Ionic Factors Affecting Aluminum Transformations and the Impact on Soil and Environmental Sciences*

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I. Introduction

Aluminum is the most abundant metallic element of minerals in soils and
the associated environments. It occurs in a series of Al-bearing minerals
(e.g., feldspars, micas, chlorites, vermiculites, smectites, kaolinite, hal-
loysite, and gibbsite). It makes up 81, 82, 25, and 4 g kg^{-1} of igneous,
shale, sandstone, and limestone rocks, respectively (Jackson, 1964; Brady,
1974; McLean, 1976).

   Analogous to carbon as a coordinator for organic matter, Al ranks in
abundance next to silicon as an oxygen coordinator in minerals in terres-
trial and aquatic environments. Aluminum can be released from minerals
to soil solutions and natural waters through chemical and biochemical
weathering reactions. Both inorganic and organic ions are an integral
part of the environment (Paul and Huang, 1980; Förstner, 1981; Robert
and Berthelin, 1986). They are important weathering agents of primary
and secondary minerals. The extent of the release of Al from minerals
to the environment has increased with time, population growth, inten-
sification of agriculture, and industrialization (Huang, 1987a). The Al re-
leased to soil solutions and natural waters undergoes a series of reactions
including hydrolysis, polymerization, complexation, precipitation, and
crystallization. These reactions are bound to be very significantly influ-
enced by prevalent ionic factors in the systems.

   Transformation products of Al as influenced by ionic factors have an
important bearing on pedogenesis and soil acidity and liming (Jackson,
1963a,b; Hsu, 1977; Thomas and Hargrove, 1984), formation (Wang *et al.*,
1986), stabilization (Stevenson, 1982), and turnover (Martin and Haider,
1986) of humic substances and soil aggregation and related soil physical
properties (Emerson *et al.*, 1986). Furthermore, these Al components have
important effects on the fate and dynamics of nutrients and toxic pollutants
in the environment (Huang, 1987a). In addition, certain Al ionic species
may pose a threat to ecological balance and human and animal health.

II. Forms and Distribution of Aluminum in Soils and Associated Environments

The total concentration of Al in soils and sediments is in general of the
same order of magnitude as that of the earth's crust (McLean, 1976). Alu-
minum is either octahedrally or tetrahedrally coordinated with oxygen in

crystalline and short-range ordered Al-bearing minerals. It also exists as exchangeable Al and hydroxy Al interlayers (Hsu, 1977; Huang and Violante, 1986; Bertsch and Barnhisel, 1987) and as coatings on the edges and external planar surfaces (Huang and Kozak, 1970). Exchangeable Al in soil environments is mainly monomeric and may be dimeric to a lesser extent (Jackson, 1963a; Thomas and Hargrove, 1984). Recent research data indicate that the association of organic carbon with exchangeable Al on clay surfaces merits attention (Goh and Huang, 1984, 1986). The hindrance of organic ligands on the hydrolysis and ploymerization of Al via complexation reactions may partially account for the restriction of exchangeable Al to monomeric and dimeric forms in soil environments.

Aluminum interacts with low-molecular-weight organic acids (Kwong and Huang, 1975, 1977, 1979a, 1981; Violante and Huang, 1984, 1985; Huang and Violante, 1986) and fulvic (FA) and humic (HA) acids (Schnitzer and Kodama, 1977; Kodama and Schnitzer, 1980; Schnitzer, 1986) to form insoluble hydroxy-Al-organic complexes, depending on the molar ratio of organic acid to Al, pH, and nature of organic acids. The reaction of Al with inorganic ions results in the formation of a series of sparingly soluble compounds. The K-taranakite is formed in fertilizer zones in soils through the reaction of concentrated K and acid phosphate solution with Al hydroxides (Taylor and Gurney, 1965). If the ionic activities of K^+, Al^{3+}, and SO_4^{2-} are sufficiently high, the K-alunite could be formed in acid soils (Adams and Rawajfih, 1977).

Substitution of Al for Fe in the structure of Fe(III) oxides is known to occur and seems to be widespread in soils (Schwertmann and Taylor, 1982). The degree of Al substitution is related to Al availability in soils and may thus vary with pedogenic environments (Fitzpatrick and Schwertmann, 1982).

In soil solutions and natural waters, Al ions can form complexes with a series of organic and inorganic ligands (Campbell et al., 1985; Huang, 1980, 1987a; Huang and Violante, 1986). However, the information on speciation of dissolved Al is rather limited. Furthermore, the chemical behavior of Al species and their ecological and health effects are even less understood.

III. Fundamental Aqueous Chemistry of Aluminum

A. Hydrolytic Reactions of Aluminum

The Al^{3+} ion, which is released from Al-bearing minerals to soil solutions and natural waters, is octahedrally coordinated with six water molecules and exists as an $Al(H_2O)_6^{3+}$ ion. The $Al(H_2O)_6^{3+}$ is a proton donor, and its K_1 for the following hydrolytic reaction is 1.12×10^{-5} (Cotton and Wilkinson, 1980):

$$Al(H_2O)_6^{3+} = Al(OH)(H_2O)_5^{2+} + H^+$$

Therefore, the $Al(H_2O)_6^{3+}$ ion is moderately acidic. The hydrolysis of $Al(H_2O)_6^{3+}$ in soil solutions and natural waters is thus the rule rather than the exception (Thomas, 1977).

Hydrolysis of $Al(H_2O)_6^{3+}$ ion can proceed through monomeric mechanism (Schofield and Taylor, 1954; Ragland and Coleman, 1960; Frink and Peech, 1963; Hunt, 1963; Frink and Sawhney, 1967; Singh, 1969; Baes and Mesmer, 1976; Stol et al., 1976) and polymeric mechanism (Brosset et al., 1954; Sillen, 1959; Hsu and Rich, 1960; Matijevic et al., 1961; Okura et al., 1962; Jackson, 1963a; Hsu and Bates, 1964b; Aveston, 1965; Fripiat et al., 1965; Hem and Roberson, 1967; Turner, 1969; Turner and Ross, 1970; Smith and Hem, 1972; Baes and Mesmer, 1976; Stol et al., 1976; Hsu, 1977). Monomeric Al ions are not the only Al species, and polymeric Al ions are important hydrolytic products in soil solutions and natural waters.

