

ADENINE, ADENOSINE, RIBOSE AND 5'-AMP ADSORPTION TO ALLOPHANE

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Abstract—We have investigated the adsorption of adenine, adenosine, ribose, and adenosine-5'-phosphate (5'-AMP) by allophane at pH 4, 6 and 8. Adenine, adenosine and ribose gave similar isotherms, *i.e.* adsorption increased regularly with solution concentration and decreased in the order: pH 8 > pH 6 > pH 4. Allophane had a greater affinity for 5'-AMP than for adenine, adenosine or ribose. Further, the extent of adsorption for 5'-AMP increased in the order: pH 8 << pH 6 ≈ pH 4. The adsorption of 5'-AMP at pH 4 and pH 6 was about 60 times greater than at pH 8. The strong adsorption of 5'-AMP accords with the well known high phosphate-retention capacity of allophane and allophane-rich soils. The experimental data may be rationalized in terms of the pH-dependent charge characteristics of the organic solutes and allophane. The large propensity of allophane to retain 5'-AMP is ascribed to ligand exchange between the phosphate of 5'-AMP and the hydroxyl of (HO)Al(OH₂) groups, exposed at perforations on the wall of allophane spherules, giving rise to a surface (chelation) complex. The high affinity of nucleotides for allophane has implications for the possible role of allophane in the abiotic formation of RNA-type polynucleotides although nucleotide 'immobilization' by surface complexation might hinder RNA oligomerization.

Key Words—Adenine, Adenosine, Allophane, 5'-AMP, Adsorption, Ribose.

INTRODUCTION

Clay minerals, because of their extensive surface area, layer structure and reactivity, can retain and catalyze the polymerization of a wide range and variety of organic molecules (Theng, 1974, 1982; Laszlo, 1987; Adams and McCabe, 2006). The role of clay minerals in chemical evolution and the origin of life has been discussed by Bernal (1965), Cairns-Smith and Hartman (1986), and Brack (2006).

It is generally accepted that ribonucleic acid is the most important biopolymer in the Earth's early life because RNA can act as both a catalyst and storehouse of genetic information (Zaug and Cech, 1986; Brack, 2006). In other words, in the 'RNA world' this molecule could assume the dual function of a protein and DNA (Gilbert, 1986).

The interactions of montmorillonite with the components of RNA have been well documented (Theng, 1974; Graf and Lagaly, 1980; Rishpon *et al.*, 1982; Winter and Zubay, 1995; Franchi *et al.*, 2003). The early work by Lailach *et al.* (1968) indicated that Li⁺, Na⁺, Mg²⁺ and Ca²⁺-montmorillonites could adsorb appreciable amounts of nucleosides and nucleotides under acid pH conditions. Subsequently, Banin *et al.* (1985) found that Fe²⁺-montmorillonite was a better adsorbent of 5'-AMP than the Ca²⁺-exchanged form at neutral and acid pH.

Similarly, Zn²⁺- and Cu²⁺-montmorillonites at pHs between 4 and 7, were shown to retain more 5'-AMP than Na⁺-, Mn²⁺-, Co²⁺- and Ni²⁺-exchanged materials (Lawless *et al.*, 1985). However, the reactivity of allophane toward individual nucleotide bases, ribose, nucleoside, and nucleotide has not been previously investigated.

Ferris and co-workers (Ferris *et al.*, 1989; Ferris and Ertem, 1993a; Ertem and Ferris, 1996; Ferris, 2005) have reported that montmorillonite was capable of catalyzing the formation of RNA from the activated monomers. Similarly, Na⁺-montmorillonite could promote the oligomerization of 5-phosphorimidazole of adenine (ImpA) as well as the formation of adducts between ImpA and diadenosinepyrophosphate. Allophane, however, was inactive in this regard (Ferris and Ertem, 1992, 1993b).

Allophane is a hydrated aluminosilicate of short-range order that occurs widely in the clay fraction of soils derived from volcanic ash (Parfitt, 1990; Harsh, 2000; Brigatti *et al.*, 2006). Unlike montmorillonite which has a permanent negative layer charge (due to isomorphous substitution), the surface charge of allophane varies with the pH of the ambient solution. The effect of pH on the adsorption of alanine by allophane has been investigated by Hashizume and Theng (1999). More recently, Hashizume *et al.* (2002) have reported that some allophanes could discriminate between the optical isomers of alanyl-alanine.

Here we determined the adsorption of adenine, adenosine, ribose and 5'-adenosine-mono-phosphate (5'-AMP) by a soil allophane as a function of pH in order to gain insight into the clay-RNA interaction.

