

## SODIUM AND CHLORIDE SORPTION BY IMOGOLITE AND ALLOPHANES<sup>1</sup>

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**Abstract**—The surface excesses of Na and Cl on synthetic imogolite and allophanes with varying Al/Si molar ratios in 0.10 M and 0.01 M NaCl solutions were determined using <sup>22</sup>Na and <sup>36</sup>Cl as ion probes. The point of zero net charge (PZNC) values ranged from 4.1 to 8.4, increasing with the Al/Si molar ratio for the allophanes, and was highest for imogolite (Al/Si = 2.01). The PZNC values were significantly lower than the point of zero charge (PZC) values previously determined by microelectrophoresis for the same material, indicating that Na resided within the shear plane to a greater extent than Cl. The PZNC values of allophanes were lower than their PZSE values, indicating that permanent charge existed in allophanes, and increased as Al/Si decreased. Conversely, the PZNC of imogolite was higher than its point of zero salt effect (PZSE) determined by potentiometric titration. Adsorption of Cl on imogolite from 0.1 and 0.01 M NaCl solutions below pH 8.4 and of Na from 0.1 M NaCl solutions between pH 5 and 8.4 exceeded the proton charge determined by potentiometric titration. There was no direct evidence of permanent charge in imogolite and excess Cl adsorption could not be entirely explained by simultaneous intercalation of Na and Cl. Isomorphic substitution of Al in tetrahedral sites was shown to increase with decreasing Al/Si by <sup>27</sup>Al high-resolution solid-state nuclear magnetic resonance (NMR) spectra of allophanes, and was absent in imogolite. The chemical shifts of Al(4) and Al(6) were similar in allophanes (63.0–64.7 ppm and 6.1–7.8 ppm, respectively) and the chemical shift of Al(6) was 9.4 in imogolite.

**Key Words**—Zero net charge, Nuclear magnetic resonance, Isomorphic substitution, PZC, Ion adsorption, Permanent charge, Salt absorption, Intercalation.

### INTRODUCTION

Extensive work on the charge properties of allophanes and imogolite (Wada, 1989) has exposed some important unanswered questions. These are the mechanism of excess Cl adsorption by imogolite, the question of permanent charge, and the existence of differences between charge properties determined by electrophoresis, ion adsorption, and structural means.

The negative surface charge of allophanes decreases and positive charge increases with increasing Al content at a given pH (e.g., Clark and McBride, 1984). This charge is due in part to the difference in acidity of aluminol and silanol surface functional groups, but may also result from Al in tetrahedral sites imparting a permanent negative charge. This substitution increases as the Al/Si ratio decreases in some natural allophanes (Goodman *et al.*, 1985) and synthetic materials (Wilson *et al.*, 1986).

The existence of Al(4) as well as Al(6) in allophane was postulated by Egawa (1964), Udagawa *et al.* (1969) and Okada *et al.* (1975); suggested by Parfitt *et al.* (1980); and demonstrated by Henmi and Wada (1976), Goodman *et al.* (1985), Wilson *et al.* (1986), and Childs

*et al.* (1990). However, Iimura (1969) stated that Al(4) atoms are few if any, and Shimizu *et al.* (1988) found that four natural allophane samples had the same <sup>27</sup>Al-NMR spectrum in spite of a variation in Al/Si molar ratio. No one has simultaneously determined charge properties and <sup>27</sup>Al-NMR spectra on the same imogolite and allophane samples to assess the effect of tetrahedral Al on ion adsorption.

An interesting phenomenon observed in imogolite is the retention of small inorganic anions such as Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> at pH values above the point where any positive charge should be observed (Clark and McBride, 1984). The same phenomenon was not observed for a large organic spin probe (TEMPO-COOH) suggesting that superequivalent “adsorption” is associated with intercalation in the imogolite tubes. Simultaneous intercalation of cation and anion (e.g., NaCl) or “salt absorption” could account for the excess sorption (Wada, 1984).

