

## TEMPERATURE EFFECTS ON BORON ADSORPTION BY REFERENCE MINERALS AND SOILS

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**Information on the effect of temperature on B adsorption by soils and soil minerals is scant. These data are needed to understand B availability. Boron adsorption on goethite, gibbsite, kaolinite, montmorillonite, calcite, and two arid zone soils was investigated as a function of solution pH (3–12) and reaction temperature (10, 25, and 40°C) after 2 h of reaction time. Boron adsorption on all materials increased from pH 3 to 7, exhibited a peak at pH 7.5 to 10, and decreased from pH 10.5 to 12. Temperature dependence measured as the increase of the B adsorption maximum at 10°C compared with 40°C on reference minerals increased in the order: calcite (3%) < goethite (7%) < gibbsite (18%) < montmorillonite (–20%) < kaolinite (26%). The kaolinitic soil exhibited greater temperature dependence than the smectitic soil. The B adsorption reaction was exothermic since B adsorption decreased with increasing temperature for all materials, except for montmorillonite at high pH. Highly specific ion adsorption is expected to be exothermic, suggesting an inner-sphere adsorption mechanism for B on all reference minerals except montmorillonite.**

Boron is a micronutrient element required in the nutrition of higher plants. The sufficiency range for B in plants is narrow; yield decrement occurs both as a result of B deficiency and B toxicity. Because plants respond only to dissolved B in solution, careful characterization of B adsorption is important both for B fertilization and for management of high-B irrigation waters.

The association of B deficiency with hot, dry summer weather is likely an interactive effect of temperature and soil moisture (Fleming 1980). Information about the effect of temperature per se on B availability and B adsorption is both scant and contradictory. Boron adsorption as a

function of temperature has been studied previously on two California soils (Biggar and Fireman 1960), one Mexican soil (Bingham et al. 1971), and three Indian soils (Singh 1971). Biggar and Fireman (1960) found decreased retention of about 35 percent for the smectitic Yolo soil and about 15 percent for the kaolinitic Aiken soil when the temperature was increased from 25 to 45°C. In contrast, Bingham et al. (1971) found an average increase of 17 percent in B adsorption as the temperature of the amorphous La Palma soil was increased from 10 to 40°C. Singh (1971) also found increases in B adsorption as a function of increasing temperature from 22°C to 45°C; adsorption increasing slightly for the sandy loam (5%) and the loam (8%), while increasing dramatically for the loamy sand (79%). The results of Biggar and Fireman (1960) and Bingham et al. (1971) are not necessarily contradictory since the mineralogical composition of the soils studied was different. Singh (1971) did not determine the mineralogy of his soil samples. Reaction time for all three studies was 24 h.

The B-adsorbing surfaces in soils are aluminum and iron oxide minerals, clay minerals, calcium carbonate, and organic matter. The effect of temperature on B adsorption has been investigated only on clay minerals (Harder 1961; Couch and Grim 1968; Singh 1971; Jasmund and Lindner 1973). For short and long reaction times, B adsorption on clays increased with increasing temperature. Adsorption on illite after 12 h and 30 days of reaction increased when the temperature was increased from 60 to 90°C and 185 to 215°C, respectively (Couch and Grim 1968). Adsorption was more than twice as great at the higher temperatures than at the lower temperatures. Adsorption at 80°C after 23 days of reaction was 4 to 5 times as great as adsorption at 15°C after 35 days of reaction on a clay containing both illite and chlorite (Harder 1961). Boron adsorption on kaolinite and montmorillonite increased with increasing temperature from 22 to 45°C when reacted for 1 day (Singh 1971). Boron fixation on Lewistown kaolinite, Otay montmorillonite, and Caslano illite

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increased with increasing temperature from 20 to 90°C using a 60-day equilibration. The mechanism of B uptake by illite is suggested to be a two-step process (Fleet 1965; Couch and Grim 1968; Jasmund and Lindner 1973). Initially, B adsorbs chemically as borate on particle edges, and it subsequently incorporates into tetrahedral sites replacing structural aluminum.

The effects of temperature on B adsorption as a function of pH has not yet been investigated. In this paper we present B adsorption data as a function of pH on aluminum and iron oxide, clay minerals, calcium carbonate, and soil samples at three different temperatures.