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MATERIALS AND METHODS

The allophane sample was obtained from a weathered pumice bed (4C horizon) of a volcanic ash soil at Kitakami in Iwate Prefecture, Japan. The soil is classified as an Alic Fulvudand (Soil Survey Staff, 1999), or a Hyperdystric Andosol (FAO/ISRIC/ISSS, 1998) (Wada, 1986; Hiradate, 2005). Imogolite gel particles, adhering to the soil (weathered pumice) peds, were removed by hand or by scraping ped surfaces with a spatula, and discarded. After gently crushing in a mortar and pestle, the soil was dispersed in water at pH 10 using an ultrasonic cleaner. This treatment would have removed any remaining imogolite as this mineral did not disperse at pH 10 (Wada, 1993). The soil suspension was then placed in a volumetric flask, and the clay (<2 μm) fraction was separated by gravity sedimentation. The clay suspension was adjusted to pH 7 by drop-wise addition of 0.1 M HCl, and coagulated with 1 M NaCl. After removing excess salt by dialysis, the material was re-dispersed in water at pH 3.5. The <2 μm particle-size fraction was separated and coagulated as before (Hall *et al.*, 1985), and centrifuged. The natural organic matter, associated with allophane particles, was removed by treating the centrifuged material five times with 10% H_2O_2 at 100°C for 12 h. The treated material was then dried in an oven at 60°C.

The Al/Si molar ratio of soil allophanes varies between 1 and 2. Irrespective of chemical composition and origin, however, the unit particle of allophane consists of a hollow spherule with an outer diameter of ~5 nm. The ~0.7 nm thick spherule wall is composed of an outer Al octahedral (gibbsitic) sheet and an inner Si sheet. Depending on the magnitude of the Al/Si ratio, the Si sheet may consist of isolated or polymerized orthosilicate (O_3SiOH) groups. Defects in the wall

structure give rise to perforations of ~0.3 nm in diameter (Wada and Wada, 1977; Hall *et al.*, 1985; Parfitt, 1990; Matsue and Henmi, 1993; Brigatti *et al.*, 2006; Khan *et al.*, 2006). The morphology and structure of an allophane unit particle are shown in Figure 1.

The allophane used here has an Al/Si molar ratio of 1.42 as determined by inductively coupled plasma (ICP) spectroscopy following dissolution in HF. The sample also contains 3.7 mol.% Fe. The specific surface area, determined by adsorption of nitrogen gas at 77 K, and applying the BET equation, is 360 m^2/g . The sample was further characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), and differential thermal analysis-thermogravimetry (DTA-TG). The XRD pattern (Figure 2a), FTIR spectrum (Figure 2b), TEM image (Figure 2c), and DTA-TG curves (Figure 2d) accord with published data (Wada, 1977; Parfitt, 1990), and confirmed that the material was essentially allophane. Notably, the electron micrograph (Figure 2c) did not indicate the presence of slender, hollow tubules (~2.2 nm diameter) of imogolite although the sample might contain some amorphous ‘allophane-like constituents’ (Brigatti *et al.*, 2006).

Adenine was purchased from Kanto Chemicals, Japan, while adenosine, ribose, and 5'-adenosine-monophosphate (5'-AMP) were supplied by Wako Pure Chemicals, Japan. The compounds were of the purest grade available, and used as received. Their molecular structures are given in Figure 3. The term ‘ribose’ in the text refers to the five-membered ring form of β -D-ribofuranose.

Adsorption isotherms at $20 \pm 3^\circ\text{C}$ were determined by equilibrating 200 mg of dry allophane with 7 mL of 0.1–2.0 mM aqueous solutions of adenine, adenosine, ribose and 5'-AMP in stoppered glass tubes. The solution