Unpublished data from our laboratory on charge properties related to proton adsorption by potentiometric titration and microelectrophoresis suggested that small cations reside in the interior of imogolite tubes but gave no information regarding charge location or anion retention. The proton charge and point of zero net proton charge (PZNPC) were determined from the titration assuming that the point of zero salt effect (PZSE) represented the PZNPC. Microelectrophoresis

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was used to determine the point of zero charge (PZC) at the shear plane of the mobile particle.

The objectives of the present study are (1) to determine if  $\text{Cl}^-$  adsorption occurs by intercalation of NaCl salt by using  $^{22}\text{Na}$  and  $^{36}\text{Cl}$  as ion probes and (2) to determine if there is permanent charge in synthetic allophanes with  $\text{Al/Si} > 1$  formed at  $\text{pH} < 7$ . We also seek to demonstrate that the relative locations of points of zero charge are valid indicators of ion adsorption properties.

## MATERIALS AND METHODS

### *Synthesis of materials*

Synthetic imogolite were obtained by the procedure of Farmer *et al.* (1983). Standardized 0.1 M  $\text{Al}(\text{ClO}_4)_3(\text{aq})$  was added to 4.5 L of standardized 2.0 mM  $\text{H}_4\text{SiO}_4(\text{aq})$  from tetraethyl orthosilicate to yield a 1.613 Al/Si molar ratio. This solution was titrated to pH 5.0 with 1.0 M NaOH at a titration rate of 0.5 mL  $\text{min}^{-1}$  and immediately acidified with a mixture of 0.40 M acetic acid-0.20 M nitric acid at a 0.818 acetic acid to Al molar ratio. After standing 8 to 12 hours, the suspension was heated in a 5.0 L round-bottom distillation flask at 95–98°C under reflux for five days.

The pH of the refluxed suspension was determined after cooling to 25°C to range from 3.2 to 3.5. The suspension was flocculated with NaCl, centrifuged, and dialyzed against distilled-deionized water until the electrolytic conductivity (EC) dropped below 0.003 ds  $\text{m}^{-1}$ .

A modified procedure of Wada *et al.* (1979) for allophane synthesis was used to accommodate large batches of material. At least 10 L of standardized 2.0 mM  $\text{H}_4\text{SiO}_4(\text{aq})$  from tetraethyl orthosilicate was mixed rapidly with an appropriate volume of standardized 0.1 M  $\text{AlCl}_3(\text{aq})$  to give parent solutions of 0.25, 1.00, and 2.00 molar ratios of Al/Si. Each solution was stirred rapidly while titrating with standardized 0.1 M NaOH(aq) at an average rate of 7.5 mL  $\text{min}^{-1}$ . When solutions became slightly opalescent, hydroxide addition was delayed for two hours to prevent formation of an  $\text{Al}(\text{OH})_3$  phase. The titration was then continued, as needed, to duplicate the pH values reached by Wada *et al.* (1979). Following the titration, the suspensions were refluxed, flocculated, centrifuged, and dialyzed.

The purified gels had final Al/Si molar ratios of 2.01 for imogolite and 1.26, 1.64, and 2.02 for allophanes. Total Al analyses were performed by inductively coupled plasma spectrophotometry. Si was determined colorimetrically by the molybdate blue method after digestion with an acid (pH 3) ammonium oxalate solution. A natural imogolite from Japan (KiG) was purified by removing organic matter with  $\text{H}_2\text{O}_2$ , removing amorphous Fe with citrate-dithionite, and dialyzing against distilled-deionized water.

Analysis by electron diffraction, electron microscop-

py, X-ray diffraction, and infrared spectroscopy showed that our materials are essentially the same as those synthesized by Wada *et al.* (1979), Farmer *et al.* (1983), and Clark and McBride (1984).