1. Monomeric Hydrolysis

There are four mononuclear species of Al; $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, and $Al(OH)_4^-$ (Table 1). Of the four mononuclear species, the formation quotients of $AlOH^{2+}$ and $Al(OH)_4^-$ are known most accurately. The formation quotients of the two intermediate species are relatively uncertain (Baes and Mesmer, 1976). May et al. (1979) found the $Al(OH)_3^0$ species to contribute insignificantly to gibbsite solubility and implicitly questioned its existence at the very low total Al concentration studied. The ^{27}Al nuclear magnetic resonance (NMR) spectroscopic investigations of diluted Al standard solutions (Bertsch et al., 1986) indirectly suggests that the $Al(OH)_3^0$ species contributes to the observed line width at half maximum ($V_{1/2}$), although its contribution is relatively insignificant over the narrow pH range investigated. Therefore, the existence of the $Al(OH)_3^0$ species in dilute acidic solution appears to be unresolved.

The solubility behavior of Al hydroxide is consistent with the formation of $Al(OH)_4^-$ in alkaline solutions. The ratio of four OH^- ions per Al^{3+} ions in solution was confirmed by Brosset (1952) and by Mesmer and Baes (1971). The solubility results (Baes and Mesmer, 1976) give:

Table 1. Mononuclear hydrolysis products of Al at 25°C

Species	Medium	Log Q_{1y}[a]
$AlOH^{2+}$	0.1 M $NaClO_4$	−5.30
	0	−4.97
$Al(OH)_2^+$	0.1 M $NaClO_4$	−9.90
$Al(OH)_3$	0.1 M $NaClO_4$	−15.60
$Al(OH)_4^-$	0	−23.00

Source: Baes and Mesmer (1976); reprinted by permission of John Wiley & Sons, Inc.

[a] Q_{1y} is an equilibrium quotient of the hydrolysis of Al.

$$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$$
$$\log K_{14} = -23.0 \pm 0.3$$
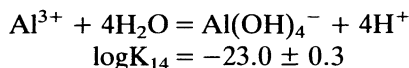
At the concentrations below 1.5 M Al, the Raman and infrared spectra (IR) of this species indicate that it is a tetrahedral ion (Moolenaar *et al.*, 1970). They also presented ^{27}Al NMR spectra of these solutions which displayed a narrow resonance line at $\approx$ 80 ppm downfield from the $Al(H_2O)_6^3$ resonance, with both the line width and chemical shift indicative of tetrahedrally coordinated Al. Studies indicating tetrahedral coordination of the $Al(OH)_4^-$ species were generally conducted at very high base concentrations. From the Raman and IR data of the Al solutions of more moderate base concentrations (1×10^{-6} to 1×10^{-2} M), Carreira *et al.* (1966) could not resolve if the $Al(OH)_4^-$ species is square planar or octahedral. In more dilute Al solutions of modest base concentrations, in which the formation quotient Q14 was determined, the $Al(OH)_4^-$ species could be a tetragonally distorted octahedral complex that may represent an intermediate in the coordination change.

The $Al(OH)_5^{2-}$ species has been used in calculations of hydrolysis reactions of Al (Lindsay, 1979) and proposed by Maksimova *et al.* (1967). However, there is no evidence to show its existence.

2. Polymeric Hydrolysis

Aluminum hydrolysis in solution containing relatively low concentrations of Al and low ligand number (ñ) may be described by monomeric hydrolysis mechanism. However, hydrolysis of Al in solutions of either higher Al concentrations or ñ is better described by polymeric hydrolysis mechanism. Generalizations are difficult to make for solutions with Al concentrations and ñ values intermediate to these conditions.

Jander and Winkel (1931) were among the first to suggest the existence of polynuclear Al species based on diffusion coefficient measured in solutions of basic Al salts. Thereafter, many theories on polynuclear Al species have been proposed (Brosset, 1952; Matijevic and Tezak, 1953; Brosset *et al.*, 1954; Sillen, 1959, 1961; Hsu and Rich, 1960; Hsu and Bates, 1964b; Aveston, 1965; Fripiat *et al.*, 1965; Patterson and Tyree, 1973). Hsu and Bates (1964b) proposed a continuous series of polynuclear Al species with the basic unit of the form $[Al_6(OH)_{12}(H_2O)_{12}]^{6+}$. The choice of the hexameric Al species as a basic structural unit is based on the theories of Brosset (1952) and Hsu and Rich (1960). This hexameric ring scheme is similar to the "core link" model of Sillen (1959, 1961) and has been supported by many researchers (Hem and Roberson, 1967; Richburg and Adams, 1970; Smith and Hem, 1972; Stol *et al.*, 1976). With additional results obtained in later studies, Hsu (1977) believes that in the absence of Dowex 50 resin or vermiculite, the hydrolyzed products are likely $[Al_{10}(OH)_{22}]^{8+}$ (double ring) or $[Al_{13}(OH)_{30}]^{9+}$ (triple ring) at NaOH/Al = 2.1 and below, as shown in Figure 1.