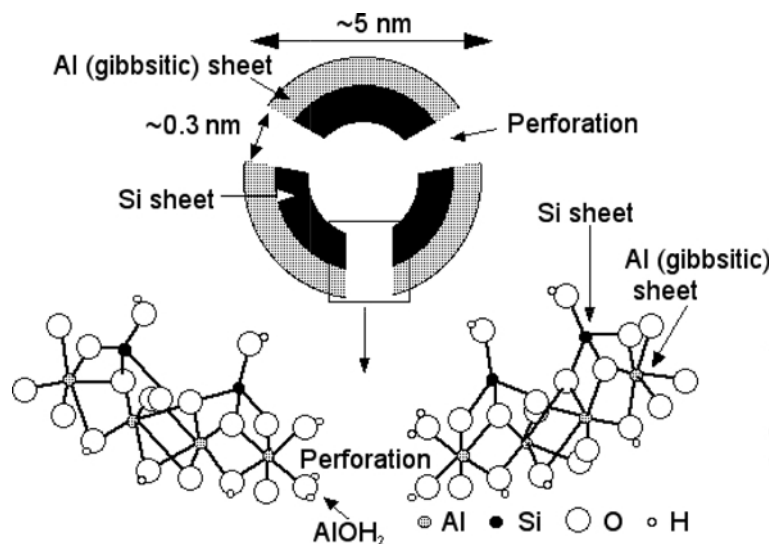


Figure 1. Diagram of a unit particle of allophane showing the hollow spherule shape and wall perforations where (HO)Al(OH)₂ groups are exposed.

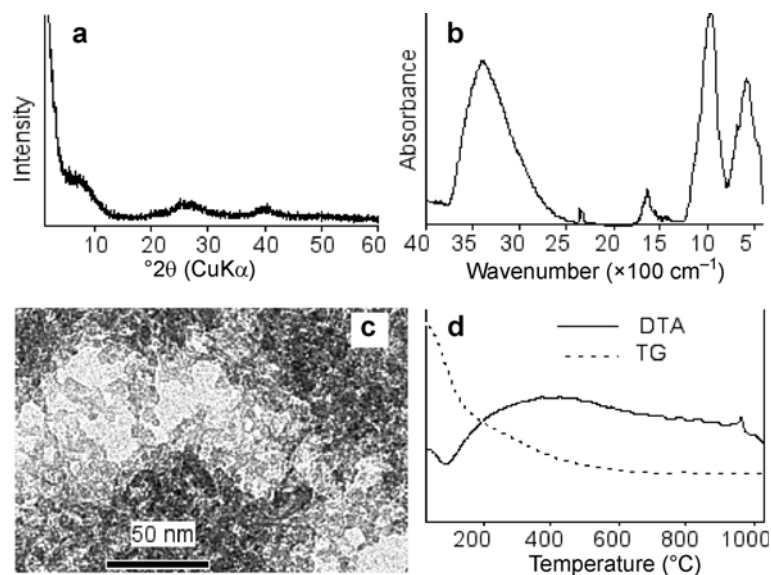


Figure 2. Some characteristics of the allophane sample: (a) XRD pattern; (b) FTIR spectrum; (c) TEM image; and (d) DTA and TG curves.

pHs were adjusted to 2, 4 and 10 by careful addition of 1 mM HCl or 1 mM NaOH to give equilibrium pHs of 4 ± 0.5 , 6 ± 0.5 , and 8 ± 0.5 , respectively. After shaking for 65 h, the suspension pHs were measured. The tubes were then centrifuged, and the supernatant solutions were separated for analysis of dissolved organic carbon. Since only a single carbon compound (adenine, adenosine, ribose or 5'-AMP) at a time was brought into contact

with allophane, total (dissolved) organic carbon can be used to measure the concentration of that compound. The total organic carbon (TOC) concentrations in the initial and equilibrium solutions were determined using a Shimadzu TOC-5000A instrument. Briefly, a specified volume of solution was sprayed into the furnace at 680°C through which pure air (nitrogen/oxygen ratio = 4/1) was circulated. The organic carbon was catalytically oxidized to CO_2 , the concentration of which was measured by infrared spectroscopy. The concentration of individual compounds was then obtained from the corresponding calibration curves. Adsorption was estimated from the difference between the TOC concentration in the initial and equilibrium (supernatant) solutions.

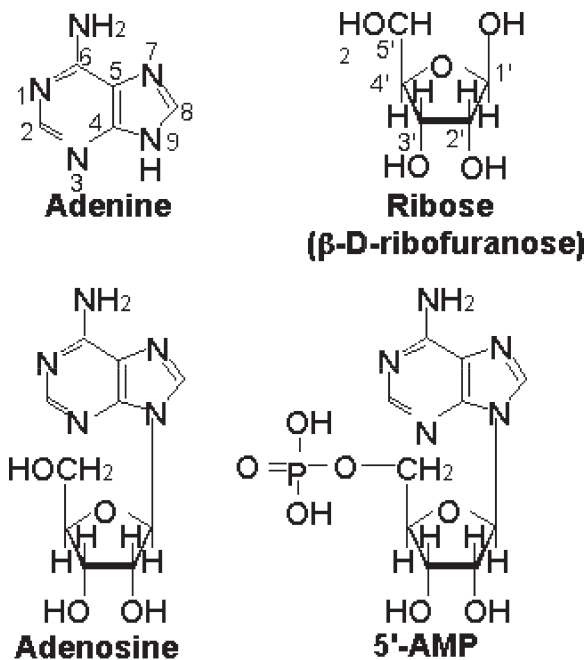


Figure 3. Molecular structures of adenine, adenosine, ribose (β -D-ribofuranose), and 5'-adenosine-mono-phosphate (5'-AMP).