#### MATERIALS AND METHODS

Boron adsorption as a function of pH and temperature was studied on various adsorbents. Gibbsite ( $\alpha$ -Al(OH)<sub>3</sub>) and goethite ( $\alpha$ -FeOOH) were synthesized according to the procedures described by Kyle et al. (1975) and McLaughlin et al. (1981), respectively. X-ray diffraction analysis was used to verify the oxide mineralogy. Samples of kaolinite (KGa-2, poorly crystallized kaolinite) and Na-montmorillonite (SWy-1, Wyoming bentonite) were obtained from the Clay Minerals Society's Source Clays Repository and used without any pretreatment. The calcium carbonate sample was Multifex calcite obtained from Pfizer Inc., identified as calcite using X-ray diffraction analysis, and used without any pretreatment. Subsurface (25–51 cm) samples of the Arlington (coarse-loamy, mixed, thermic Haplic Durixeralf) and Bonsall (fine, montmorillonitic, thermic Natric Palexeralf) soil series were sieved to contain the <2-mm fraction. Although the Bonsall soil is classified as montmorillonitic, the clay mineralogy of our

particular subsample was dominated by kaolinite. Clay content was 140 g kg<sup>-1</sup> for the Arlington soil and 309 g kg<sup>-1</sup> for the Bonsall soil as determined with the hydrometer method of Day (1965). Organic carbon content of the soil samples was determined by the method of Nelson and Sommers (1982) and found to be low ( $\leq 0.2\%$ ).

Trace impurities in the oxides, clay minerals, and calcite were determined using X-ray diffraction powder mounts and are provided in Table 1. Dominant clay minerals in the soils, listed in Table 1, were determined by converting X-ray diffraction peak areas obtained with oriented mounts directly to clay mineral contents using the method of Klages and Hopper (1982). Specific surface areas of all materials were determined using a single point BET-N<sub>2</sub> adsorption isotherm with a Quantachrome Quantasorb Jr. surface area analyzer. Points of zero charge were determined using a Zeta-Meter 3.0 system as described by Goldberg et al. (1993).

Boron adsorption envelopes (amount of B adsorbed as a function of solution pH per fixed total B concentration) were determined in batch systems. Samples of adsorbent (0.375 g for oxides, 0.75 g for montmorillonite, 2.5 g for kaolinite, and 5.0 g for calcite and soils) were added to 50-ml polypropylene centrifuge tubes and equilibrated with aliquots (25 ml for clays, calcite, and soils and 15 ml for oxides) of a 0.1 M NaCl solution by reciprocal shaking for 2 h in a Grant heating and cooling water bath. The bath temperature was maintained at 10, 25, or 40°C with a sensitivity of  $\pm 0.1^\circ\text{C}$ . The equilibrating solution contained 5.0 mg B L<sup>-1</sup> and had been adjusted to the desired pH values using 1 M HCl or 1 M NaOH additions that changed the total

TABLE 1  
Characterization of adsorbent materials

Reference minerals	Trace impurities	B.E.T. Surface area (m <sup>2</sup> g <sup>-1</sup> )	PZC
gibbsite, $\alpha$ -Al(OH) <sub>3</sub>	bayerite	32.9	9.6
goethite, $\alpha$ -FeOOH	hematite	42.5	8.5
KGa-2 kaolinite	chlorite	19.3	3.3
SWy-1 montmorillonite	mica	18.6	<2.0
calcite, CaCO <sub>3</sub>	none	22.0	>11.8
<i>Soils</i>	<i>Dominant minerals</i>		
Arlington	smectite, vermiculite, kaolinite	13.7	<2.0
Bonsall	kaolinite, illite, smectite	22.2	<2.0

volume by <2%. The samples were centrifuged for 20 min in a Sorvall Superspeed Centrifuge at 7800 RCF (10,000 rpm). The decantates were analyzed for pH, filtered through a 0.45- $\mu\text{m}$  Whatman filter, and analyzed for B concentration. Boron was determined on a Technicon Auto Analyzer II using the Azomethine-H method described by Bingham (1982).

