

# $^{11}\text{B}$ NMR investigation of boron interaction with mineral surfaces: Results for boehmite, silica gel and illite

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## Abstract

Boron is an important micronutrient for plants but is toxic at high pore solution concentrations. Its mobility and migration in many geochemical environments is often controlled by reactions with mineral surfaces, and thus its speciation on mineral surfaces has been extensively investigated. Most previous studies have used IR spectroscopy to characterize the surface B-environments. We present here the first  $^{11}\text{B}$  MAS NMR study of surface sorbed boron on minerals. The results demonstrate the capability of this method to effectively probe the local structure of the sorption sites at total B-concentrations in the samples as small as 0.03 wt% and to provide insight into the mechanisms of sorption. Signal is readily resolved for both trigonal (B(3)) and tetrahedral (B(4)) boron exchanged onto boehmite, silica gel and illite, and the resonances are readily assigned on the basis of chemical shift and quadrupole coupling constant. Boron surface densities on illite are approximately order of magnitude greater than on silica gel or boehmite. For boehmite, both B(3) and B(4) occur dominantly as inner-sphere complexes formed by ligand exchange reaction with surface aluminol sites. The B(3)/[B(3) + B(4)] ratio of approximately 0.87 does not vary significantly with pH from 3 to 11, with solution B-concentration, or with washing. The occurrence of B(3) and B(4) as inner-sphere complexes is in agreement with previous suggestions from IR studies of B-sorption on iron hydroxide, allophone, kaolinite, and hydrous ferric oxide. For silica gel, B(3) and B(4) occur principally as outer-sphere complexes or as residual precipitate from un-removed solution. The B(3)/B(4) ratio decreases with increasing pH paralleling the speciation in solution, but the relative abundance of B(4) is greater than in solution. A small fraction of the B(4) occurs as inner-sphere complexes with B(4)–O–Si linkages formed by ligand exchange reaction with silanol sites. For illite, surface boron occurs as outer-sphere B(3) and B(4), as for silica gel, and as inner-sphere B(3) and B(4), as for boehmite. Outer-sphere B(3) and B(4) are dominant at pH 3 and 5, whereas inner-sphere B(3) and B(4) are dominant at pH 9 and 11. The inner-sphere complexes probably form dominantly by ligand exchange reactions involving sites on the broken edges of illite layers.

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## 1. Introduction

Boron is a geochemically important element and an essential plant nutrient, but there is only a narrow concentration range in soil pore solution in which plants exhibit neither boron deficiency nor toxicity (Romero and Aquilar, 1986). The adsorption of boron on mineral surfaces controls its mobilization and migration in natural environments, and thus understanding its reaction with mineral

surfaces and its speciation on these surfaces is a key to understanding its transport and biological activity (Goldberg, 1999, 2004; Peak et al., 2003). Sorption isotherm and infrared (IR) spectroscopic studies of high surface area phases such as hydrous aluminum and iron oxide, iron hydroxide, and allophone have shown that boron occurs in both trigonal (B(3)) and tetrahedral (B(4)) coordination on mineral surfaces and that the B(4)/[B(3) + B(4)] ratio increases with increasing pH. This variation parallels its occurrence in solution as  $\text{B}(\text{OH})_3^0$  at low pH and  $\text{B}(\text{OH})_4^-$  at high pH (De Bussetti et al., 1995; Su and Suarez, 1995, 1997; Peak et al., 2003). Several sets of adsorption experiments have indicated that B(4) species

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are preferentially adsorbed from solution relative to B(3) and that they occur as both inner-sphere (ligand-exchanged, chemisorbed) and outer-sphere (physisorbed) complexes on mineral phases including goethite, Al oxide, and clay minerals (Goldberg et al., 1993; Keren et al., 1994; De Bussetti et al., 1995). Isotopic studies also suggest strong adsorption of borate on marine clay and marine carbonates (Palmer et al., 1987; Hemming and Hanson, 1992).

Boron adsorption on minerals is affected by many factors including pH, ionic strength, competing ions or organic matter, and the mineral species (De Bussetti et al., 1995; Goldberg et al., 1996, 2004; Prodromou, 2004). The pH is very important, with maximum B-sorption occurring at pH 8–10 for many phases including goethite, Al oxyhydroxides, and clay minerals (Bloesch et al., 1987; De Bussetti et al., 1995; Goldberg et al., 1996; Prodromou and Thessaloniki, 2000). The presence of other anions and increasing ionic strength generally increase B-sorption (Goldberg et al., 1993, 1996; De Bussetti et al., 1995), although the effect of ionic strength is different on different minerals. For example, Goldberg et al. (1993) found that boron adsorption increases with increasing ionic strength for montmorillonite, a montmorillonite soil, goethite, kaolinite, a kaolinite soil, but gibbsite. Increasing adsorption with increasing ionic strength indirectly indicates inner-sphere surface complexation (McBride, 1997) because the higher cation activity in solution is thought to compensate the surface negative charge generated by specific adsorption of borate. FTIR studies by Su and Suarez (1995, 1997) indicate that B(3) and B(4) are adsorbed via ligand exchange on the surfaces of amorphous aluminum and iron hydroxides, allophane, and kaolinite. Recently, Peak et al. (2003) identified both B(3) and B(4) on hydrous ferric oxide using ATR-FTIR spectroscopy. From these data, they proposed multiple surface inner-sphere surface complexes for both and also formation of outer-sphere surface complexes for boric acid.