Table 1. Values for the constant, K_F , and the exponent, $1/n$, derived by fitting the Freundlich equation to the experimental points for the adsorption of adenine, adenosine, ribose and 5'-AMP at pH 4, 6 and 8.

	pH	K_F	$1/n$
Adenine	4	0.00143	0.590
	6	0.00197	0.475
	8	0.00351	0.296
Adenosine	4	0.000741	0.899
	6	0.00164	0.745
	8	0.00439	0.456
Ribose	4	0.00172	0.505
	6	0.00228	0.665
	8	0.00322	0.613
5'-AMP	4	1.068	0.839
	6	2.551	0.897
	8	0.0444	1.344

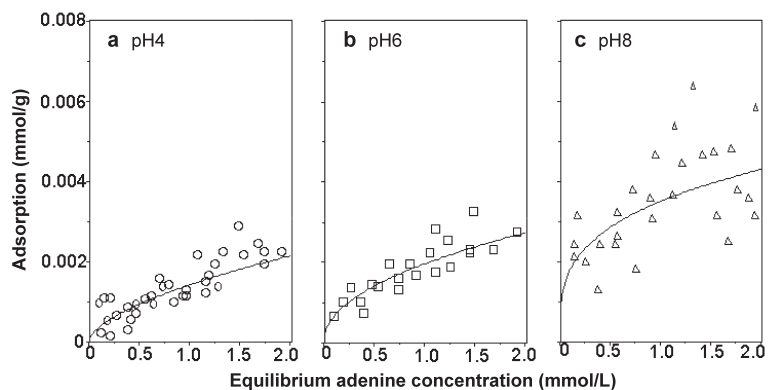


Figure 4. Isotherms for the adsorption of adenine by allophane at (a) pH 4, (b) pH 6 and (c) pH 8.

RESULTS AND DISCUSSION

Effect of pH

Figure 4 shows the isotherms for the adsorption of adenine by Kitakami allophane. Adsorption increased regularly with solution concentration without any indication of levelling off to a plateau. Adsorption was markedly influenced by solution pH, decreasing in the order pH 8 > pH 6 > pH 4. The isotherms for the adsorption of adenosine (Figure 5) and ribose (Figure 6) were similar to those of adenine but the experimental points for ribose were relatively more scattered. Compared to adenine, adenosine and ribose, the adsorption of 5'-AMP to allophane was much stronger (Figure 7). Thus, at pH 8 and an equilibrium concentration of 1.0 mmol/L, the adsorption of 5'-AMP was about an order of magnitude greater than that of the other three compounds at the same pH and concentration. Further, the extent of adsorption for 5'-AMP increased in the order: pH 8 \ll pH 6 \approx pH 4. Indeed, at pH 4 and 6, nearly all of the added nucleotide was adsorbed from dilute (<0.01 mmol/L) solutions. Although adsorption of 5'-AMP at pH 8 was much reduced, the amount adsorbed was still appreciably larger than that for adenine, adenosine and ribose at the same pH.

The experimental points for the adsorption of adenine, adenosine, ribose and 5'-AMP at pHs 4, 6 and 8 were fitted to the Freundlich equation, indicated by the solid lines in Figures 4–7. This equation takes the form

$$A = K_F C^{1/n} \quad (1)$$

where A denotes adsorption, *i.e.* the amount of solute adsorbed per unit weight of allophane (mmol/g), C is the equilibrium solute concentration (mmol/L), while K_F and $1/n$ are empirical constants. The values of K_F and $1/n$, derived from the experimental data (Figures 4–7), are listed in Table 1. Only 5'-AMP adsorption to allophane at pH 8 yielded a Freundlich $1/n$ value >1 and a concave isotherm (Figure 7).