Increasing NaOH/Al $\longrightarrow$

$\dfrac{NaOH}{Al} = 0.3\text{-}2.1$ $\longleftarrow$ $\dfrac{NaOH}{Al} = 2.2\text{-}2.7$ $\longrightarrow$ $\dfrac{NaOH}{Al} = 3.0\text{-}3.3$

$\left(\infty\right)^{8+}$ $\longrightarrow \left(\triangle\!\!\!\triangle\right)^{9+} \cdots\cdots \longrightarrow \left(\hexagon\right)^{12+} \cdots\cdots \longrightarrow \left(\hexagon\right)^{18+} \cdots\cdots$ → Crystalline aluminum hydroxides

$[Al_{10}(OH)_{22}]^{8+}\cdot16\,H_2O$ $[Al_{13}(OH)_{30}]^{9+}\cdot18\,H_2O$ $[Al_{24}(OH)_{60}]^{12+}\cdot24\,H_2O$ $[Al_{54}(OH)_{144}]^{18+}\cdot36\,H_2O$ $Al_p(OH)_{3p}$

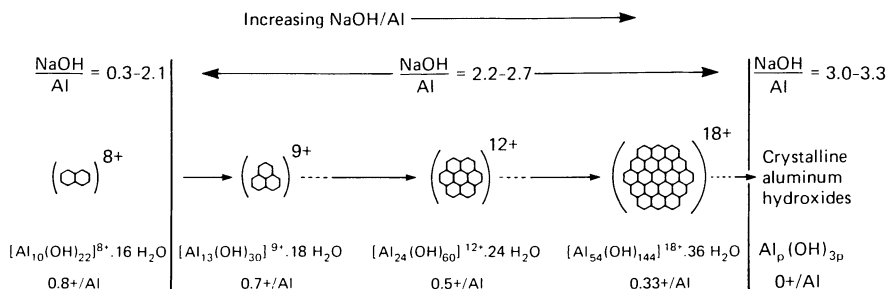0.8+/Al   0.7+/Al   0.5+/Al   0.33+/Al   0+/Al

Figure 1. Proposed development of aluminum hydroxides (Hsu, 1977; reprinted with permission of Soil Science Society of America).

Using ultracentrifugation, Aveston (1965) derived average degrees of polymerization (Nw) as a function of ñ and concluded that the $[Al_6(OH)_{15}]^{3+}$ species (Brosset *et al.*, 1954) did not fit the data and the octameric $[Al_8(OH)_{20}]^{4+}$ species (Matijevic *et al.*, 1961) was unlikely. He interpreted his results in terms of the species $Al_2(OH)_2^{4+}$ and $Al_{13}O_4(OH)_{24}^{7+}$. He perferred these two species, because they have been identified in crystalline solids precipitated from hydrolyzed Al solutions. The first occurs as a complex ion in basic aluminum sulfate, $[Al_2(OH)_2(H_2O)_8](SO_4)_2 \cdot 2H_2O$, and in the isomorphous selenate. It consists of two AlO_6 octahedra with a shared edge formed by bridging OH^- ions (Johansson, 1962). The second occurs as the symmetrical ion $Al_{13}O_4(OH)_{24} (H_2O)_{12}^{7+}$ (Figure 2). Aveston (1965) also cited the small-angle X-ray work of Rausch and Bale (1964) who suggested a polymer with
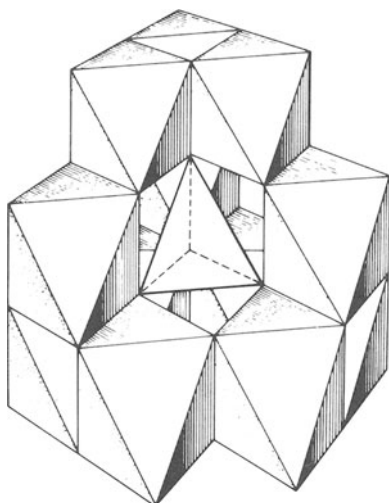
Figure 2. The $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ion. The drawing shows how the 12 AlO_6 octahedra are joined together by common edges. The tetrahedra of oxygen atoms in the center of the structure contains one 4-coordinate Al atom (Johansson, 1960; reprinted with permission of *Acta Chemica Scandinavica*).

Table 2. Polynuclear hydrolysis products of Al at 25°C

| | | Log Q_{xy}[a] | |
Medium	$Al_2(OH)_2^{4+}$	$Al_3(OH)_4^{5+}$	$Al_{13}O_4(OH)_{24}^{7+}$
1 M NaClO$_4$	−8.0	−13.47	−104.81

Source: Base and Mesmer (1976); reprinted by permission of John Wiley & Sons, Inc.

[a] Q_{xy} is an equilibrium quotient of the polynuclear hydrolysis of Al.

a radius of gyration of 0.43 nm, which was assumed to be the Al_{13} polymer, predominated in the solutions investigated.

Baes and Mesmer (1976) conclude that the polynuclear species formed by Al hydrolysis are $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, and $Al_{13}O_4(OH)_{24}^{7+}$ (Table 2). The interpretation of their data indicates acceptable fit with Al_{13} polymer, which is in concurrence with the conclusions of Aveston (1965). Based on ^{27}Al NMR spectroscopic work, Akitt et al. (1972) and Akitt and Farthing (1978, 1981a–d) also proposed the Al_{13} cation. They suggested the predominance of the Al_{13} cation along with small amounts of the dimer and monomeric hexaqua Al ions in similar solutions. Indirect potentiometric studies (Kubota, 1956; Mesmer and Baes, 1971; Bottero et al., 1980) also suggest that the $Al_2(OH)_2(H_2O)_8^{4+}$ species could be a stable polymeric species. More recent evidence from direct NMR spectroscopic investigations (Akitt et al., 1972; Akitt and Farthing, 1981c; Bertsch et al., 1986) further substantiates this contention. The existence of the Al_{13} polynuclear species has been confirmed in crystals of basic Al sulfates precipitated from partially neutralized Al solution (Johansson, 1960) and inferred from small-angle X-ray scattering (Rausch and Bale, 1964), ultracentrifugation (Aveston, 1965), and potentiometric data (Baes and Mesmer, 1976). The charge on the Al_{13} polynuclear species has been reported to range from +3 to +7 (Bottero et al., 1980; Vaughan and Lussier, 1980).