Although IR spectroscopy can readily differentiate between B(3) and B(4) on mineral surfaces, analysis of the spectra is often limited by overlap from bands arising from the substrate. In contrast, NMR spectroscopy is element-specific and often shows high resolution for different surface species (see e.g., Kirkpatrick, 1988). Thus, although NMR is spectroscopically less sensitive than IR, it does not suffer signal interference from the substrate unless it has a significant B-content. In addition, interpretation of NMR spectra is not affected by the existence of impurity elements unless there is a significant concentration of paramagnetic species (typically Fe or Mn in natural samples), which can destroy observable signal in the spectrum. NMR has been used successfully to investigate mineral surface reactions in many systems, including alkali metals on clay minerals (Kim et al., 1996; Kim and Kirkpatrick, 1997) and phosphate on oxyhydroxide and oxide phases (Kim and Kirkpatrick, 2004). For instance,  $^{31}\text{P}$  MAS NMR can readily differentiate phosphate adsorbed on the surface from that in hydrous Al-phosphate phases

formed by surface precipitation reactions (Kim and Kirkpatrick, 2004).

This paper describes the first use of  $^{11}\text{B}$  NMR to study B-sorption on mineral surfaces. Data are presented for B-exchanged boehmite ( $\text{AlOOH}$ ; a model for Al- and possibly  $\text{Fe}^{+3}$  oxyhydroxides), silica gel (a high surface area model for quartz and other silica phases) and the clay mineral illite. The results demonstrate the ability of  $^{11}\text{B}$  NMR to detect well-resolved signal at B-concentrations as small as 0.03 wt.%, to distinguish B(3) and B(4) in inner-sphere and outer-sphere complexes, and to provide information about the next-nearest atomic neighbor linkages of these species. Illite is abundant in many geological environments. It has a dioctahedral 2:1 phyllosilicate structure similar to muscovite mica, but with typically a lower tetrahedral Al/Si ratio and often interlayer expandable (smectite) layers (Środoń and Eberl, 1984; Altaner et al., 1988). Even though B-sorption on clays plays an important role in controlling its migration and distribution in soils and water (Romero and Aquilar, 1986), its reaction with illite has not been systematically studied.

$^{11}\text{B}$  is a quite sensitive NMR nucleus (nuclear spin  $I = 3/2$ , 81.17% natural abundance, Larmor frequency = 160.3 MHz at  $H_0 = 11.7$  T) and has been widely applied to structural studies of borate and borosilicate minerals and borosilicate, boroaluminate, and borophosphate glasses (Turner et al., 1986; Bunker et al., 1990, 1991a,b; Gan et al., 1994; Du and Stebbins, 2003; Hansen et al., 2005). The spectral characteristics of these materials provide an essential basis for interpretation of the data for the sorbed B-containing species described here.

## 2. Experimental

The illite used here is from the Yangsan area, Korea, and was formed by hydrothermal alteration of rhyolite (Kim and Kirkpatrick, 1997). Its structural formula is  $(\text{K}_{0.82}\text{Na}_{0.04}\text{Ca}_{0.01})(\text{Si}_{3.12}\text{Al}_{0.88})(\text{Al}_{1.98}\text{Mg}_{0.02})\text{O}_{10}(\text{OH})_2$ , its polytype is  $2\text{M}_1$ , and it contains essentially no expandable layers. It was prepared for the exchange experiments by gravity settling to remove anatase impurity followed by drying in air. The boehmite was obtained from Alpha Products and the silica gel from Brinkmann. All were used as-received. Surface areas measured by  $\text{N}_2$  BET using an ASAP 2400 Micrometrics instrument are 7.8, 159, and 390  $\text{m}^2/\text{g}$  for the illite, boehmite, and silica gel, respectively.

For the main sets of adsorption experiments, 0.5 g of each sample was reacted with 50 mL of boric acid solution at pH 3, 5, 7, 9, and 11. The boric acid was reagent grade from Aldrich. The boric acid concentrations were 0.01 M for boehmite and 0.1 M for silica gel and illite. The pHs of the solutions were adjusted by HCl and NaOH addition. In a second set of experiments, boehmite was also reacted with 0.1, 0.001, and 0.0001 M boric acid solutions at pH 5 using the same procedures. All reaction mixtures were held in Teflon bottles in a rocking water bath at 25 °C for 24 h. No additional background electrolyte was used

in any of the experiments, and the NMR results are correlated with the analyzed B-contents of the solid samples after exchange. The exchange experiments were done in air, and no effort was made to exclude carbonate species, which are reported to not effectively compete with B adsorption and desorption (Saha and Singh, 1998).

After reaction, all samples were vacuum filtered using a Millipore filter system and air-dried. A portion of the boehmite samples reacted with 0.01 M boric acid solution at pH 5 and the silica gel sample reacted with 0.1 M boric acid at pH 7 and 9 were washed with water with the same pH as the reaction. None of the other samples were washed. The boron content of the vacuum-filtered samples was measured by inductively coupled plasma (ICP) spectrometry (Perkins-Elmore Model P2000).