Comparison of adsorption isotherms

The adsorption isotherms (at pHs 4, 6 and 8) for adenine were similar in shape and extent to those for adenosine and ribose. All three compounds are presumably adsorbed by a combination of electrostatic, hydrogen bonding, and van der Waals interactions. Thus, condensation of the NH group at the 9 position of adenine with the OH group at the 1' position of ribose to form adenosine (Figure 3) had little effect on adsorption. In contrast, the addition of a phosphate group to the OH

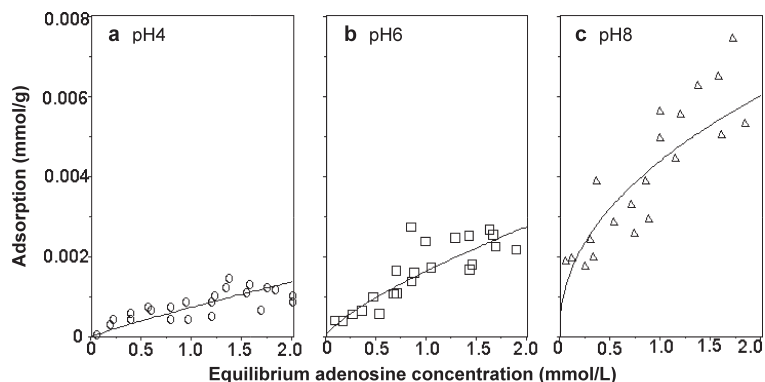


Figure 5. Isotherms for the adsorption of adenosine by allophane at (a) pH 4, (b) pH 6 and (c) pH 8.

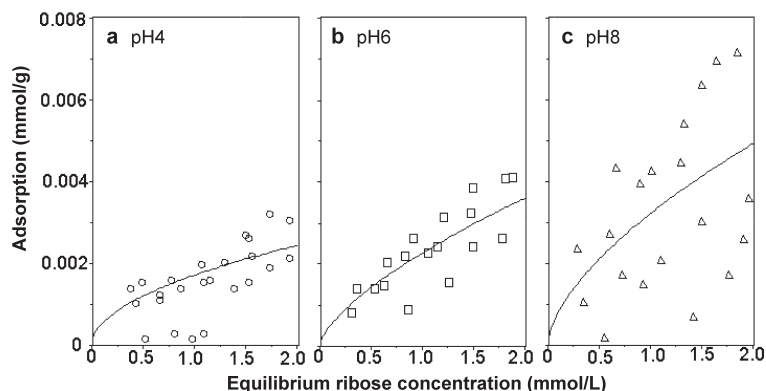


Figure 6. Isotherms for the adsorption of ribose by allophane at (a) pH 4, (b) pH 6 and (c) pH 8.

at 5' position of adenosine to yield 5'-AMP (Figure 3) was highly conducive to adsorption. As discussed below, the high affinity of 5'-AMP for allophane is ascribable to the formation of surface complexes.

Charge characteristics of adsorbates and allophane

The pH-dependent charge characteristics of allophane may be ascribed to the protonation and deprotonation of (HO)Al(OH)₂ groups, exposed at perforations (surface defects) along the spherule wall (Figure 1). In other words, these groups can gain protons on the acid side of the point of zero net charge (p.z.n.c.), and lose protons on the alkaline side of the p.z.n.c. Since the p.z.n.c. of allophane (Al/Si molar ratio ~1.5) is close to pH 6 (Theng *et al.*, 1982; Harsh, 2000) the net charge of the mineral at pH 4 is positive, essentially neutral (zero) at pH 6, and negative at pH 8. The dissociation constants and net charge of adenine, adenosine and 5'-AMP together with the p.z.n.c. and charge characteristics of allophane are summarized in Table 2.

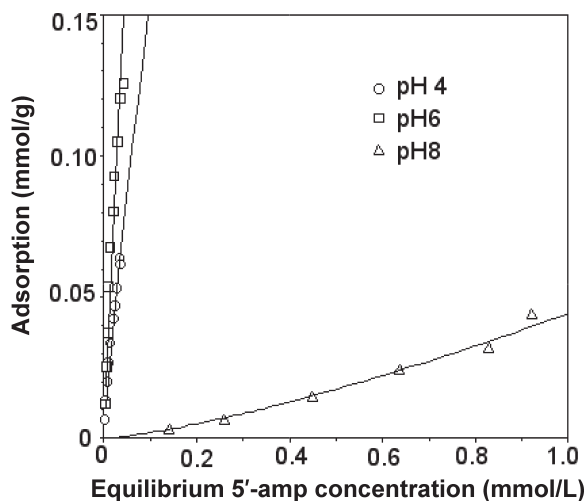


Figure 7. Isotherms for the adsorption of 5'-AMP by allophane at pH 4, 6 and 8.