Direct NMR evidence indicates that the Al_{13} polynuclear species exists in partially neutralized Al solutions ranging widely in Al concentration, ñ, and the methods of the synthesis (Bottero et al., 1980; Akitt et al., 1972; Akitt and Farthing, 1981a–d; Bertsch et al., 1986). The resonance peak at ~ 63 ppm, which is assigned to the Al_{13} polynuclear species, is clearly in the region characteristic of tetrahedrally coordinated Al (Figure 3). Furthermore, the very sharp resonance line with a characteristic line width $V_{1/2}$ of 6–7 Hz suggests both a symmetrical environment with a very weak electric field gradient at its position and general lack of exchange with other Al species. The other 12 octahedrally coordinated Al atoms in the structure display a very broad resonance as a result of their rather asymmetric environment producing a large electric field gradient at their positions. For a given Al concentration, the amount of Al_{13} polynuclear species in partially neutralized Al solutions increases linerally with ñ until high ñ values,
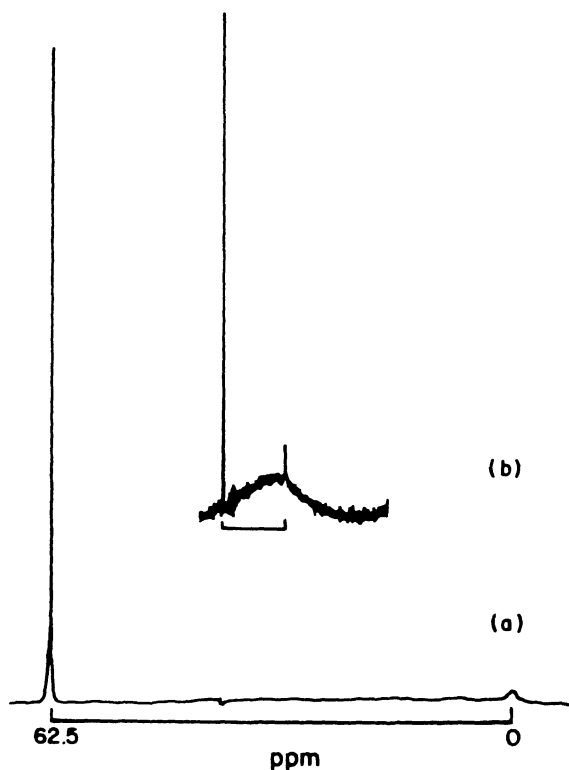
Figure 3. ^{27}Al NMR spectrum of a 0.1-M partially neutralized $AlCl_3$ solution $\bar{n} = 2.5$ demonstrating the monomeric Al species at 0 ppm and the tetrahedrally coordinated Al of the Al_{13} polymer at 63 ppm downfield from the monomeric Al peak. In the condensed spectrum (b), the broad resonance resulting from the 12 octahedrally coordinated Al atoms in the Al_{13} structure is apparent (Bertsch *et al.*, 1986; reprinted with permission of Soil Science Society of America).

where the Al_{13} polynuclear species begins to decrease (Bottero *et al.*, 1980; Bertsch *et al.*, 1986). The $\bar{n}$ values at which this polynuclear species first forms or begins to decrease depend on many factors including Al concentrations, mode of base addition, base injection rate, and mixing conditions during synthesis (Bottero *et al.*, 1980; Bertsch *et al.*, 1986).

The influence of preparation parameters on the relative amounts of monomeric Al, the Al_{13} polynuclear species, and more polymerized Al species formed during synthesis suggests that the Al_{13} polymers may be formed under inhomogeneous pH conditions at the point of base addition or at the solid solution interface of dissolving carbonate phases (Akitt and Farthing, 1981c; Teagarden *et al.*, 1982; Bertsch *et al.*, 1986). Therefore, it appears that $Al(OH)_4^-$ is a required precursor to the formation of the Al_{13}

polynuclear species. The Al_{13} polynuclear species appears to form rapidly when $Al(OH)_4^-$ interacts with 12 octahedrally coordinated Al ions and not to form on aging via polynuclear intermediates (Bottero et $al.$, 1980; Bertsch et $al.$, 1986). The Al_{13} structure could be viewed as being composed of six oxygen-sharing dimeric units which bridge the edges of the central tetrahedron (Akitt and Farthing, 1981c). This species has been shown to be the primary polynuclear species of Al solutions of high ñ (Bottero et $al.$, 1980; Akitt et $al.$, 1972; Akitt and Farthing, 1981a–c; Bertsch et $al.$, 1986).

Recent studies using ^{27}Al NMR, Al-ferron (or hydroxyquinoline) reactions, and sulfate precipitation show that Al polynuclear species in solution gradually change in nature with time, even when the solution maintains similar pH, turbidity, and concentration of mononuclear Al species (Hsu, 1984). These results suggest that the model postulated by Hsu and Bates (1964b) may be oversimplified. The Al_{13} species are present in significant amounts only in freshly prepared solutions of OH/Al molar ratios of 1.5 and above and gradually disappear during aging. Some polynuclear species are not detectable with ^{27}Al NMR spectroscopy. Therefore, no definite conclusion can be drawn at present. Further research on the factors governing the formation and stability of Al_{13} polynuclear species merits close attention in understanding the chemistry of Al pertaining to soil and environmental sciences.

Species other than hexamers and their cyclic derivatives may be present, but their contribution toward the total Al species is much less than that of the hexameric species (Stol et $al.$, 1976). Some species that are deduced from the solid-state structure are shown in Figure 4. Some less stable Al species in solution or transient precipitates may occur in aqueous systems of natural importance. Therefore, the kinetic behavior of these intermediate entities should not be overlooked.
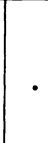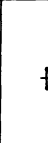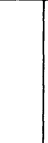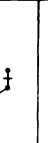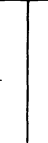
	Al^{3+}	$Al_2(OH)_2^{4+}$	$Al_3(OH)_4^{5+}$	$Al_6(OH)_{12}^{6+}$	$Al_9(OH)_{18}^{9+}$	$Al_{10}(OH)_{22}^{8+}$	$Al_{16}(OH)_{38}^{10+}$	$Al_{24}(OH)_{60}^{12+}$
Average charge/$_{Al}$	3.0	2.0	1.67	1.0	1.0	0.80	0.63	0.50
OH/$_{Al}$ ratio	0	1.0	1.33	2.0	2.0	2.20	2.38	2.50

Figure 4. Summary of species, which can be deduced from the solid-state structure. The OH/Al ratio refers to the molar ratio in the complexes and not the OH/Al ratio of the system (Stol et $al.$, 1976; reprinted with permission of $Journal$ of $Colloid$ $Interface$ $Science$).