Boron adsorption isotherms (amount of B adsorbed as a function of equilibrium B concentration) were also determined in batch systems. The procedure was modified so that the equilibrating solution contained 1, 2, 5, 10, 15, 25, 50, or 100 mg B L<sup>-1</sup>, and no acid or base additions were used. Boron adsorption isotherms were determined at 10 and 40°C and average pH values of 5.8 for gibbsite, 7.0 for goethite, 3.7 for kaolinite, 8.1 for montmorillonite, 7.4 for Arlington soil, and 6.0 for Bonsall soil. Standard deviations ranged from 0.04 for kaolinite at 10°C to 0.86 for gibbsite at 40°C.

#### RESULTS AND DISCUSSION

Boron adsorption on all materials could be described by the Langmuir and Freundlich isotherms up to an initial B concentration of 50 mg B L<sup>-1</sup>. The fit of the equations to the data, as measured by the coefficient of determination,  $r^2$ , was significant at the 99% level of confidence. Langmuir and Freundlich isotherms were fit to the B adsorption data using the nonlinear least squares optimization program ISOTHERM (Kinniburgh 1985). In using this computer program, linearization of adsorption isotherm equations is not required, avoiding the introduction of changes in error distribution and biased parameters. For calcite and the two soils, Langmuir adsorption maxima for 40°C were statistically larger than for 10°C at the 95% level of confidence. For the other materials, there was no statistical difference.

Boron adsorption as a function of pH and temperature is shown in Fig. 1a for gibbsite and in Fig. 1b for goethite. Adsorption increased with increasing solution pH to an adsorption peak near pH 9 and then decreased as the pH continued to increase. Boron adsorption on oxides decreased with increasing temperature. The temperature dependence of B adsorption was slight on goethite. On gibbsite, temperature dependence of B adsorption was significant near the adsorption maximum but slight at low and high pH values.

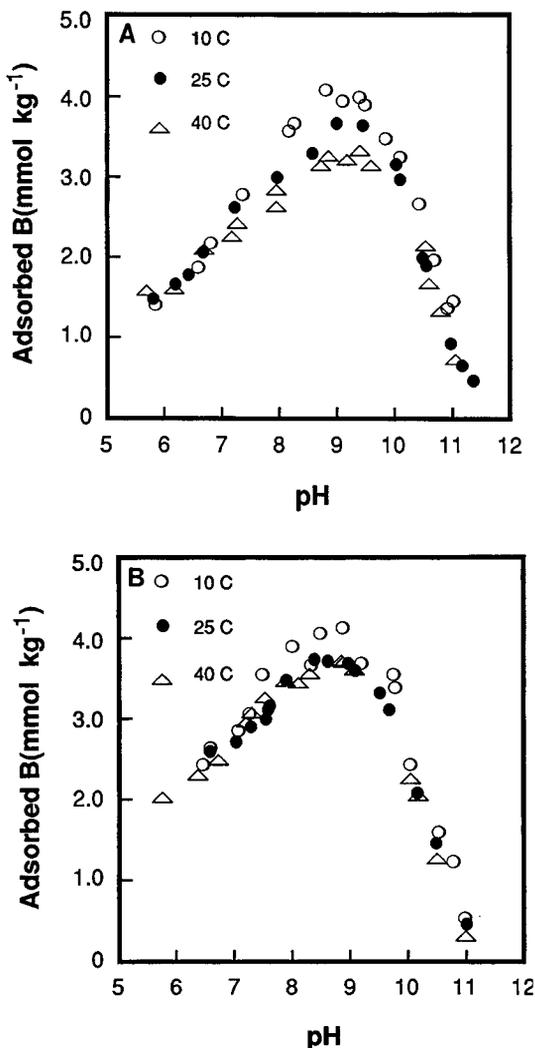


FIG. 1. Boron adsorption as a function of pH and temperature on oxides: (a) gibbsite,  $\alpha\text{-Al}(\text{OH})_3$ ; (b) goethite,  $\alpha\text{-FeOOH}$ .