If electrostatic (Coulombic) interactions largely control adsorption, little adenine and adenosine retention by allophane would be expected at pH 4 because both the organic solutes and allophane were positively charged. That measurable amounts of adenine and adenosine retention occurred at pH 4 suggests that other attractive forces, such as van der Waals and H bonding, were operative. Based on the pH-dependent charge characteristics (Table 2), electrostatic attraction between adenine or adenosine and allophane should increase with solution pH. The extent of adsorption should, therefore, decrease in the order pH 8 > pH 6 > pH 4 as the experiments revealed (Figures 4 and 5).

By comparison with adenine and adenosine, 5'-AMP shows an extraordinarily high affinity for allophane at pH 4 and 6 (Figure 7). Indeed, at low concentrations (<0.01 mmol/L) very little, if any, solute was detectable in the equilibrium solution at these pH values. This observation accords with the early finding by Theng *et al.* (1982) that allophane (of a similar composition) could adsorb up to 0.12 mmol/g phosphate at very dilute solution concentrations. Apparently, 5'-AMP is adsorbed by a different mode of interaction in which electrostatic attraction plays a relatively minor role. We propose that

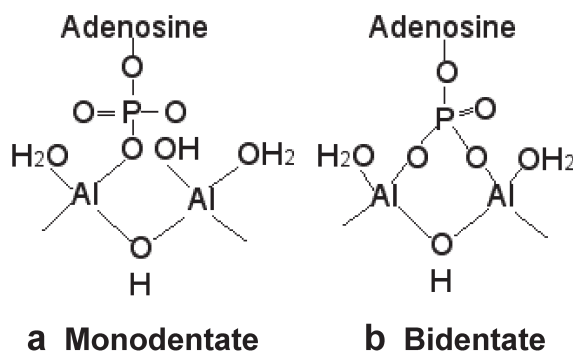


Figure 8. Possible surface complexes formed as a result of ligand exchange between 5'-AMP and allophane: (a) monodentate (mononuclear) complex; (b) bidentate (binuclear) complex.

Table 2. Dissociation constants of adenine, adenosine and 5'-AMP (at 25°C) together with the point of zero net charge (p.z.n.c.) of allophane. The charge characteristics of the organic solutes and allophane at pH 4, 6 and 8 are also shown.

	pK ₁	pK ₂	pK ₃	pH 4	pH 6	pH 8
Adenine*	4.15	9.8		++	(+)N	N(+)
Adenosine*	3.5	12.5		++	N(+)	N
5'-AMP**	3.80	6.19	13.06	+–	–	– –
		p.z.n.c.		pH 4	pH 6	pH 8
Allophane***		~6		++	N	– –

+ = positively charged; – = negatively charged; N = neutral (uncharged); (+) = weakly positive; ++ = strongly positive; – – = strongly negative

* Winter and Zubay (1995), **Banin *et al.* (1985), ***Theng *et al.* (1982)

5'-AMP, like phosphate, is adsorbed by ligand exchange reactions between the phosphate group of 5'-AMP and allophane hydroxyls associated with the (HO)Al(OH₂) groups that are exposed at perforations on the spherule surface (see Figure 1). When the phosphate group of 5'-AMP replaces one hydroxyl, a monodentate (mononuclear) surface complex is formed, while the replacement of two hydroxyls from adjacent (HO)Al(OH₂) groups would yield a bidentate (binuclear) surface complex (Rajan, 1975; McBride, 2000) as depicted in Figure 8. Adsorption was much reduced at pH 8 (Figure 7) when both 5'-AMP and allophane were negatively charged, and hence tended to repel each other. Even then, however, ligand exchange could still take place.

CONCLUDING REMARKS

By serving both to adsorb and concentrate nucleotides at the surface, allophane might also facilitate nucleotide polymerization as Ferris and Ertem (1993a, 1993b) and Ferris (2005) have demonstrated for montmorillonite. One model of the primitive Earth would have favored allophane formation because CO₂ was apparently abundant, air temperatures were high, and precipitation was heavy (Julg, 1990). The soil solution would, therefore, have been moderately acidic and enriched in dissolved silicic acid and hydroxy-aluminum cations that derived from the intense leaching of aluminosilicate minerals. These conditions would have been conducive to allophane formation from volcanic glass, feldspar and/or biotite. Alternatively, allophane could have formed by coprecipitation of Al- and Si-rich constituents when the solution pH exceeded 4.7 (Parfitt and Kimble, 1989).

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