The  $^{11}\text{B}$  NMR spectra were collected under magic-angle spinning (MAS) at 160.3 MHz using a home-built spectrometer based on an 11.7 T superconducting magnet (Oxford Instruments) and a Nicolet model 1280 computer and pulse programmer. The samples were spun at 5–9 kHz in 5 mm silicon nitride or alumina rotors using a sample probe manufactured by Doty Scientific (Columbia, South Carolina, USA). The excitation pulses were about 4  $\mu\text{s}$  (solution  $\pi/2 = 12 \mu\text{s}$ ), and a 4 s recycle delay was used routinely. No changes in peak shape or intensity were observed at longer recycle delays. The  $^{11}\text{B}$  chemical shifts are reported in parts per million (ppm) relative to external boron trifluoride diethyl etherate ( $\text{BF}_3\text{OEt}_2$ ). The  $^{11}\text{B}$  isotropic chemical shifts ( $\delta_i$ ), quadrupole coupling constants (QCC) and quadrupole asymmetry parameters ( $\eta$ ) were determined by spectral simulation using the simulation program QMASS used by Phillips et al. (1988). Evaluation of the accuracy of simulated signal intensities representing different sites in MAS NMR spectra of quadrupolar nuclei such as  $^{11}\text{B}$  is difficult due to the effects of potentially different quadrupole coupling constants and therefore different  $90^\circ$  pulse lengths. Experience with determining B(3)/B(4) ratios of known materials suggests that this can be done well under our experimental conditions (Turner et al., 1986; Bunker et al., 1988). However, the conservative way to interpret the data, which we use here, is to focus on changes in the signal intensities and to not rely heavily on the absolute values. In our experiment there are no observable changes in relative signal intensities with different pulse lengths.

### 3. Results and discussion

#### 3.1. B-content of exchanged samples

The elemental boron content of the exchanged samples ranges from about 0.03 to 0.35 wt% and varies substantially with mineral substrate and pH (Fig. 1). For all three phases, the B-concentration generally increases with increasing pH, and for boehmite and silica gel reaches a maximum at pH 9 and decreases at pH 11. These observations are in agreement with those of previous studies, which

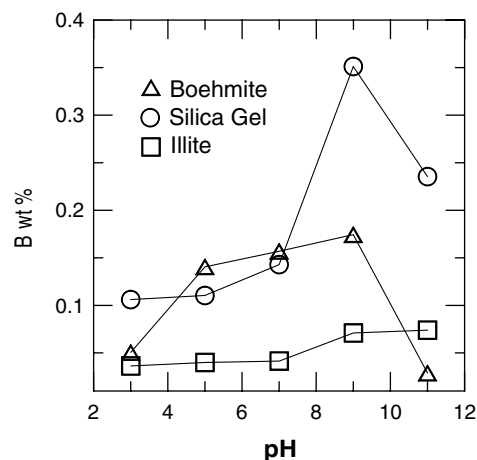


Fig. 1. Analyzed elemental B-content (wt%) of B-exchanged boehmite, silica gel, and illite after reaction in 0.01 M (boehmite) and 0.1 M (silica gel and illite) boric acid as a function of pH.

show B-sorption maxima at pH 8–9 for clay minerals and aluminum hydroxides (Bloesch et al., 1987; De Bussetti et al., 1995; Goldberg et al., 1996; Prodromou and Thessaloniki, 2000). The reaction  $\text{B}(\text{OH})_3^0 + \text{OH}^- \leftrightarrow \text{B}(\text{OH})_4^-$  has an equilibrium constant  $\log K = 9.2$  in aqueous solution at 25  $^\circ\text{C}$  (Shriver et al., 1994), and the maximum amount of sorption on mineral surfaces occurs ideally at pH = 9.2, (Singh and Mattigod, 1992), in agreement with the observations for silica gel and boehmite here. The amount of boron in our boehmite samples increases linearly with increasing boric acid concentration in solution at pH 5 (Fig. 2). Overall, illite shows the least total B-exchange but has the largest amounts per unit edge surface area. For the illite reacted with 0.1 M boric acid, there are 2.6–5.1 atoms/ $\text{nm}^2$ , whereas for the silica gel reacted with 0.1 M boric acid and boehmite reacted with 0.01 M

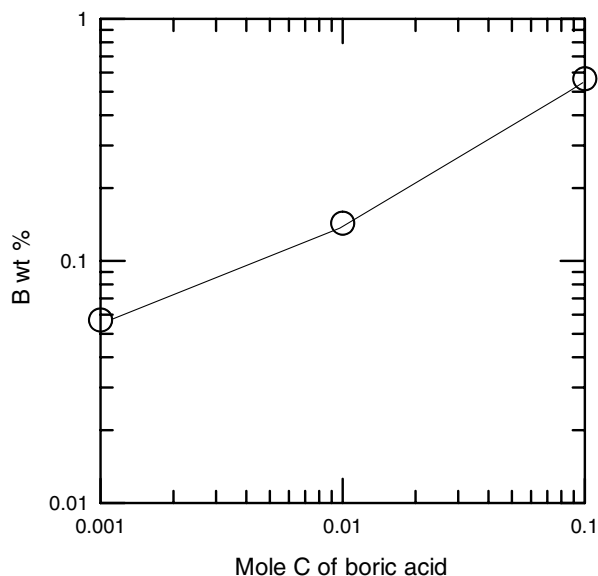


Fig. 2. Analyzed elemental B-content (wt%) of B-exchanged boehmite after reaction in  $10^{-3}$ ,  $10^{-2}$ , and  $10^{-1}$  M boric acid solutions at pH 5.