Boron adsorption on clay minerals as a function of temperature and pH is shown in Fig. 2a for kaolinite and Fig. 2b for montmorillonite. Boron adsorption on kaolinite exhibits a peak near pH 8. Temperature dependence of B adsorption is pronounced, with adsorption decreasing with increasing temperature. Boron adsorption on montmorillonite decreases with increasing temperature at low pH and increases with increasing temperature at high pH. The adsorption maximum is shifted to higher pH values with increasing temperature; maximum adsorption occurs near pH 9.5 at 10°C and near

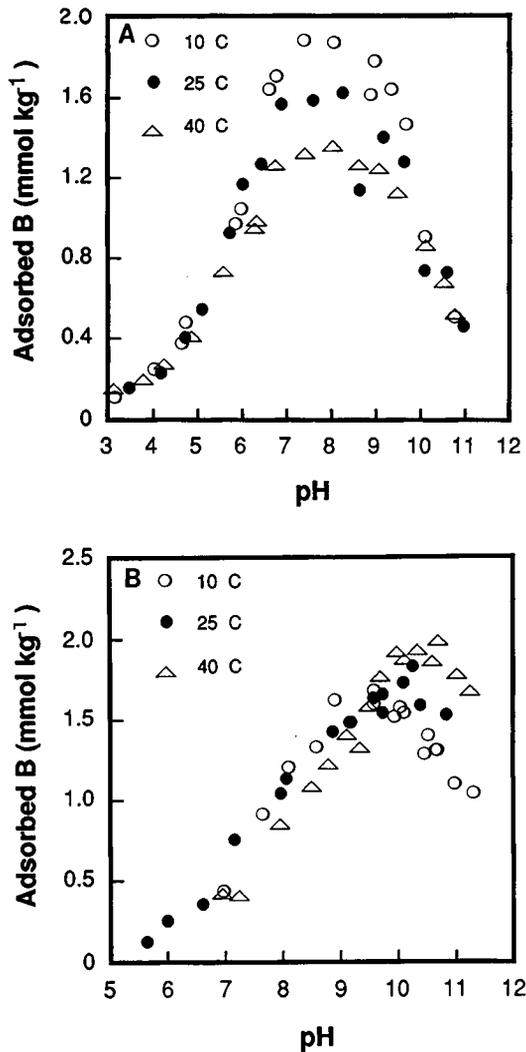


FIG. 2. Boron adsorption as a function of pH and temperature on clay minerals: (a) kaolinite; (b) montmorillonite.

pH 10.5 at 40°C. The shift in the adsorption maximum may result because the pH of the point of zero charge (PZC) on aluminum oxide increases with increasing temperature from 4.5 at 10°C to 7.5 at 40°C (Akratopulu et al. 1986). Thus, as the PZC value increases, the particles retain a positive charge over a greater pH range, allowing greater adsorption of anions. The pH shift in PZC is much greater than the decrease in  $pK_a$  value for boric acid, with increasing temperature from 9.38 at 10°C to 9.13 at 40°C (CRC Press 1983). However, since no similar shift in adsorption maximum was observed for gibbsite,

the shift may be due to a change of adsorption mechanism or dissolution of montmorillonite at high pH.

Figure 3 shows B adsorption on calcite as a function of pH and temperature. The B adsorption maxima occur near pH 10. Temperature dependence of B adsorption is very slight, but adsorption is higher at lower temperatures.

Boron adsorption on soils as a function of temperature and pH is shown in Fig. 4a for the kaolinitic Bonsall soil and in Fig. 4b for the smectitic Arlington soil. Boron adsorption on the Bonsall soil exhibits a peak near pH 9. As for reference kaolinite, temperature dependence of B adsorption on the kaolinitic soil is pronounced, with adsorption increasing with decreasing temperature. Boron adsorption on the Arlington soil peaks near pH 10. As for reference montmorillonite, B adsorption on the smectitic soil decreases with increasing temperature. Unlike for montmorillonite, temperature dependence of B adsorption is very slight at high pH and does not reverse with increasing temperature.

