BORON ADSORPTION ON ALLOPHANE WITH NANO-BALL MORPHOLOGY

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ABSTRACT

Two types of reaction scheme were proposed for boron (B) adsorption at equilibrium B concentrations of less than 2 mM on nano-ball shaped allophane with its fundamental structure of aluminum orthosilicate.

(i) Al-OH + B(OH)₃ → Al-O-B(OH)₂ + H₂O
(ii) Al-OH + B(OH)₄⁻ → Al-(OH)-B(OH)₃ + OH⁻

With the aluminol groups (Al-OH) included in the structure, the reaction (i) occurs below equilibrium pH of about 10, whereas the reaction (ii) does at equilibrium pH of higher than about 8. Calculated Langmuir parameters suggested that the aluminol groups of nano-ball allophane had higher affinity for B(OH)₄⁻ than B(OH)₃. Because the content of the aluminol groups increase with decreasing Si/Al ratio of allophane, B adsorption maxima were higher for KyP sample (Si/Al=1.34:2) than for KnP sample (Si/Al=1.98:2) irrespective of equilibrium pH. Release of Si from allophane samples during B adsorption on them was much smaller than the case of phosphate (P) adsorption previously studied. This indicates that B has less ability than P for replacing Si in the structure of nanoball allophane and the main B adsorption site is the aluminol group at the pore of the allophane nano-ball.

Key words: Adsorption, boron, Langmuir equation, nano-ball allophane

INTRODUCTION

Boron (B) is an important element for agricultural production because it is one of the microelements most plants inevitably require for their normal growth. The element has a marked effect on plants and crops from the standpoint of both nutrition and toxicity, being a relatively narrow range between levels of its content which cause deficiency and toxicity symptoms (Keren and Bingham, 1985). Behavior of boric acid as well as other oxo-acids in soils and surface waters is also very important in environmental and ecological aspects.

The amount of B adsorbed by soil varies depending on types and contents of soil constituents such as clay minerals and organic matter (Parfitt, 1978). Volcanic-ash-derived soils adsorb large amounts of boric acid and the adsorption has been ascribable to allophanic clays in the soils (Schalcha et al., 1973). However, the detailed mechanism of B adsorption is not well known with respect to micromorphology and chemical structure of allophane.

Allophane, a main component in allophanic clays, is a series name of naturally occurring amorphous hydrous aluminosilicates with various chemical compositions (Wada
and Harward, 1974). The aluminosilicates had not been believed to have a definite morphology and structure. Henmi and Wada (1976) found that allophane, at least separated from volcanic ash soils and weathered pumice grains, had definite hollow spherical morphology (nano-ball with diameter of about 5nm) and a narrow range of chemical compositions from 1:2 to 2:2 with respect to Si/Al atomic ratio. Hereafter, allophane with hollow spherical morphology is referred to nano-ball allophane. With combination of detailed mineralogical analyses, physico-chemical properties have been investigated for allophane with nano-ball morphology, which was collected carefully not to involve impurities in it, in order to make clear the chemical structure of wall of the ball in relation to its Si/Al ratio (Henmi, 1977; Henmi, 1980; Henmi et al., 1983; Henmi, 1985; Henmi and Huang, 1985). The wall structure of nano-ball allophane has been proposed as aluminum-nesosilicate structure composed of curved gibbsite sheet with monomeric SiO₄ tetrahedra combined to it (Parfitt and Henmi, 1980). The proposed chemical structure has been proved truthful by NMR study for allophane with nano-ball morphology (Shimizu et al., 1988).

The purpose of the present paper was to investigate the behavior and mechanism of boric acid adsorption on allophane in relation to the nano-ball morphology and detailed chemical structure of the wall of the aluminosilicate. Allophane samples used in this study have nano-ball morphology with the fundamental chemical structure composed of aluminum orthosilicate described above.