### *$^{27}\text{Al}$ -NMR analyses*

The solid state magic angle spinning  $^{27}\text{Al}$ -NMR spectra were recorded on a Varian XL-400 spectrometer operating at 9.4 T, corresponding to a resonance frequency for  $^{27}\text{Al}$  of 104.21 MHz, with spinning rates of about 3 and 4 KHz. The spectra were accumulated over 512 to 1024 transients at a pulse width of 1.5  $\mu\text{s}$  (90°) and a pulse delay of 1 s. Chemical shifts of the Al nuclei were referenced in ppm from the  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  ion in an acidified 1 M solution of  $\text{Al}(\text{NO}_3)_3$  in water. The intensities of the Al(4) and Al(6) were obtained by measuring the integrated peak areas. They were expressed as a percentage of the total Al by assuming that all the Al present was observable by NMR spectroscopy.

### *Ion adsorption isotherms*

A preliminary batch study using  $^{22}\text{Na}$  and  $^{36}\text{Cl}$  as ion probes in 0.10 and 0.010 M NaCl showed that isotope exchange at  $23 \pm 1^\circ\text{C}$  and one bar P was complete in less than 15 minutes.

Three replicate suspension samples containing 50.0 mg of imogolite or allophane were weighted into centrifuge tubes. The ionic strength of the suspensions was adjusted to 0.10 or 0.01 using 1.00 M and 0.100 M NaCl. The desired pH levels were achieved with 0.1 M HCl or NaOH. The suspensions were shaken on a reciprocal shaker for one or three days. Isotopes of Na ( $^{22}\text{NaCl}$ ) or Cl ( $\text{Na}^{36}\text{Cl}$ ) were added to the equilibrated suspensions. The labelled samples were shaken for two days and centrifuged. The pH of the supernatant solutions was determined using a combination glass electrode immediately after centrifugation. Activity of  $^{22}\text{Na}$  or  $^{36}\text{Cl}$  was measured with a liquid scintillation spectrometer. Adsorbed  $\text{Na}^+$  or  $\text{Cl}^-$  was calculated by the isotopic dilution analysis formula (Harsh and Doner, 1984).

The adsorption isotherms were fitted to fourth or fifth order polynomial functions and the point of zero net charge (PZNC) was obtained from the intersection of the  $\text{Na}^+$  and  $\text{Cl}^-$  curves.

## RESULTS

### *Adsorption isotherms*

The isotherms of  $\text{Na}^+$  and  $\text{Cl}^-$  adsorption (Figure 1a–d) were constructed to determine the PZNC of imogolite and allophanes. Proton charge curves from unpublished results from our laboratory are superimposed on the isotherms. The proton charge data were determined by potentiometric titration for materials with slightly different Al/Si ratios, namely, 2.02, 2.04,