boric acid, there are 0.14–0.5 and 0.10 to 0.6 atoms/nm<sup>2</sup>, respectively. The comparable exchange on boehmite at the lower solution concentration suggests stronger B-bonding with boehmite than with the other phases.

### 3.2. <sup>11</sup>B NMR

#### 3.2.1. Boehmite

The <sup>11</sup>B MAS NMR results for the B-exchanged boehmite samples illustrate well the typical features of the spectra for our samples and provide a basis for interpreting the spectra of illite. For boehmite reacted with 0.01 M boric acid solution, the spectral features do not vary significantly with pH (Fig. 3). There is a resonance for B(3) with intensity between 7 and 20 ppm that shows resolved quadrupolar splitting, along with a narrow, symmetrical resonance for B(4) with a peak maximum between 0.7 and 1.6 ppm. The calculated isotropic chemical shifts ( $\delta_i$ ) and quadrupole coupling constants (QCC) of these two resonances are B(3): 19.3–19.9 ppm and 2.6 MHz and B(4): 1.7–2.1 ppm and  $\sim$ 0.5 MHz. The quadrupole asymmetry parameters ( $\eta$ ) cannot be accurately fit at  $H_0 = 11.7$  T (Turner et al., 1986), but values  $< 0.2$  for B(3) give good fits to our spectra, indicating a quite symmetric bonding environment. The B(3) and B(4) fractional signal intensities can typically be determined well under MAS at  $H_0 = 11.7$  T (Turner et al., 1986; Bunker et al., 1988), although as dis-

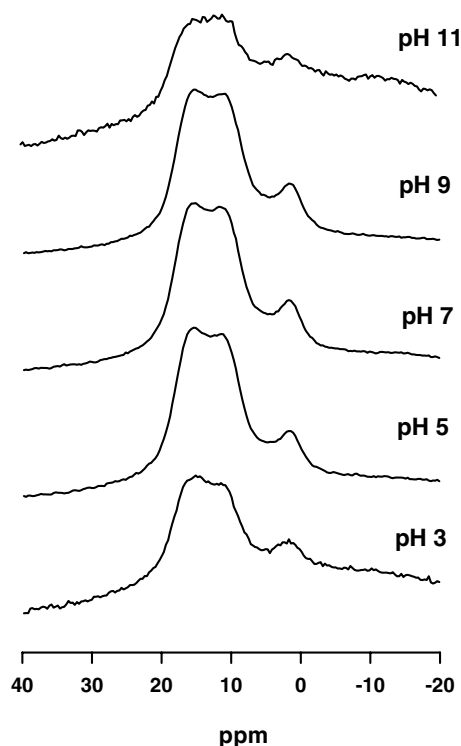


Fig. 3. <sup>11</sup>B MAS NMR spectra of B-exchanged boehmite collected at 11.7 T after reaction in 0.01 M boric acid solution at the indicated pH for 24 h. The irregular base line of the pH 3 and 11 samples is due to probe background and reflects the low B-content of these samples.

cussed above, caution is needed in the use of the absolute B(3)/B(4) ratios. For boehmite, the B(3)/B(4) ratios do not vary significantly from pH 3 to 11 (Fig. 4), even though in solution B(3) dominates at low pH and B(4) at high pH.

Decreasing solution concentration from 10<sup>-1</sup> to 10<sup>-3</sup> M at pH 5 results in lower B-content of the solid (Fig. 2) and lower signal/noise ratios in the <sup>11</sup>B NMR spectra (Fig. 5), but there is no significant change in  $\delta_i$  or QCC of the B(3) and B(4) resonances or in the fitted relative abundances of B(3) and B(4). In addition, washing with water with the same pH as the exchange-solution does not effect  $\delta_i$  or QCC and does not significantly change the B(3)/B(4) ratio (Fig. 6).

The absence of variation in the <sup>11</sup>B NMR spectra of the exchanged boehmite samples and the insolubility of the boron clearly indicate formation of a quite specific borooaluminate structure. The B could be exchanged onto the boehmite surface or a reconstructed boehmite surface via ligand exchange with surface aluminol sites, or it could be in borooaluminate precipitates. Our previous <sup>31</sup>P NMR study of P-exchanged boehmite and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> suggests that both surface aluminophosphates and aluminophosphate precipitates can occur (Kim and Kirkpatrick, 2004). For the results reported here, the sensitivity of NMR chemical shifts and quadrupolar coupling parameters to only nearest and next-nearest neighbor atomic structure and the absence of distinct resonances for boron on the surface and in precipitates prevents us from distinguishing these possibilities with assurance. Previous IR-spectroscopic studies of B-exchange onto amorphous aluminum and iron hydroxides, allophane, and kaolinite by Su and Suarez (1995, 1997) and hydrous ferric oxide by Peak et al. (2003) have suggested reaction via ligand exchange and the occurrence of surface B(3) and B(4) on those surfaces. Peak et al. (2003) proposed multiple inner-sphere complexes for B(3) and B(4) and also formation of outer-sphere B(3) surface complexes.