MATERIALS AND METHODS

Samples

The allophane samples used in this study were obtained from weathered pumices originated from different volcanoes in Japan. The sample KyP was collected from Kurayoshi, Tottori prefecture, and the sample KnP from Kakino, Kumamoto prefecture. Fine clay fraction (<0.2μm) was used to eliminate possible contamination of allophane samples with volcanic glasses, opaline silica, and imogolite. The fraction was separated carefully from the inner part of pumice grains after removing their outer part. The separation was carried out by ultrasonification at 28 kHz and dispersion at pH4 for KyP sample with low Si/Al ratio or at pH10 for KnP sample with high Si/Al ratio (Henmi and Wada, 1976). The collected samples were flocculated by NaCl solution and washed with water, then stored as suspension. The Si/Al atomic ratios of the samples were 1.34:2 and 1.98:2 for KyP and KnP, respectively. The KyP sample belongs to allophane with low Si/Al atomic ratio, and the KnP sample to that with high Si/Al ratio. The prepared allophane samples were examined by infrared spectroscopy, X-ray diffraction analysis, electron microscopy and thermal analysis (data not shown), and characterized as the relevant allophane with nano-ball morphology and aluminum-nesosilicate structure (Fig. 1).

Boron adsorption experiment

Boron adsorption experiment was carried out with 5mL of suspension (containing 50mg of allophane sample on 105°C oven dry basis) in 200mL polypropylene centrifuge bottle. Various volumes of B (10mM boric acid) solution, NaCl solution and water were
Fig. 1. Morphology and structure of a unit particle of nano-ball allophane. A: molecular morphology in section; B: atomic arrangement near the pore of the hollow particle; C: atomic arrangement in the cross section of the particle.
added to give total volume of 100 mL with final B concentrations of 0 to 2200 μmol L⁻¹ and NaCl concentration of 10 mmol L⁻¹. Initial pH of the mixed suspension was adjusted to about 4, 7 or 9. For the purpose, pH of each suspension or solution (allophane sample, B and NaCl) was adjusted to the same value (4, 7 or 9) with HCl or NaOH solution before mixing. The mixture was shaken for 24 h at room temperature and centrifuged. The supernatant was analyzed for B concentration by azomethine-H method (Gupta and Steward, 1975), for Si by metholsulphite method (Strickland and Pason, 1968), for Al by ferron method (Davenport, 1949) and for equilibrium pH. The amount of B adsorbed on allophane samples was estimated from the difference between initial and equilibrium B concentrations.

RESULTS AND DISCUSSION

B adsorption isotherm and Langmuir plot

Fig. 2 shows B adsorption isotherms for the two samples at different initial pH values. For all the cases, the amounts of B adsorption increased with increase in equilibrium B concentrations. For each curve, the increase is steep at lower equilibrium B concentrations, then the curve gradually becomes nearly plateau at higher equilibrium B concentrations. It is suggested that KyP, allophane with lower Si/Al atomic ratio, has more capacity for B adsorption than KnP, and that with an increase in initial solution pH values the amounts

![Graph showing B adsorption isotherms](image)

Fig. 2. Boron (B) adsorption isotherms on nano-ball allophane samples (KnP and KyP, <0.2 μm) at initial pHs of 4, 7 and 9 in 10 mmol L⁻¹ NaCl background solution. One hundred ml of 0 to 2200 μmol L⁻¹ boric acid was added to 50 mg allophane sample.
of B adsorption for both the samples increase.

The results in Fig. 2 seem to obey Langmuir adsorption equation shown below.

\[ X = \frac{X_m K C}{1 + K C} \]  

(1)

Where \( X \) = amount of B adsorption (\( \mu \text{mol g}^{-1} \)), \( K \) = a constant related to the binding energy (\( L \mu \text{mol}^{-1} \)), \( X_m \) = maximum B adsorption (\( \mu \text{mol g}^{-1} \)), \( C \) = equilibrium B concentration (\( \mu \text{mol L}^{-1} \)). In order to check the fitness to Langmuir equation, the adsorption data in Fig. 2 were plotted according to the linear form of Langmuir equation:

\[ \frac{C}{X} = \frac{C}{X_m} + \frac{1}{K X_m} \]  

(2)

Fig. 3 shows the results of the plots. For all cases, two straight lines were obtained with a break (conjunction) at the equilibrium B concentrations of about 500 to 1000 \( \mu \text{mol L}^{-1} \). From Fig. 3, we assumed that there are two different sites responsible for B adsorption in the allophane samples.