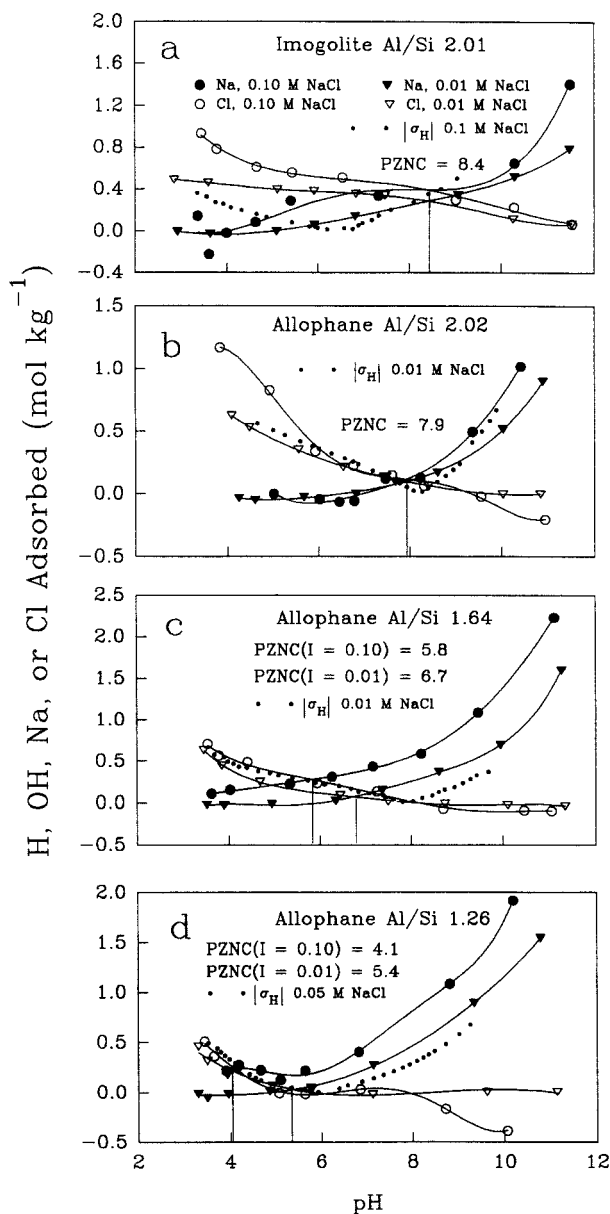


Figure 1. Adsorption isotherms of H<sup>+</sup>, OH<sup>-</sup>, Na<sup>+</sup>, and Cl<sup>-</sup> as a function of pH and initial NaCl concentration. a: imogolite; b, c, and d: allophanes of 2.04, 1.56, and 1.12 Al/Si molar ratio for the absolute proton charge, and 2.02, 1.64, and 1.26 Al/Si molar ratios for Na<sup>+</sup> and Cl<sup>-</sup> adsorption.

1.56, and 1.12 for imogolite and three allophanes. There is no correspondence between Na<sup>+</sup> or Cl<sup>-</sup> adsorption and proton charge in imogolite, whereas Cl<sup>-</sup> adsorption corresponds quantitatively with the proton charge in all the allophanes. Sodium adsorption is higher than the proton charge in all but the 2.02 allophane. As expected, the Na<sup>+</sup> adsorption increases with increasing pH, whereas Cl<sup>-</sup> adsorption decreases with increasing pH. Imogolite shows negative Na<sup>+</sup> adsorption at pH < 4, and positive Cl<sup>-</sup> adsorption up to pH 12. All three

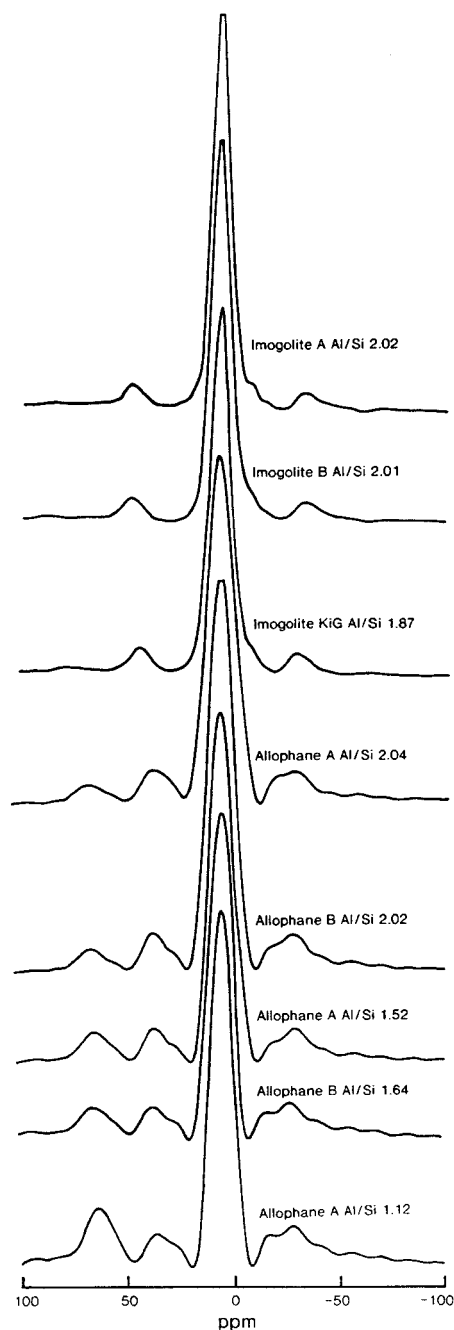


Figure 2. High-resolution solid-state <sup>27</sup>Al-NMR spectra of imogolite and allophanes.

allophanes show negative Cl<sup>-</sup> adsorption at high pH. Higher initial NaCl concentration (I = 0.10 M) shows greater negative Cl<sup>-</sup> adsorption than lower NaCl concentration (I = 0.01 M).