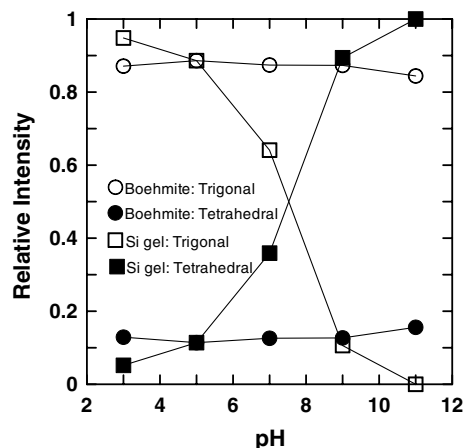


Fig. 4. Relative intensities of B(3) and B(4) in B-exchanged boehmite and silica gel as functions of pH obtained from curve fitting of the <sup>11</sup>B MAS NMR spectra.

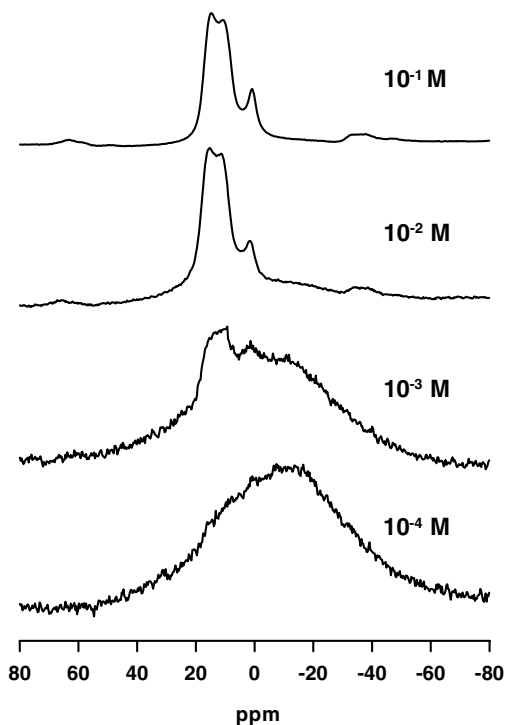


Fig. 5.  $^{11}\text{B}$  MAS NMR spectra of boehmite exchanged with pH 5 boric acid solutions with the indicated concentrations for 24 h. Signal for the  $10^{-4}$  M sample contains only broad probe background, but the  $10^{-3}$  M sample yields resolvable signal for B(3) and B(4) on top of the background.

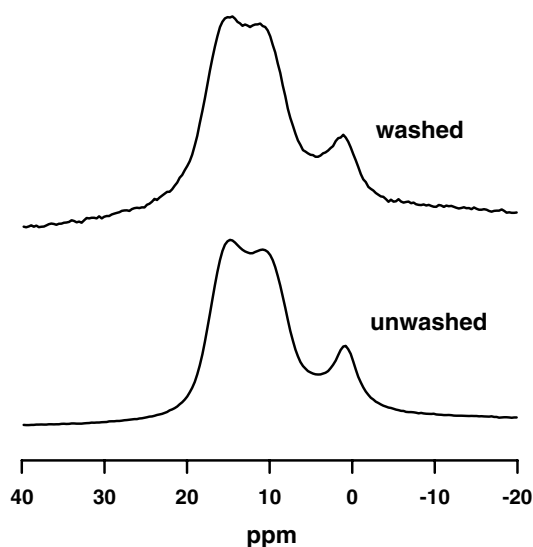


Fig. 6.  $^{11}\text{B}$  MAS NMR spectra of boehmite reacted with 0.01 M boric acid solutions at pH 5 for 24 h, before and after washing in water at the same pH as the exchange.

The invariance of the surface B-environments with solution pH and composition in the face of large changes in B(3)/B(4) ratio in solution (Peak et al., 2003) suggest the formation of a borosilicate structure that is stable over a wide range of conditions. The  $^{11}\text{B}$  NMR characteristics combined with fundamental crystal chemical bonding con-