Henmi and Huang (1985) obtained isotherms of the similar shape for adsorption of phosphate on allophane. They interpreted the isotherms by suggesting that there were two sets of adsorption sites which have their own binding energy constants and adsorption maxima, each of which can be described by different Langmuir equation. We rewrote the equation (1) as a two-term Langmuir equation according to Henmi and Huang (1985):

\[ X = X^I + X^II = X_m^I K^I C/(1 + K^I C) + X_m^II K^II C/(1 + K^II C) \]  

(3)
Where superscripts I and II refer to adsorption site I and site II, respectively. The $X_m^I$ and $K^I$ values were calculated from isotherm data at lower $C$ values by assuming all of the $B$ were adsorbed on site I, and the amount of $B$ adsorption due to site I, $X^I$, was calculated for all $C$ values. Then the amount of $B$ adsorption due to site II, $X^II$, was obtained by subtracting $X^I$ from $X$ at each $C$ value, and $X_m^II$ and $K^{II}$ were calculated.

The values of $X_m^I$, $X_m^{II}$, $K^I$ and $K^{II}$ are given in Table 1. At initial pH of 4, KnP showed adsorption maxima of 238 and 95 $\mu$mol g$^{-1}$ and binding energy constant of 0.0017 and 0.0005 L$\mu$mol$^{-1}$ for site I and site II, respectively. This means that the $B$ adsorption capacity of the site I is about 2.5 times larger than that of the site II, and that the site I can adsorb $B$ with binding strength more than three times greater than the site II. Similar results were obtained at initial pHs of 7 and 9 for KnP, and at all initial pHs for KyP (Table 1). It is known that allophanes, even in suspension, form aggregates made of nano-ball unit particles and have outer and inner surfaces on and in the aggregates (Wada, 1989). The site I could roughly correspond to the unit particles at the inner surface (micropore) and the site II to the unit particles at the outer surface (macropore). It is common fact that micropore is first filled by adsorbent and has greater adsorption capacity and energy than macropore.

When compared the two allophane samples, KyP had more capacity for $B$ adsorption than KnP. This may be simply ascribed to the difference in contents of functional groups, aluminol and silanol groups, per unit sample mass. The fundamental structure of nano-ball allophane is that of allophane composed of aluminum orthosilicate with Si/Al atomic ratio of 1:2 (Fig. 1), and the structure of allophane with the ratio higher than 1:2 is composed of both the aluminum orthosilicate (Si/Al = 1:2) and accessory polymeric silicon weakly attached to SiO$_4$ tetrahedra in the fundamental structure (Shimizu et al., 1988; Henmi et al., 1997). As a result, the content of aluminol and silanol groups per an unit nano-ball of allophane is independent upon the Si/Al ratio, but that of the groups per unit mass of allophane sample decrease with increasing Si/Al ratio of the sample. Because the formula weight of allophanes with Si/Al ratio of 1:2 and 2:2 are SiO$_2$. Al$_2$O$_3$. 2H$_2$O = 198 and 2SiO$_2$. Al$_2$O$_3$. 2H$_2$O = 258, respectively, the content of functional groups per unit mass of the allophane with Si/Al = 2:2 is about 77% of that of the allophane with Si/Al = 1:2.

Obtained $X_m$ and $K$ values increased with increasing initial pH of the sample suspensions. The increase in the values is clearer when the initial pH increased from 7 to 9,

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X_m^I$</th>
<th>$X_m^{II}$</th>
<th>$K^I$</th>
<th>$K^{II}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4, 7, 9 KnP</td>
<td>238, 323, 526</td>
<td>95, 119, 247</td>
<td>0.0017, 0.0022, 0.0028</td>
<td>0.0005, 0.0008, 0.0011</td>
</tr>
<tr>
<td>pH 4, 7, 9 KyP</td>
<td>385, 434, 588</td>
<td>106, 169, 390</td>
<td>0.0018, 0.0025</td>
<td>0.0005, 0.0010</td>
</tr>
</tbody>
</table>

