.8	2 Unkr	7 10WD	9	20
(2) Deedmennerite	Nobel O Duckana Co Hack	2.3	16.0 J	~0.5	0.2	Unkr	IOWD	1	_
Alkali Feldspar	NadoijOs, Ducnesne Co., Ulan NaAlSi <sub>3</sub> Os (B)	q a	9		-1.9 -1.1, -2.5				

TABLE 1

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<sup>a</sup> Quadrupole coupling constant, in MHz. Error is  $\pm 0.1$  MHz. <sup>b</sup> In ppm from BF<sub>3</sub>, Et<sub>2</sub>O. Error is  $\pm 0.2$  ppm. <sup>c</sup> Error is  $\pm 10\%$ . <sup>d</sup> No boron of this coordination present. <sup>e</sup> Not determined. <sup>/</sup>Center of peak.



FIG. 1. 11.7 T boron-11 static and MASS NMR spectra of kernite (Na<sub>2</sub>B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>·3H<sub>2</sub>O), inderite (Mg[B<sub>3</sub>O<sub>3</sub>(OH)<sub>5</sub>]·(H<sub>2</sub>O)<sub>4</sub>·H<sub>2</sub>O), and borax (Na<sub>2</sub>B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>·8H<sub>2</sub>O) showing the effects of specimen rotation rate, and of <sup>1</sup>H decoupling, on spectral appearance. H/B refers to the hydrogen-to-boron ratio. (A) Static, coupled spectra. (B) Static, decoupled spectra. (C) ~3.8 kHz MASS, coupled. (D) ~3.8 kHz MASS, decoupled. (E) ~6.4 kHz MASS, coupled. (F) ~6.4 kHz MASS, decoupled. Spectra were recorded using 2  $\mu$ s pulses (2/9 the solution value), the recycle time was 1 s, and a 10 Hz linebroadening due to exponential multiplication was applied.

field lines arise from the tetrahedral  $BO_4$  units. We now use this information to interpret the structures of a variety of other boron-containing mineral phases and glasses (Fig. 2 and Table 1), paying particular attention to the *quantitative* determination of the relative intensities of the two types of site.

We show in Figs. 2A, C the 11.7 T boron-11 MASS NMR spectra of the borate minerals kernite and ulexite (NaCaB<sub>5</sub>O<sub>6</sub>(OH)<sub>6</sub> · 5H<sub>2</sub>O), together with their spectral simulations (Figs. 2B, D). For kernite, we expect a 1:1 trigonal/tetrahedral ratio based on X-ray results (12), or simply on compositional grounds (13). This is in excellent agreement with the results of the spectral simulation: BO<sub>3</sub>  $e^2qQ/h = 2.4$  MHz,  $\delta_i$ 

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FIG. 2. 11.7 T boron-11 MASS NMR spectra (left) of kernite, ulexite (NaCaB<sub>5</sub>O<sub>6</sub>(OH)<sub>6</sub>  $\cdot$  5H<sub>2</sub>O), and Pyrex, together with (right) their spectral simulations. Spectral conditions as in Fig. 1F. Simulation parameters are given in Table 1, except for the linewidths, which were Lorentzian and varied between 150 and 250 Hz. (A) kernite. (C) ulexite. (E) Pyrex.

= 18.5 ppm, intensity = 1 boron; BO<sub>4</sub>  $e^2 qQ/h = 0.2$  MHz,  $\delta_i = 0.9$  ppm, intensity = 1 boron, as shown in Figs. 2A, B. Similar results are obtained with ulexite, Figs. 2C, D. Ulexite has the formula NaCaB<sub>5</sub>O<sub>6</sub>(OH)<sub>6</sub> · 5H<sub>2</sub>O, and has two BO<sub>3</sub> and three BO<sub>4</sub> units (14). The results (Fig. 2D) of our simulation of the spectrum of ulexite (Fig. 2C) yield BO<sub>3</sub>  $e^2 qQ/h = 2.45$  MHz,  $\delta_i = 18.2$  ppm, intensity = 2 borons; BO<sub>4</sub>  $e^2 qQ/h \approx 0.3$  MHz,  $\delta_i = 1.2$  ppm, intensity = 3 borons, in excellent agreement with the intensity ratios expected.

These results, and the additional results listed in Table 1, indicate that quantitatively reliable intensity ratios (BO<sub>3</sub>/BO<sub>4</sub>) may be obtained using high-field boron-11 MASS NMR spectroscopy, at least under the instrumental conditions (2  $\mu$ s pulses, 2/9th the solution 90° pulse values) we have used. This implies that primarily the  $\frac{1}{2}$ ,  $-\frac{1}{2}$  transition is being excited (and observed) (15, 16), and that it should be a straightforward matter to obtain *absolute* quantitation under similar conditions (17).

Our  $e^2 qQ/h$  values are in the range 2.3 to 2.6 MHz for all trigonal borons, and  $\sim 0.0$  to 0.5 MHz for tetrahedral ones. Where it is possible to compare, our values are very close to those determined by others. In all cases, we could not detect deviations from a zero asymmetry parameter, while Bray *et al.* found, using wide-line methods, values of  $\sim 0.06$  to 0.12 for trigonal and 0.48 to 0.60 for tetrahedral boron in a wide range of crystalline borates (9). When the  $e^2 qQ/h$  values are small, as they are for the tetrahedral borons in this study, it is difficult to accurately measure the asymmetry parameters using MASS NMR, thus the values that Bray *et al.* report are more reliable.