cepts provide significant insight into the structure of this complex. The spectral characteristics of B(3) and B(4) in minerals and glasses are well documented and provide the basis for the interpretation of the spectra here (Turner et al., 1986; Bunker et al., 1988, 1990, 1991b; Gan et al., 1994; Du and Stebbins, 2003). B(3) has  $\delta_i$  values between about +12 and +19 ppm and QCCs between 2.3 and 2.6 MHz. The B(3)  $\delta_i$  values fall into two ranges, one near +12 to +13 for B(3) with B(3)–O–Si linkages and the other between about +16 and +19 for B(3) with B(3)–O–B and B(3)–O–Al linkages (Turner et al., 1986; Bunker et al., 1988, 1990, 1991b). B(OH)<sub>3</sub> resonates near 19 ppm. B(4) has  $\delta_i$  values from about –2.5 to +2 ppm and QCCs from 0 to 0.3 MHz, although the QCCs are too small to determine accurately under MAS at  $H_0 = 11.7$  T. Negative B(4) chemical shifts occur only for B(4) with B(4)–O–Si linkages, and positive chemical shifts indicate B(4) with dominantly B(4)–O–B and B(4)–O–Al linkages. B(3) and B(4) in aqueous solution resonate near +20 and +2 ppm, respectively (How et al., 1969). The increased shielding of both B(3) and B(4) with B–O–Si linkages relative to those with B–O–B or B–O–Al linkages parallels the well known trends of increasing shielding with increasing electronegativity of the next-nearest atomic neighbor cation observed for other nuclei such as  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ , and  $^{31}\text{P}$  (e.g., Kirkpatrick, 1988). Indeed, the  $^{11}\text{B}$   $\delta_i$  for BPO<sub>4</sub>, which has B(4)–O–P linkages is even more shielded at  $\delta_i = -3.3$  ppm (Turner et al., 1986). The  $^{11}\text{B}$  chemical shift range is smaller than those of  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ , and  $^{31}\text{P}$ , because B has a lower atomic number. None-the-less, the chemical shift ranges for the different B-species are clear and consistent with the behavior of all other cations studied.

For the B-exchanged boehmite, the  $\delta_i$  and QCC values of 19.3–19.9 ppm and 2.6 MHz for B(3) and 1.7–2.1 ppm and  $\sim 0.5$  MHz for B(4) are clearly consistent with dominance of B(3)–O–B,Al and B(4)–O–B,Al linkages. Indeed, the spectra here are essentially identical to those of borosilicate glass with low modifier cation (alkali or alkaline earth) content (Bunker et al., 1991b). In addition, the relatively low  $\eta$  value for B(3) here suggests symmetrical B(3) environments with each B(3)–O–X linkage having X = B or Al, rather than an alkali cation. The stability of structures involving B and Al have been analyzed in terms of the charge neutrality of the bond strengths donated by the cations to the oxygen atoms (Bunker et al., 1991a), and structures involving B(3), B(4), and octahedral Al (Al(6), the coordination in boehmite) are highly stable. Specifically, the oxygen atoms coordinated to two B(3)s (B(3)–O–B(3) linkages), to 1 B(3) and 2 Al(6) (B(3)–O–2Al(6)), and to 1 Al(6) and any combination of two Al(4) and B(4) (Al(6)–O–2Al,B(4)) receive a formal charge from their NN cations of exactly +2, making them highly stable (Bunker et al., 1991a). The dominance of B(3) coordination for our boehmite samples suggests that its stabilization occurs via ligand exchange reactions involving B(OH)<sub>3</sub> in solution with aluminols, such as B(3)–OH + HO–2Al(6) = B(3)–O–2Al(6) + H<sub>2</sub>O.

### 3.2.2. Silica gel

The  $^{11}\text{B}$  MAS NMR spectra of the B-exchanged silica gel are very different from those of the boehmite and indicate very different surface interactions (Fig. 7). The peak for B(3) does not show the well resolved quadrupole peak splitting of the boehmite samples, borate minerals or B-containing glasses and appears to be a composite of several resonances. The maximum near 18 ppm suggests significant  $\text{B}(\text{OH})_3$  (Bunker et al., 1988), but we have not attempted to simulate the overlapping components. The B(4) peak is narrow and symmetrical with a peak maximum of  $-0.4$  to  $0.4$  ppm that does not change systematically with pH but is slightly negative for pH 9 and 11 ( $-0.2$  and  $-0.4$  ppm). In contrast to boehmite, the B(3)/B(4) ratio decreases with increasing pH, paralleling the trend in solution (Fig. 7). At pH 3 B(3) is by far dominant, whereas at pH 9 and 11 B(4) is dominant. Washing the pH 7 and 9 samples in water with the same pH as the reactant solution removes almost all the B(3), resulting in spectra with poorer signal/noise ratios, a weak B(4) resonance for the pH 7 sample, and a relatively strong B(4) for the pH 9 sample. The B(4) resonances for both washed samples have maximum at  $-0.6$  ppm, indicating inner sphere complexes with B(4)–O–Si linkages (Fig. 8). The broad component under the signals for pH 7 sample is dominantly probe background.