$X_m: \mu$mol g$^{-1}$, $K: (\mu$M)$^{-1}$

**Table 1.** Maximum adsorption ($X_m$) and binding energy ($K$) for boron adsorption on nano-ball allophane samples at initial pHs of 4, 7 and 9
especially for Xm. For example, for KnP, ratio of Xm\textsuperscript{II} at pH 7 to pH 4 is 1.25, while the ratio at pH 9 to pH 7 is 2.08. Similar trend is observed for Xm\textsuperscript{I} of KnP, and for Xm\textsuperscript{I} and Xm\textsuperscript{II} of KyP. The increase in B adsorption with increasing initial suspension pH should be coming from the change in chemical structure of allophanes and/or B with pH.

At pH 4, it is known that the adsorbents, nano-ball allophanes, have positive charges (Al–OH\textsuperscript{+2}) at pore of the ball irrespective of Si/Al ratio of the sample (Wada, 1987). At pHs of 7 and 9, allophanes have no positive charge, but have negative charges (Si–O\textsuperscript{−}) at inner surface of the ball and the negative charges increase with increasing solution pH (Wada, 1987). On the other hand, the adsorbate, B, exist as B(OH)\textsubscript{3} at solution pHs of 4 and 7, but at pH 9, about half of B exist as anion, B(OH)\textsubscript{4}\textsuperscript{−}, because the pKa value of the following reaction is 9.24 at ionic strength of 0 (Bassett, 1980).

\[
\text{B(OH)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_4\textsuperscript{−} + \text{H}^+
\]

Both the boron hydroxide species exist as monomer in aqueous solutions at B concentrations of less than 25 mM. The B(OH)\textsubscript{3} is a planer molecule, while the B(OH)\textsubscript{4}\textsuperscript{−} tetrahedron. The pKa value indicates that most of B exist as B(OH)\textsubscript{3} below pH of about 8, and as B(OH)\textsubscript{4}\textsuperscript{−} above pH of about 10. At initial pH of 9, the final suspension pH exceeded 10 for both the samples, indicating most of B were in the form of anion, B(OH)\textsubscript{4}\textsuperscript{−}. Therefore, it is difficult to consider that negative charge development (Si–O\textsuperscript{−}) on allophane caused increase in B adsorption with increase in pH. Therefore, it can be concluded that the B(OH)\textsubscript{4}\textsuperscript{−} has higher adsorption affinity for nano-ball allophane than the B(OH)\textsubscript{3}, resulting higher B adsorption at initial pH of 9 than initial pHs of 4 and 7.

Change in pH and release of Si and Al with B adsorption

With the B adsorption on allophane, the suspension pH increased in almost cases. Fig. 4 shows that measured pH values for the suspensions. For each case, pH value of blank run, B concentration of 0, is considered to be the initial pH of the B and allophane mixed suspension before B adsorption on allophane. At initial pHs of 4 and 7, increases in pH due to B adsorption are small (less than 0.15 pH units) for both the allophane samples. On the other hand, at initial pH of 9, the suspension pH increased after B adsorption up to about 1.0 and 1.5 pH units for KnP and KyP, respectively. This indicates that much OH\textsuperscript{−} were released from allophane into solution at initial pH of 9 than at pHs 4 and 7, and that adsorption mechanism at initial pH of 9 is different from that at initial pHs of 4 and 7.

In the course of B adsorption, release of Si and Al from allophane were observed in all cases. Fig. 5 shows the amounts of Si and Al released from allophane with B adsorption for both the allophane samples at initial pHs of 4, 7 and 9. The release of Al at initial pHs of 7 and 9 is almost constant irrespective of B adsorption, while the release of Al increased with increasing B adsorption at initial pH of 4 for both KnP and KyP samples. This means that, at lower suspension pH, B adsorption causes partial destruction of the allophane structure resulting in the release of Al into solution. The destruction may occur at the pore region of nano-ball wall, by the co-existence of proton and boric acid. Detailed mechanism for the destruction and Al release at acidic region by B adsorption is now in consideration using spectroscopic and molecular orbital method.