#### Point of zero net charge

The PZNC of imogolite was half a pH unit higher than that of allophane of the same Al/Si molar ratio.

Table 1. Comparison of the PZNC, PZSE, and PZC values of synthetic imogolite and allophanes.

Material <sup>1</sup>	Al/Si	PZNC in NaCl		Material <sup>2</sup>	Al/Si <sup>2</sup>	PZSE <sup>2</sup>	PZC <sup>2</sup>
		0.10 M	0.01 M				
Imogolite B	2.01	8.4	8.4	Imogolite A	2.02	6.5	>10
Allophane B	2.02	7.9	7.9	Allophane A	2.04	8.3	10
Allophane B	1.64	5.8	6.7	Allophane A	1.56	7.7	9
Allophane B	1.26	4.1	5.4	Allophane A	1.12	5.9	7.6

<sup>1</sup> Synthesized by Chunming Su.

<sup>2</sup> Unpublished results from our laboratory.

This is due in part to the higher adsorption of Cl<sup>-</sup> on imogolite at pH 6–12.

The Na<sup>+</sup> and Cl<sup>-</sup> adsorption isotherms of the remaining allophanes were distinguished by their positive Na<sup>+</sup> adsorption at very low pH, the higher Na<sup>+</sup> adsorption by allophane of the 1.26 Al/Si molar ratio, and the lack of correspondence between the PZNC and PZSE for both allophanes. That the Na<sup>+</sup> adsorption remained positive at very low pH implies negative permanent structural charge due to Al substitution for Si in tetrahedral sites of allophanes. The difference between the PZNC and PZSE for allophanes (Table 1) increased with decreasing Al/Si ratios, implying increasing structural charge with decreasing Al/Si ratios.

#### <sup>27</sup>Al-NMR spectra

Figure 2 shows the high-resolution solid-state <sup>27</sup>Al-NMR spectra of imogolite and allophanes and the natural imogolite KiG from Japan. Table 2 shows ratios of integrated peaks of tetrahedral and octahedral Al, and their chemical shifts in imogolite, allophanes, and related minerals. The <sup>27</sup>Al-NMR spectra of synthetic imogolite (Figure 2) show that the Al atoms are mainly in 6-coordination with a chemical shift of 9.4 ppm. Aluminum atoms in 4-coordination may be represented by a chemical shift of 67.3 ppm but are prac-

tically negligible. The spectra for the two synthetic imogolite materials prepared by different persons in our laboratory were almost identical, demonstrating the reproducibility of the synthesis process. In another study, Goodman *et al.* (1985) obtained chemical shifts of 63 and 58 ppm for Al(4), and 5.5 and 3.5 ppm for Al(6), in imogolite and Al/Si 1:1 gel, respectively, and 5 percent of the Al(4)/Al(6) peak ratio for imogolite (Table 2). The natural imogolite KiG had essentially the same spectrum as its synthetic analog. The Al(4) atoms in imogolite KiG are also negligible. Shimizu (Table 2) found a chemical shift of 6-coordinated Al of 0.4 ppm and negligible 4-coordinated Al for KiG.

Figure 3 shows the details of imogolite spectra. The main peak is flanked by a set of spinning-sidebands. The chemical shift of 9.4 ppm for the synthetic and natural imogolites indicates that aluminum is six-coordinated with oxygen (Kinsey *et al.*, 1985; Goodman *et al.*, 1985), and is close to that found for gibbsite (7.8 ppm; Kinsey, 1984) but different from that found for kaolinite, pyrophyllite, smectite, and muscovite (4 ppm; Kinsey *et al.*, 1985). These spectra also exhibit a very small peak of less than 1 percent of the intensity of the main peak, at 67.3 ppm for the synthetic and natural imogolites, due presumably to Al in four-fold coordination, together with a small contribution from the

Table 2. Distribution of Al in tetrahedral and octahedral sites and the <sup>27</sup>Al chemical shifts in imogolite, allophanes, and related minerals.