Boron adsorption on all materials studied decreased with increasing temperature, with the exception of adsorption on montmorillonite above pH 9.5. The reaction is thus exothermic, as is usually the case for adsorption. Highly specific adsorption of electrolyte ions is expected to decrease with increasing temperature (Helfferich 1962). Previous research performed in

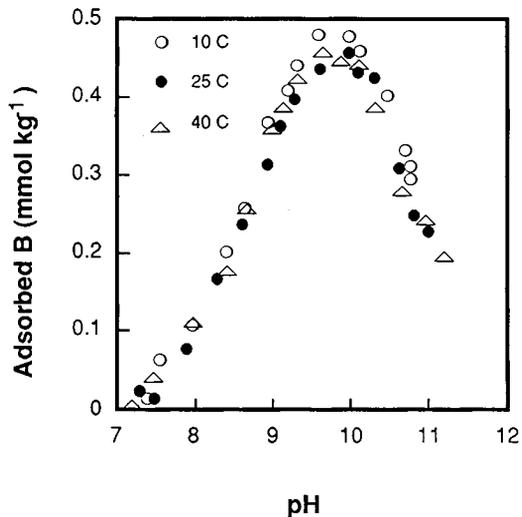


FIG. 3. Boron adsorption as a function of pH and temperature on Multiflex calcite.

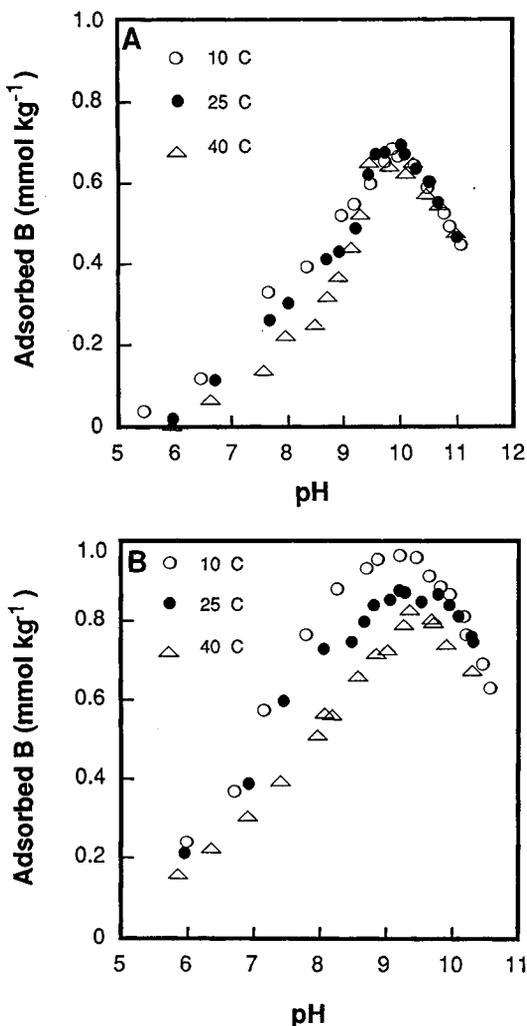


FIG. 4. Boron adsorption as a function of pH and temperature on soils: (a) kaolinitic Bonsall soil; (b) smectitic Arlington soil.

our laboratory using PZC determinations and ionic strength dependence of B adsorption measurements has suggested a specific inner-sphere adsorption mechanism for B on goethite, gibbsite, and kaolinite (Goldberg et al. 1993). An inner-sphere surface complex contains no water molecules between the adsorbate ion and the surface functional group (Sposito 1984). Shifts in PZC were also obtained for B adsorption on calcite indicating an inner-sphere adsorption mechanism (data not shown). Previous determinations of ionic strength dependence of B adsorption performed in our laboratory have suggested an outer-sphere adsorption mecha-

nism for B on montmorillonite (Goldberg et al. 1993). An outer-sphere surface complex contains at least one water molecule between the adsorbate ion and the surface functional group (Sposito 1984). This difference in B adsorption mechanism may explain the reversal of the temperature dependence of B adsorption by montmorillonite at high pH. Temperature dependence was measured as the percentage increase in B adsorption maximum at 10°C as compared with 40°C. The temperature dependence of B adsorption by the reference minerals increased in the order: calcite (3%) < goethite (7%) < gibbsite (18%) < montmorillonite (20%) < kaolinite (26%). The kaolinitic Bonsall soil exhibited greater temperature dependence of B adsorption than the smectitic Arlington soil. Thus the temperature dependence of B adsorption on soil may perhaps be governed by the dominant clay mineralogy of the soil. The increase in B adsorption on soils with increasing temperature explains the decreased availability and increased deficiency of B associated with hot, dry weather.

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