We have also obtained the boron-11 MASS NMR spectra of several borosilicate minerals and glasses (Fig. 2 and Table 1). Danburite  $(CaB_2Si_2O_8)$  contains tetrahedral



FIG. 3. 11.7 T boron-11 MASS NMR spectra of (A) reedmergnerite and (B) alkali feldspar containing  $\sim 2$  wt% B<sub>2</sub>O<sub>3</sub>. Spectral conditions basically as in Fig. 1F.

boron coordinated to silicate tetrahedra and gives rise to a sharp resonance at -0.7 ppm. Tourmaline ((Na, Ca)(Li, Mg, Al)(Al, Fe, Mn)<sub>6</sub>(BO<sub>3</sub>)<sub>3</sub> (Si<sub>6</sub>O<sub>18</sub>)(OH<sub>4</sub>)) contains trigonal boron coordinated to a (Si<sub>6</sub>O<sub>18</sub>)<sup>-12</sup> cyclosilicate and yields a much broader resonance centered at ~12.7 ppm, together with evidence of spinning sidebands, which probably originate from the paramagnetic Fe and Mn impurities (*18*). These chemical shifts for natural borosilicate minerals suggest that the presence of silicon (rather than boron) as a next-nearest neighbor to boron may cause a slight shielding, both for BO<sub>4</sub> and BO<sub>3</sub> units. This idea is consistent with the ~1-2 ppm chemical-shift values noted by Gabelica *et al.* (2) for randomly distributed BO<sub>4</sub> units (in, e.g., Pyrex or an aluminosilicate gel), compared with the ~ -3 ppm value observed for BO<sub>4</sub> incorporated into a zeolite framework (where solely B-O-Si bonds might be expected (2)), or for BO<sub>4</sub> units in feldspar minerals (~ -2.5 ppm) or in reedmergnerite (-1.9 ppm), as shown in Fig. 3.

Finally, we show in Figs. 2E and F the boron-11 MASS NMR spectrum of a Pyrex glass, together with its computer simulation. To adequately reproduce the experimental result we find it necessary to use a four-component simulation, comprising the following parameters:  $e^2qQ/h = 2.5$  MHz,  $\delta_i = 12.6$  ppm, intensity = 60%;  $e^2qQ/h = 2.3$  MHz,  $\delta_i = 16.0$  ppm, intensity = 10%;  $e^2qQ/h \approx 0.5$  MHz,  $\delta_i = 1.8$  ppm, intensity = 20%;  $e^2qQ/h = 0.5$  MHz,  $\delta_i = 0.2$  ppm, intensity = 10%. These results suggest the presence of essentially unmodified BO<sub>3</sub>/BO<sub>4</sub> units (BO<sub>3</sub>,  $\delta_i = 16.0$  ppm; BO<sub>4</sub>,  $\delta_i = 1.8$  ppm) together with the presence of BO<sub>3</sub>/BO<sub>4</sub> units whose structures are modified by incorporation into the silicate structure (BO<sub>3</sub>,  $\delta_i = 12.6$  ppm; BO<sub>4</sub>,  $\delta_i = 0.2$  ppm). One possible explanation is that the slightly shielded resonances arise from BO<sub>3</sub>/BO<sub>4</sub> units linked to one (or more) SiO<sub>4</sub> tetrahedra, causing the observed shifts to be closer to those for danburite-datolite (Table 1), and perhaps for tourmaline. Also, we note that

the relatively large shielding found for reedmergnerite (Fig. 3A), reedmergnerite  $B(OSi)_4$ units in a zeolite (2) and a feldspar (Fig. 3B) (19) are also consistent with this idea. However, the more shielded resonance could also arise from the presence of nonbridging oxygens. Extensive boron-10 and boron-11 NMR results on sodium borate and sodium borosilicate glasses indicate that boron in the reedmergnerite structure, as well as boron with nonbridging oxygens, both exist (3, 20-22). Further work to quantitate next-nearest neighbor effects on chemical shift is indicated.

In conclusion, the results we have presented above indicate that rapid "magicangle" sample-spinning boron-11 NMR spectra of borates (and borosilicates) can yield quantitatively reliable BO<sub>3</sub>/BO<sub>4</sub> ratios. BO<sub>3</sub> chemical shifts occur in the range  $\sim 12.7$ – 19.0 ppm, while BO<sub>4</sub> shifts occur in the range  $\sim -3.3$  to 2.0 ppm. However, the simple borates we have investigated resonate at  $\sim 17 \pm 1$  ppm (BO<sub>3</sub>) and  $1.5 \pm 0.5$ ppm (BO<sub>4</sub>) from BF<sub>3</sub> · Et<sub>2</sub>O. Our results also indicate that unless high-speed ( $\geq 6$  kHz) sample-rotation rates are employed, then all spectra of hydrogen-containing borates should be recorded in the presence of <sup>1</sup>H dipolar decoupling.

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