Material	Al/Si	Al(4) Chemical shift ppm	Al(6) Chemical shift ppm	Al(4)/Al(6) Integrated peak ratio %	Al(4)%	References
Imogolite A	2.02	67.3	9.4	—	Trace	This study
Imogolite B	2.01	67.3	9.4	—	Trace	This study
Imogolite	2.0	63.0	5.5	5.0	—	Goodman <i>et al.</i> , 1985
Imogolite KiG	1.87 <sup>1</sup>	67.3	9.4	—	Trace	This study
Imogolite KiG	2.08	—	0.4	—	Trace	Shimizu <i>et al.</i> , 1988
Allophane A	2.04	64.7	6.1	15.19	13.19	This study
Allophane B	2.02	63.0	6.1	14.06	12.33	This study
Allophane A	1.52	64.7	6.1	18.62	15.70	This study
Allophane B	1.64	64.7	6.1	18.16	15.37	This study
Allophane A	1.12	64.7	7.8	35.75	26.34	This study
Allophane gel	1.00	58.0	3.5	—	—	Goodman <i>et al.</i> , 1985
Gibbsite	—	—	7.8	—	—	Kinsey, 1984
Kaolinite	1.0	—	4.0	—	—	Kinsey, 1985
Pyrophyllite	0.5	—	4.0	—	—	Kinsey, 1985
Smectite	0.5	—	4.0	—	—	Kinsey, 1985
Muscovite	1.0	—	4.0	—	—	Kinsey, 1985

<sup>1</sup> Clark and McBride (1984).

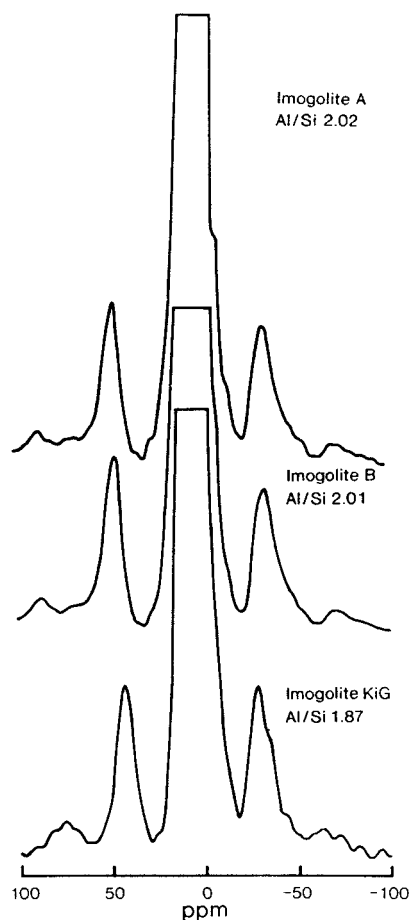


Figure 3. High-resolution solid-state  $^{27}\text{Al}$ -NMR spectra of imogolite showing spinning-sidebands.

second spinning-sideband from the main, six-coordinate peak. The weak Al(4) peak could be derived from a small amount of more-disordered gel-like material (Goodman *et al.*, 1985).

The Al(6) atoms in allophanes with Al/Si molar ratios of 1.52–2.04 have identical chemical shifts of 6.1 ppm whereas the Al(6) atoms in allophane of 1.12 Al/Si molar ratio have a slightly greater chemical shift of 7.8 ppm (Table 2). The Al(4) atoms in all the allophanes have similar chemical shifts (63.0–64.7 ppm).