The precise differentiation of polynuclear and mononuclear Al species has been difficult. Indirect methods of differentiation used include conductometry, light scattering, ultracentrifugation, ion exchange, dialysis, and kinetic methods based on the interaction of Al with a complexation agent (Kentamma, 1955; Hem and Roberson, 1967; Hsu and Bates, 1964b; Aveston, 1965; Bersillon et al., 1980; Okura et al., 1962; Turner, 1969, 1971, 1976; Turner and Sulaiman, 1971; Smith, 1971; Smith and Hem, 1972; Patterson and Tyree, 1973; Bertsch et al., 1986; Tsai and Hsu, 1984, 1985). More recently, direct ^{27}Al NMR spectroscopy has provided a unique tool for investigation of the distribution of mononuclear and polynuclear Al species coexisting in solution and the nature of some of the polynuclear species (Akitt et al., 1972; Bottero et al., 1980; Akitt and Farthing, 1981a–d; Bertsch et al., 1986; Buffle et al., 1985; Parthasarthy and Buffle, 1985). ^{27}Al NMR spectroscopy has also cast light on applicability, limitations, and boundary conditions of some indirect differentiation methods. However, even NMR spectroscopy has been unable to provide unequivocal evidence for all the polynuclear Al species present. Continued efforts in differentiating solution Al species would lead to further advancement of knowledge on the chemistry of Al in soils and the associated environments.

B. Precipitation and Crystallization of Hydrolytic Products of Aluminum

Mononuclear and polynuclear Al species can be transformed into colloidal or distinct solid phases. Many of colloidal solid phases initially formed are of very fine particulates that may not settle upon centrifugation and may easily pass membrane filters. The precipitation products of Al can be either short-range ordered materials or crystalline Al hydroxides, depending on solution composition and formation conditions.

In the scheme of polymeric hydrolysis of Al (Figure 1), Hsu (1977) stated that below the OH/Al molar ratio of 3, hydroxyl ions repel each other. As the OH/Al molar ratio reaches 3, net charge per Al is 0; the repulsion becomes negligible, and polynuclear species cluster and form crystals. The transformation of soluble Al species to a solid structure involves the orientation of platelets (the *001* sheets) relative to one another with the help of H bonding and van der Waals forces. During this ordering process, severe constraints exist in the systems.

Aluminum hydroxide may crystallize in three modifications—bayerite, gibbsite, and nordstrandite. In all three of these structures, the a and b crystallographic axes have the same length. Therefore, the (*001*) planes must be identical in structure (Wells, 1962). The differences among three Al hydroxide polymers lie in the stacking of these sheets along the c-crystallographic axis.

Rapid precipitation favors the bayerite structure, and slow crystal growth favors the gibbsite structure (Hsu, 1966). pH also plays an impor-

tant role in governing the formation of the Al hydroxide polymorphs (Barn-hisel and Rich, 1965; Schoen and Roberson, 1970. The acidic medium promotes gibbsite structure, whereas the alkaline medium favors bayerite structure (Barnhisel and Rich, 1965). In acidic medium, Al is present mainly as mononuclear Al^{3+} or $Al(OH)^{2+}$. These Al species have strong hydrolyzing power and therefore favor the formation of gibbsite (Schoen and Roberson, 1970). In alkaline medium, Al is present as $Al(OH)_4^-$. Aluminum is thus precipitated in the form of bayerite. However, gibbsite can be prepared at pH > 12 on an industrial scale, whereas bayerite forms between pH 9 and 12 when a supersaturated sodium aluminate solution is allowed to cool (Hsu, 1977). Furthermore, nordstrandite and gibbsite are more common than bayerite in alkaline soils and bauxite deposits (Lodding, 1961; Keller, 1964; Violante and Jackson, 1979).

The development of aluminum hydroxide polymorphs appears to be related to the rate of precipitation, pH of the system, clay surface, and the nature and concentration of inorganic and organic anions (Hsu and Bates, 1964b; Barnhisel and Rich, 1965; Schoen and Roberson, 1970; Davis and Hill, 1974; Hsu, 1977; Violante and Jackson, 1979, 1981; Violante and Violante, 1980; Violante and Huang, 1985; Huang and Violante, 1986). However, the mechanisms of their formation remain obscure.

Besides Al hydroxide polymorphs, metastable precipitation products are formed during hydrolytic reactions of Al. In several studies where colloidal precipitate was formed during rapid neutralization, it was observed that upon dissolution, polynuclear Al species would result (Turner, 1971; Turner and Sulaiman, 1971). The data obtained from ^{27}Al NMR studies show that heating cloudy solutions resulted in the appearance of Al_{13} polynuclear species in solution, suggesting that the solid phase consisted of discrete Al_{13} units stabilized by a bridging mechanism (Bertsch, 1988). Turner (1971) and Turner and Sulaiman (1971) suggested that some of the initial solid phases formed on rapid neutralization of Al solutions redissolved on aging yielding increase in the polynuclear Al species as estimated by the 8-hydroxy quinoline method. These data appear to indicate the existence of Al_{13} polynuclear units within a colloidal precipitate matrix. ^{27}Al NMR spectroscopic data show that some Al precipitates retained by ultrafilter (13-nm pore size) was composed of Al_{13} polynuclear species, providing further support for the nucleation of this Al species to form discrete units (Bertsch, 1988).