The release of Si increased with increasing B adsorption for all the cases. The slopes of
FIG. 4. Changes in equilibrium pH with boron (B) adsorption on nano-ball allophane samples (KnP and KyP, <0.2μm) at initial pHs of 4, 7 and 9.

The plots in Fig. 5 are, however, not so steep. The ratio of Si release to B adsorption are at most 0.15 (KnP, pH9), and less than 0.05 for other cases. Nanzyo (1988) reported Si release from allophane in phosphate adsorption on allophane, and the ratio of Si release to P adsorption were about 0.18 at pH 4.0, and 0.14 at pH 6.0. Johan et al. (1997) also observed Si release in phosphate adsorption experiment for the same allophane samples, KyP and KnP, and found that the ratios of Si release to P adsorption were 0.40 for KnP and 0.16 for KyP. In all cases, there were linear relationships between P adsorption and Si release. Johan et al. (1997) showed that some P adsorbed on allophane with replacing Si on allophane structure. Also in case of B adsorption on allophane (Fig. 5), the almost linear relationship was recognized between B adsorption and Si released, but the slopes are much smaller than P adsorption on allophane (Nanzyo, 1988; Johan et al., 1997). It is reasonable to consider that the aluminol groups [Al(OH)OH2] can work as binding sites with B and the adsorption of B on nano-ball allophane occurs almost with the aluminol groups, which located at the pore sites of allophane nano-ball (Fig. 1).

B adsorption mechanism

With above information, now we can write the reaction formula for B adsorption on nano-ball allophane at initial pHs of 4 and 7.

\[ \text{Al–OH} + \text{B(OH)}_3 \rightarrow \text{Al–O–B(OH)}_2 + \text{H}_2\text{O} \]  

Because the B exists in the form of B(OH)3 in solution, and few amounts of OH– were released from allophane during B adsorption at the initial pH values (Fig. 4). At initial pH
of 9, following reaction may occur in addition to the reaction in formula (4).

\[
\text{Al} - \text{OH} + \text{B(OH)}_4^- \rightarrow \text{Al} - (\text{OH}) - \text{B(OH)}_3 + \text{OH}^- \quad (5)
\]

This reaction formula can explain the release of \(\text{OH}^-\) at this initial pH (Fig. 4), and the B atom keeps the same coordination number before and after the reaction. In formula (5), \(\text{OH}\) bridges Al atom and B atom after the adsorption. This type of bridging is necessary to explain the release of \(\text{OH}^-\) with B adsorption at initial pH 9 and to keep the same coordination number of B atom before and after the adsorption.

In general, a condensation reaction between two \(\text{OH}\) groups followed by dehydration, e.g. esterification reaction, results in a \(-\text{O}^-\) bonding. For phosphate adsorption on allophane, Al and P are also bridged by O (Johan et al., 1997), and the formation of Al(Fe)–O–P bonding is common for phosphate adsorption on hydroxides and clay minerals (Parfitt, 1978). In aluminosilicates and silicates, structural O also bridges between Al and Si or Si and Si (Al–O–Si or Si–O–Si). However, in the structure of hydroxides and clay minerals, coordination number of structural O atoms are usually three or four, such as Fe–OH–Fe, Al–OH–Al and 3Mg=OH. Also in nano-ball allophane, the outer surface of the ball is composed of Al–OH–Al functional groups. Above facts suggest that the
protonation of the bridging O atom in the X–O–X (X = Al, Fe, Mg, Si or P) bonding become possible when the O atom is only surrounded by Al, Fe or Mg with coordination number of 6. Since the bonding between O atom and the three atoms are relatively weak, and are somewhat ionic in nature.

Therefore, the formation of Al–OH–B bonding proposed in formula (5) might become possible if the bonding energy between B and O is weak enough to allow protonation of the O atom. Our molecular orbital calculation results (unpublished) showed that the bond order of the AlOH–B is lower than the other three B–OH bonds in right side of formula (5), and that the O–H bond order in the Al–OH–B is higher than those in Al–OH–P and Al–OH–Si. Detailed molecular orbital calculation results on the protonation of bridging O atom including Al–O–B bonding will be published elsewhere.

REFERENCES