#### DISCUSSION

The NaCl concentration had little effect on the PZNC of imogolite and Al/Si 2.02 allophane, indicating that the dominant exchangeable cations and anions near the PZNCs of these two minerals are  $\text{Na}^+$  and  $\text{Cl}^-$ . This is expected because the activities or concentrations of  $\text{Al}^{3+}$  from mineral dissolution near their PZNCs would be too low to compete against the  $\text{Na}^+$  for adsorption sites. The PZNC of 8.4 of imogolite in this study coincided with the PZNC of 8.5 from the  $\text{Na}^+$  and  $\text{Cl}^-$  adsorption isotherms of Clark and McBride (1984).

Differences in the PZNCs obtained from this study and those from Clark and McBride (1984) for allophanes may result from different preparations for the materials or from different techniques for determining  $\text{Na}^+$  and  $\text{Cl}^-$  adsorption isotherms.

The PZNC of  $\text{Na}^+$  and  $\text{Cl}^-$  adsorption on allophanes decreased with decreasing Al/Si molar ratio while  $\text{Na}^+$  adsorption increased. We find this consistent with a variable charge model of allophane in which Si-O groups impart negative charge and Al-OH<sub>2</sub> groups impart mostly positive charge. Negative adsorption of  $\text{Cl}^-$  above pH 9 is consistent with the model of variable charge Si-O sites which are primarily negative in this system (pure  $\text{SiO}_2$  has a PZNPC  $\approx 2$ ) and Al-OH sites which have a net negative charge above pH 9 [the PZNPC of  $\text{Al}(\text{OH})_3$  is near pH 9] (Sposito, 1984). Negative adsorption is known to increase with ionic strength (Sposito, 1984). Negative adsorption of  $\text{Na}^+$  is only observed with high Al/Si ratio allophane where there is no permanent negative charge, including imogolite.

More noteworthy,  $\text{Na}^+$  and  $\text{Cl}^-$  adsorption correspond quantitatively with the amount of proton charge except that  $\text{Na}^+$  adsorption is higher than the proton charge for Al/Si 1.26 and 1.64 allophanes. In the Al/Si 1.26 allophane this cannot be attributed to the different Al/Si ratios for the two materials (proton charge was determined on Al/Si 1.12 allophane and  $\text{Na}^+$  adsorption on 1.26 allophane) because the Al/Si 1.12 allophane should have even more proton charge than the 1.26 allophane due to more Si-O groups. Therefore, the excess  $\text{Na}^+$  must be due to the existence of permanent charge sites from tetrahedral Al atoms. The existence of permanent charge sites would also explain (1) the fact that the PZNC is lower than the PZSE (Sposito, 1984) and (2) the fact that positive adsorption of  $\text{Na}^+$  exists even at low pH and increases with decreasing Al/Si ratio.

The  $^{27}\text{Al}$ -NMR results strongly support our preliminary hypotheses that (1) there is substantial Al substitution for Si in allophanes, resulting in permanent negative charge; (2) the amount of substitution is inversely related to the molar Al/Si ratio of allophanes, and; (3) there is little such substitution in imogolite. Our ion adsorption results were also shown to support these hypotheses. Unfortunately, a quantitative measure of Al(6)/Al(4) is difficult for two reasons. First, the Al(6) signal can be broadened by quadrupolar effects for Al in less symmetrical sites and, hence, underestimated in noncrystalline materials (Bleam *et al.*, 1989a, 1989b; Childs *et al.*, 1990). Second, Al(4) can be overestimated because of the intensity overlap of the spinning side-bands. In fact, we found that the magnitude of permanent negative charge in allophanes indicated by the Na cation adsorption [ $<0.5 \text{ mol}(-) \text{ kg}^{-1}$ ] was much less than that suggested by  $^{27}\text{Al}$ -NMR data [ $1.0\text{--}2.0 \text{ mol}(-) \text{ kg}^{-1}$ ] (Table 3). Childs *et al.* (1990) also found more substitution than charge in high silica



Table 3. The estimated permanent negative charges of imogolite and allophanes based on the total chemical analyses and  $^{27}\text{Al}$ -NMR data, assuming the total Al is the sum of Al(4) and Al(6). Tetrahedral Al is listed first in the formula for allophanes.