The experimental variables affecting nucleation-precipitation reactions of polynuclear Al species include rates and methods of base addition, pH, localized hydroxyl ion concentrations, nature and concentration of inorganic and organic anions, the sequence of anion introduction to the Al solution, and effects of temperature during synthesis or aging of solutions (Turner, 1971; Turner and Sulaiman, 1971; Mesmer and Baes, 1971; Patterson and Tyree, 1973; Vermeulen et al., 1975; Huang and Violante, 1986).
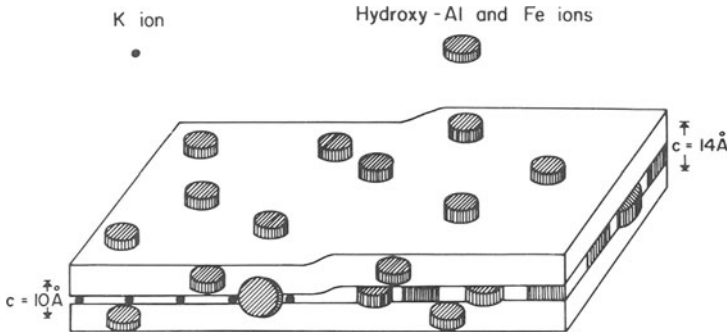
Figure 5. Structural models depicting the hydroxy-Al and Fe coatings on the inter-lamellar and external planar surfaces and edges of mica-vermiculite (Huang, 1980).

IV. Influence of Clay Minerals on Aluminum Transformations

Clay minerals can be considered as solid-state ions and affect Al trans-formations. Aluminum released to the soil solution through chemical weathering of minerals can be adsorbed by interlayers of 2:1 expansible clay minerals (Jackson, 1963b; Rich, 1968) and external surfaces of phyllo-silicates (Huang and Kozak, 1970), as illustrated in Figure 5. The adsorption of hydroxy-Al ions on the external surfaces of phyllosilicates is espe-cially important when the particle size is smaller than 0.2 μm (Table 3). Brosset *et al.* (1954) suggested a six-membered ring structure for the hy-drolysis product of Al, having a formula of $Al_6(OH)_{15}^{3+}$ and an OH/Al molar ratio of 2.5. A similar structure was proposed for hydroxy-Al poly-mers fixed by exchange resins (Hsu and Rich, 1960; Jackson, 1960).

Table 3. Adsorption of hydroxy Al polymers by various-size fractions of muscovite and biotite

	mg of Al adsorbed/g of mineral					
	Muscovite Ratio of hydroxy Al solution to mineral (ml/g)			Biotite Ratio of hydroxy Al solution to mineral (ml/g)		
Size fraction (μm)	25	50	100	25	50	100
5–2	1.4	1.6	3.7	1.7	1.8	3.0
2–0.2	4.0	4.6	5.7	4.5	4.5	5.0
0.2–0.08	13.8	16.5	19.1	13.1	14.8	18.1
< 0.08	13.6	28.4	37.9	13.8	28.3	38.9

Source: Huang and Kozak (1970).

Hydroxy-Al interlayers may consist of these or similar polymers (Jackson, 1962, 1963b; Hsu and Bates, 1964a,b; Hsu, 1977). The existing evidence shows that the OH/Al molar ratio of the nonexchangeable Al occurs in a rather narrow range of about 2.5–2.7. If the OH/Al molar ratio exceeds 2.7, the Al interlayers are metastable (Turner, 1965; Turner and Brydon, 1965, 1967b). The conclusion as to this narrow range of OH/Al molar ratios of nonexchangeable Al is supported by many observations in both natural and synthetic systems (Schwertmann and Jackson, 1964; Singh and Brydon, 1967; De Villiers and Jackson, 1967a,b; Huang and Lee, 1969; Richburg and Adams, 1970; Kirkland and Hajek, 1972).

Smectite with synthetic interlayers resembles natural hydroxy-interlayered smectite in mineralogical and chemical properties. In contrast, this has not been the case for vermiculite. Synthetically prepared hydroxy-interlayered vermiculite often did not remain at a 1.4-nm d-spacing when K-saturated or when subjected to heat treatments. Naturally interlayered vermiculites can be heated to at least 100 or 300°C with little change in the d-spacing, whereas synthetically prepared vermiculite tends to collapse toward a 1.0-nm d-spacing at a lower heat treatment (Barnhisel, 1965). Many factors may be responsible for the low stability of Al interlayers in vermiculite in the synthetic systems. In contrast to a more uniform distribution of hydroxy-Al polymers in smectites, an "atoll" structure is formed in synthetic Al interlayers in vermiculites (Frink, 1965). This concept of two types of structures is supported by the work of Sawhney (1968), Barnhisel (1969), Novak et al., (1971), and Kozak and Huang (1971). The atoll structure results in a steric blocking of exchange sites in the center of the particles and insufficient numbers of props. Therefore, synthetically prepared Al-interlayered vermiculites cannot maintain the d-spacing in the c-axis at 1.4 nm when heated and K-saturated, and the structure collapses toward 1.0 nm. The interlayer space of vermiculites is less than for smectites. The particles of vermiculites are in general larger and likely more rigid than smectites. The charge density of vermiculites is higher than that of smectites, and hydroxy Al polymers may thus deposit more frequently along the crystal edges. The OH/Al molar ratio of Al interlayers in vermiculites may be smaller than in smectites. These factors may contribute to the lower thermal stability of synthetic Al interlayers in vermiculites. In nature, the formation of Al-interlayered vermiculites may proceed over long periods. Therefore, the above-noted factors may be relatively insignificant.

Besides the OH/Al molar ratio, nature of clay surfaces, and particle size and charge density of clays (Barnhisel and Rich, 1963, 1965; Jackson, 1963b; Hsu and Bates, 1964a; Carstea, 1968; Jackson et al., 1973; Hsu, 1977), other factors affecting the stability of synthetic Al interlayers include: (1) nature and amount of hydroxy Al ions (Turner and Brydon, 1965, 1967a; Brydon and Kodama, 1966); (2) anions or salts present during formation of interlayers (Barnhisel and Rich, 1965; Singh and Brydon, 1967); (3) presence of gibbsite in the system (Turner and Brydon, 1967b);

and (4) temperature at which aging is conducted (Carstea, 1968; Singh, 1972). Although optimum conditions for hydroxy-Al interlayer formation in nature are not entirely known, the favorable conditions appear to be as follows: (1) moderately active weathering must be in progress or have occurred to furnish Al ions; and (2) the pH should be moderately acid, about pH 5.0, organic matter content should be low, and there should be frequent wetting and drying of the soils (Rich, 1968). The ability of 2:1 expansible clays to fix polynuclear Al has been proposed as a reason for the absence of gibbsite in temperate soils and is referred to as the "antigibbsite" effect (Jackson, 1963a,b).