The  $\text{B}(4)/[\text{B}(3) + \text{B}(4)]$  signal intensity ratio for the silica gel samples is greater than that in solution at all pHs except

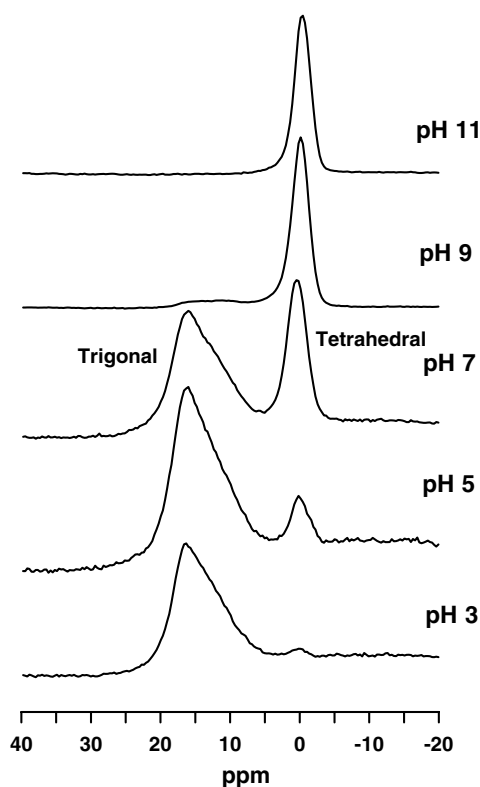


Fig. 7.  $^{11}\text{B}$  MAS NMR spectra of silica gel after reaction with 0.1 M boric acid solutions at the indicated pH values for 24 h.

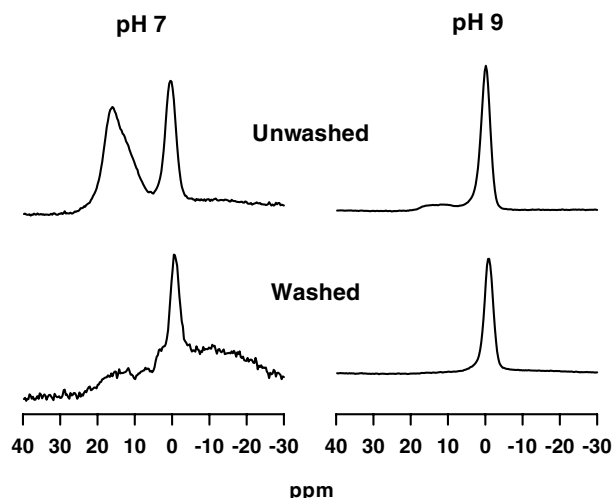


Fig. 8.  $^{11}\text{B}$  MAS NMR spectra of silica gel reacted with 0.1 M boric acid solution at pH 7 and 9 for 24 h, before and after washing with DI water.

11, suggesting its preferential adsorption in agreement with previous suggestions by Palmer et al. (1987) and Hemming and Hanson (1992) for marine clays and carbonate. The dissociation constant of boric acid is  $10^{-9.2}$  leading to negligible B(4) concentrations in solution at pH 3, 5, and 7, a  $\text{B}(3)/[\text{B}(3) + \text{B}(4)]$  ratio of 0.63 at pH 9, and essentially all B(4) at pH 11. However, the spectra of the exchanged samples have  $\text{B}(3)/[\text{B}(3) + \text{B}(4)]$  ratios of 0.05, 0.11, 0.36, and 0.90 at pH 3, 5, 7, and 9, respectively. Even if the fitted relative signal intensities are somewhat in error due to NMR quadrupolar effects, the presence of significant B(4) at low pHs strongly supports its preferential sorption. The removal of the bulk of the B(3) and B(4) by mild washing indicates that the bulk of the boron binding to silica gel occurs in weakly held outer-sphere complexes and not via ligand exchange as for boehmite. The low surface coverage determined from chemical analysis is consistent with this conclusion. Some of the B present may also be precipitate from un-removed solution. Although the points of zero charge (PZC) of silica phases such as quartz and silica gel are reported to be near two (Parks and De Brnyn, 1962; Parks, 1965), there is evidence that silica surfaces typically remain quite highly protonated up to pH 10 (Roose et al., 1999; Zhuravlev, 2000; Sahai, 2002; Cardenas, 2005). Thus, the preference for B(4) may be due to preferential H-bond interactions between surface  $\text{Si}-\text{OH}$  and  $\text{BO}_4^-$ .

The washed pH 7 and 9 samples, however, do yield detectable signal for unremoved B(4) (Fig. 8), and the negative peak maximum of  $-0.6$  ppm shows that it is involved in B(4)–O–Si structural linkages. These probably occur on the surface by ligand exchange reaction with silanols,  $\text{B}(4)-\text{OH} + \text{HO}-\text{Si} = \text{B}(4)-\text{O}-\text{Si} + \text{H}_2\text{O}$ , or in precipitates. Each B(4) may be linked to more than one Si. The oxygen atom in a B(4)–O–Si linkage is underbonded with a formal donated charge of  $+1.75$ . In crystals and glasses this deficiency is typically balanced by nearby alkali or alkaline earth counterions. In our samples, the  $\text{Na}^+$  from the

NaOH added to adjust pH may play this role.  $\text{Na}^+$  may also charge balance non-bridging B(4)–O sites.

Polymerization of the boron species may also affect the surface reaction discussed here. At boric acid concentrations greater than 25 mM, polyborates including B(3) and B(4) can be formed in alkaline conditions (Cotton and Wilkinson, 1980). This was not the case for our experiments with boehmite reacted at lower concentration of boric acid. The spectra for the silica gel sample, however, show a continuous decrease in B(3)/B(4) ratio with increasing pH, paralleling the speciation in solution. There are no other specific changes at high pH values, consistent with the absence of an affect of borate polymerization on the surface reactions.