Material			$M_w$	Chemical formula	Permanent charge mol(-)/kg
Imogolite	Al/Si	2.01	198.3	$\text{Al}_2\text{SiO}_3(\text{OH})_4$	0.000
Allophane	Al/Si	2.02	215.5	$\text{Al}_{0.255}\text{Al}_{1.745}\text{O}_3 \cdot 0.990\text{SiO}_2 \cdot 3\text{H}_2\text{O}$	1.183
Allophane	Al/Si	1.64	229.3	$\text{Al}_{0.331}\text{Al}_{1.669}\text{O}_3 \cdot 1.220\text{SiO}_2 \cdot 3\text{H}_2\text{O}$	1.356
Allophane	Al/Si	1.12	263.3	$\text{Al}_{0.527}\text{Al}_{1.473}\text{O}_3 \cdot 1.587\text{SiO}_2 \cdot 3\text{H}_2\text{O}$	2.001

allophane, but suggested the lack of negative charge was due to neutralization by  $\text{Al-OH}_2^+$  sites. Another explanation could be that the adsorption of positively charged Al polymers helped balance the negative charge.

The unusual shape of the  $\text{Na}^+$  isotherm at low pH and  $I = 0.1$  for Al/Si 1.26 allophane and the resulting drop in the PZNC relative to the  $I = 0.01$  isotherm may be related to nonexchangeable OH-Al monomers and/or polymers blocking exchange sites as found on clay minerals (Harsh and Doner, 1984). As pH drops, exchangeable  $\text{Al}^{3+}$  is formed and is replaced by  $\text{Na}^+$  at  $\text{Na}^+$  concentration  $>0.01$  M. In the Al/Si 1.64 system, the same phenomenon seems to be operating but to a lesser extent, presumably because there is less negative charge. We were not able to remove adsorbed Al with  $\text{Ba}^{2+}$ , indicating that the Al, if present, is nonexchangeable. Nonexchangeable Al may also explain the discrepancy between negative charge and Al(4).

The  $\text{Cl}^-$  adsorption on imogolite is much higher than the positive proton charge throughout the isotherm. This is probably the major cause of the high PZNC relative to the Al/Si 2.02 allophane PZNC and the imogolite PZSE. Other researchers have attributed the excess  $\text{Cl}^-$  adsorption to "salt absorption." Our data demonstrate that at low pH,  $\text{Cl}^-$  adsorption exceeds proton charge even though no  $\text{Na}^+$  is adsorbed. Also, at the PZNC,  $\text{Na}^+$  adsorption is exactly balanced by the net proton charge and yet  $\text{Cl}^-$  adsorption is still positive. Therefore the excess  $\text{Cl}^-$  cannot be attributed entirely to adsorption of NaCl, indicating "specific" adsorption of  $\text{Cl}^-$ . A similar phenomenon is noted for  $\text{Na}^+$  on imogolite, which exceeds the net negative proton charge from pH 4.5 to 8 at  $I = 0.1$ .

### CONCLUSIONS

The PZNC values of the allophanes increased with increasing Al/Si molar ratio (from 1.26 to 2.02) and those measured in 0.10 M NaCl are lower than in 0.01 M NaCl except for the allophane with Al/Si = 2.02. The PZNC values of the 1.64 and 1.26 Al/Si allophanes were lower than their PZSE values, implying the existence of permanent structural charge, whereas the PZNC of imogolite was higher than its PZSE.

High-resolution solid-state  $^{27}\text{Al}$ -NMR spectroscopy indicated a negligible amount of tetrahedral Al in imogolite, but significant tetrahedral Al in the three allophanes. The Al(4) increased with decreasing Al/Si mo-

lar ratio. The  $^{27}\text{Al}$ -NMR results support the contention that the downward shift in the PZNC relative to the PZSE is due to the presence of permanent charge from isomorphic substitution of Al in tetrahedral sites.

Excess adsorption of  $\text{Na}^+$  and  $\text{Cl}^-$  by imogolite cannot be explained entirely by intercalation of NaCl into the tubes. Therefore, some specific adsorption mechanism appears to be operative.

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