In addition to the formation of Al-interlayered clays displaying a stable 1.4-nm d-spacing, it has recently been reported that direct magic-angle spinning NMR evidence substantiates the reasoning that Al_{13} polynuclear species can be deposited in the interlayer space of the 2:1 clay minerals with a stable 1.8-nm d-spacing (Bertsch and Barnhisel, 1987). However, the structural and surface properties of these clay minerals in affecting the formation of Al_{13} interlayers remain obscure.

Little is known about the mechanisms of the polymerization reactions of Al at the mineral water interface and the importance to the formation of polynuclear Al species, particularly in moderately acid environments, where solution Al concentrations are low. Even though Al concentrations in bulk solutions are low, the Al concentrations on the clay surfaces can be several orders of magnitude higher, thus facilitating the formation of polynuclear species. Hydrolysis of Al on clay surfaces has been demonstrated (Barnhisel and Bertsch, 1982; Bertsch and Barnhisel, 1987). Polynuclear Al species can form on the surfaces of clay minerals by simply washing a partially Al saturated clay with water; there is some indication that Al_{13} polynuclear species may form in this manner (Perrott, 1981). High concentrations of Al on clay mineral surfaces and the influence of surface charge on hydrolytic reactions of Al are certainly favorable for the formation of polynuclear Al species, even in systems with relatively low concentrations of Al. However, the influence of surface properties of clay minerals on the kind of polynuclear Al species formed at moderate Al surface coverage is not known. The surfaces of clay minerals may serve as sites for the formation of polynuclear Al species in soil solutions and natural waters, since some polynuclear Al species are exchangeable to other cations (Bertsch and Barnhisel, 1987).

V. Influence of Inorganic Ligands on Aluminum Transformations

The nature and concentration of inorganic ligands play an important role in influencing the hydrolysis and polymerization of Al (Marion and Thomas, 1946; Ross and Turner, 1971; De Hek et al., 1978; Nordstrom, 1982;

Violante and Huang, 1984, 1985). The residual positive charge of poly-
nuclear Al (Figure 1) must be balanced by the counteranions, giving rise
to basic salts.

With anions such as Cl^-, ClO_4^-, and NO_3^- (Hsu, 1966; Ross and Tur-
ner, 1971), which do not have strong affinity for Al, the basic salts are
highly solube and yield clear solutions (Hsu, 1977). Furthermore, polynu-
clear Al ions continue to hydrolyze and polymerize into larger units during
prolonged aging unless a high concentration of the counteranion is present.

Pseudoboehmite is formed in the presence of a high concentration of
indifferent electrolytes such as NaCl (Hsu, 1967; Chesworth, 1972). The
data suggest that pseudoboehmite may form in a saline environment. Hsu
(1967) also provides evidence showing the gradual transformation of
pseudoboehmite to Al hydroxide during aging. The pseudoboehmite
formed in a saline environment may persist in nature for a very long time if
it is dried before its conversion to Al hydroxide. Materials similar to
pseudoboehmite formed in the laboratory have been found in submicro-
scopic particles in most of the European bauxites (Lippens and Steggerda,
1970). Noncrystalline alumina of boehmite character has been found in
certain tropical soils (De Villiers, 1969). Although pseudoboehmite is not
identical with the typical boehmite, both of them consist of Al-O-Al link-
ages. The difference between pseudoboehmite and typical boehmite is a
matter of rate rather than the basic nature of the reaction.

In the presence of ligands that have strong affinity for Al, such as sulfate
(Hsu, 1973), phosphate (Hsu, 1975), silicic acid (Luciuk and Huang, 1974),
carbonate (White and Hem, 1975; Serna et al., 1977; Bardossy and White,
1979), and fluoride (Violante and Huang, 1985), the further hydrolysis of
polynuclear Al species is prevented or at least retarded. These counter-
polyvalent anions tend to link polynuclear Al species together but in dis-
torted arrangement because of steric reasons. Most of such precipitation
products are thus short-range ordered materials and different from Al hy-
droxide polymorphs. These ligands, with strong affinity for Al, can also
promote physical flocculation resulting from reduction in electrostatic
repulsion between polynuclear Al ions (Serna et al., 1977; De Hek et al.,
1978). Nail et al. (1976a,b) proposed that the initial precipitation products
of Al was composed of polynuclear Al species with the gibbsite fragment
structure bound together by anions, which was also thought to inhibit
further crystallization by restricting growth along edges. The same type of
mechanism has been suggested for the interactions of complexing ligands
with Al_{13} polynuclear species (Teagarden et al., 1981).

Inorganic ligands that have strong affinity for Al, such as phosphate
(Violante and Huang, 1985) and sulfate (Hsu and Bates, 1964b; Violante
and Huang, 1984, 1985), promote and stabilize the formation of pseudo-
boehmites in the optimum range of the ligand/Al molar ratios. Pseudo-
boehmite has never been found to be formed in the presence of fluoride. If
the ligand/Al molar ratios are sufficiently high, these ligands inhibit the

Table 4. Precipitation products of aluminum formed in the presence of inorganic ligands after 5 months of aging at 20°C[a]

Ligand/Al molar ratio (R)	Ligand			
	Sulfate	Silicate	Fluoride	Phosphate
0.005	B[b]	—	B	B
0.01	B	—	—	—
0.02	B, (G)	B	B	G, P
0.05	B, (G)	B, (P)	B, S	P
0.1	B, (G)	B, G, (P)	B, S	P
0.2	B, G	B, P	B, S	A
0.5	B, G	A	A	A
1.0	G, (BP)	A	A	A
3.0	G, P	A	A	A

Source: Violante and Huang (1985); reprinted by permission of Clay Minerals Society.
[a] Initial pH = 8.2.
[b] B = bayerite; G = gibbsite; N = nordstrandite, A = X-ray-amorphous material; P = pseudoboehmite; ( ) = small amount; S = gelatinous, shapeless material detected by transmission electron microscopy.

crystallization of Al hydroxides and oxyhydroxides and promote the formation of noncrystalline precipitation products of Al (Violante and Huang, 1985). The influence of these inorganic ligands on the formation of Al hydroxides and oxyhydroxides is shown in Table 4.