### 3.2.3. Illite

The  $^{11}\text{B}$  NMR spectra of the B-exchanged illite samples show the presence of surface B-sites similar to those of both boehmite and silica gel (Fig. 9), reflecting its more complex dioctahedral 2:1 phyllosilicate structure (Środoń and Eberl, 1984). At pH 3 and 5 the spectra resemble those of the B-exchanged silica gel samples, except that the B(3)/B(4) ratios are smaller. There is poorly resolved B(3) signal with a peak maximum near +18 ppm and a narrow B(4) peak with a maximum at 0.2–0.4 ppm. The chemical shifts and peak shapes, thus, suggest that these signals are due dominantly to B(3) and B(4) adsorbed in outer sphere complexes and perhaps to residual precipitate from un-removed solution. The illite samples showed the poorest removal of solution by vacuum filtration of all our samples.

Signal for a B(4) site with a maximum near +2.5 ppm occurs as a small shoulder at pH 5 and increases in intensity with increasing pH. This signal is similar to that for

B(4) on boehmite. In parallel, the signal in the B(3) region becomes somewhat better resolved and the intensity maxima move to less positive values. Again, this signal is quite similar to the B(3) signal for boehmite. Thus, the chemical shifts and peaks shapes for these two sites indicate that they represent inner-sphere surface complexes or precipitates containing B–O–Al bonds and formed by ligand exchange reactions of the type described for boehmite. Relative to boehmite, however, the fitted signal intensity for inner-sphere B(4) is more abundant, suggesting a different overall structure. The structure of illite is composed of a dioctahedral Al sheet sandwiched between two (Si,Al) tetrahedral sheets (Środoń and Eberl, 1984). The tetrahedral sheet is thought to expose only the basal oxygens involved in Si(4)–O–Si,Al(4) linkages. Broken edges on illite crystallites, however, are thought to expose more reactive sites, and if the boron is on the illite surface, it is most likely that the ligand exchange reactions with aluminols occur dominantly on broken edges. This structural environment appears to favor B(4) compared to boehmite, but the current data do not allow more detailed structural analysis. Previous isotope fractionation studies of boron have suggested strong sorption of B(4) on marine clays including illite, mixed-layer illite–smectite, and kaolinite (Palmer et al., 1987) and results here support this conclusions.

## 4. Conclusions

$^{11}\text{B}$  MAS NMR spectroscopy readily detects and resolves signal for trigonal (B(3)) and tetrahedral (B(4)) boron in exchanged samples of boehmite, silica gel, and illite at total B-concentrations as small as 0.03 wt% B. These borate species may be surface adsorbed or in precipitates. The  $^{11}\text{B}$  resonances are readily assigned on the basis of chemical shift and quadrupole coupling constant. For boehmite ( $\text{AlOOH}$ ), both B(3) and B(4) occur dominantly as inner-sphere complexes formed by ligand exchange reaction with aluminols on the surface or in solution. The B(3)/[B(3) + B(4)] ratio of approximately 0.87 does not vary significantly with pH from 3 to 11, with solution B-concentration, or with washing. Our interpretations are in agreement with previous suggestions from IR studies of B-sorption on amorphous aluminum and iron hydroxides, allophane, and kaolinite (Su and Suarez, 1995, 1997; Peak et al., 2003). For silica gel B(3) and B(4) occur principally as sorbed outer-sphere complexes or are in residual precipitates from un-removed solution. The B(3)/B(4) ratio decreases with increasing pH, but the relative abundance of B(4) is greater than in solution. A small fraction of the B(4) occurs as surface complexes or precipitates with B(4)–O–Si linkages formed by ligand exchange reaction. Illite has higher boron surface atomic densities than the other two phases, and boron occurs as outer-sphere B(3) and B(4), as for silica gel, and as inner-sphere B(3) and B(4), as for boehmite. Outer-sphere B(3) and B(4) appear to dominate at pH 3 and 5, whereas inner-sphere B(3) and B(4) dominant at pH 9 and 11.

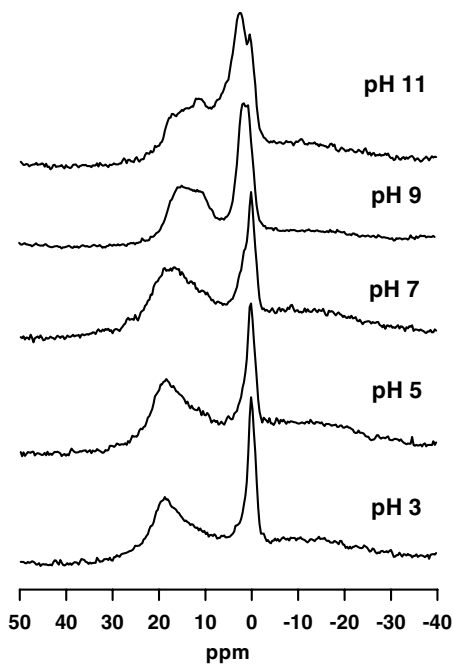


Fig. 9.  $^{11}\text{B}$  MAS NMR spectra of illite reacted with 0.1 M boric acid solution at the indicated pH values for 24 h.

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