The sequence of inorganic ligand introduction to the Al solution also influences Al transformations. The introduction of complexing ligands to the Al solution prior to neutralization results in the inhibitory influence on the hydrolysis-precipitation reactions of Al. On the other hand, if complexing ligands are interacted with a partially neutralized Al solution, even the addition of F^- results in rapid precipitation of polynuclear Al species, with efficient removal of dissolved F^- (Buffle *et al.*, 1985; Parthasarthy and Buffle, 1985).

Complexation of Al by a series of inorganic ligands may have a considerable influence on the behavior of Al in soil solutions and natural waters (Hem, 1968; Roberson and Hem, 1969; Johnson *et al.*, 1981; Huang and Violante, 1986). The ecological significance of such complexation reactions and the impact on human health need to be investigated.

VI. Influence of Organic Acids on Aluminum Transformations

A. Organic Acids in Soils and Associated Environments

The importance of organic acids in the weathering of minerals was reported in the classical studies by Sprengel (1826), Thenard (1870), Julien (1879), and Bolton (1880, 1882). Organic acids are agents for the mobiliza-

tion and transport of metals in soils and natural waters (Kaurichev and Nozdrunova, 1961; Schnitzer, 1968; Zunino and Martin, 1977; Förstner, 1981; Stevenson, 1982). The carboxyl and hydroxyl groups are the principal functional groups involved in the reactions of metal ions with organic acids in soil solutions and natural waters. These functional groups are present in both the humic and nonhumic fractions of soil organic components (Schnitzer and Skinner, 1965; Schnitzer and Kodama, 1977; Stevenson, 1982). The significance of the humic fractions, such as fulvic acids (FAs), in complexing with Al in solution has been intensively studied (Schnitzer and Kodama, 1977; Kodama and Schnitzer, 1980). The nonhumic fractions, such as the low-molecular-weight organic acids, are of great importance in the translocation of Al and Fe and pedogenesis (Bloomfield, 1964; Bruckert, 1970a,b; Stevenson and Ardakani, 1972; Stevenson, 1982).

The soluble humic substances comprise two major fractions. The low-molecular-weight materials with fairly high functional group acidity (FAs) are not precipitated at pH 2, whereas the larger humic acids (HAs), with molecular weights of 20,000–100,000, are precipitated. The materials that are so intimately associated with the clays that they are not removed by the basic solution or sequestering agents are known as humins. HAs isolated from a wide range of soils have a carbon content ranging from 53.6% to 58.8% with an average of 56.2%. The FAs have a lower carbon content and also show greater variability in composition. They have higher hydrogen, sulfur, and oxygen, but lower nitrogen contents. This is expressed in the functional groups with FAs having a much higher total acidity, carboxylic acid content, and alcoholic OH than the HAs isolated from the same soil (Schnitzer, 1977).

HAs and FAs behave like linear flexible polyelectrolytes that are readily aggregated at low pH with the aid of hydrogen bonding, van der Waal's interactions, and interactions with the π electron systems of adjacent molecules (Flaig et al., 1975). FAs at pH values above 2–3 occur as elongated fibers and bundles of fibers with a relatively open structure. With increases in pH, the fibers tend to mesh into a woven network, yielding a spongelike structure. HAs show similar structures, but because of the lower solubility in water the same structures are observed over a narrower pH range. A contemporary view of the structure of humic substances has been presented by Hayes and Himes (1986). The composition of humic materials is not identical in all soils. These substances are associated to varying extents (as much as 40–50% of the dry weight) with hydrolyzable carbohydrates and peptide or polypeptide materials. They are virtually bound to soil mineral colloids.

The sources of low-molecular-weight organic acids in soil environments include root exudates, canopy drip, decay of plant and animal residues, and microbial metabolites. The organic acids in soils can be broadly grouped into three categories: the volatile aliphatic acids, the nonvolatile aliphatic acids, and the aromatic acids (Stevenson, 1967). The relative abundance of these three categories of organic acids in soils generally

Table 5. Levels of some common organic acids in soil solutions

Nomenclature of acids	Concentration of acids (M) $\times 10^5$	Reference
Acetic	370–500	Stevenson and Ardakani (1972)
	265–570	Rao and Mikkelsen (1977)
Amino	8–60	Stevenson and Ardakani (1972)
Benzoic	7.5	Whitehead (1964)
Citric	1.4	Bruckert (1970b)
Ferulic	0.1–3.2	Whitehead (1964)
	0.0–0.3	Wang et al. (1967)
Formic	250–435	Stevenson (1967)
Malic + malonic + tartaric	100–400	Stevenson and Ardakani (1972)
Oxalic	6.2	Bruckert (1970b)
p-Coumaric	0.9–4.2	Whitehead (1964)
	0.0–2.2	Wang et al. (1967)
p-Hydroxybenzoic	0.8–3.9	Whitehead (1964)
	0.0–0.9	Wang et al. (1967)
Propionic	19	Walters (1916)
Vanillic	0.7–4.9	Whitehead (1964)
	0.0–0.7	Wang et al. (1967)
Tannic acid–related compounds	5–30	Coulson et al. (1960); Davies (1971); Stevenson (1982)

follows the order volatile aliphatic acids > nonvolatile aliphatic acids > aromatic acids (Wang et al., 1967; Casalicchio and Rossi, 1970). The levels of organic acids in soils are affected by a number of variables. Anaerobic conditions are particularly favorable for the microbial synthesis of organic acids (Desai and Rao, 1957; Sato and Yamane, 1967). Their concentration range in soil solutions is presented in Table 5.

Living plants contribute organic acids to the soil in root exudates and leaf washings. The exudates contain a range of organic acids such as oxalic, citric (Rovira and McDougall, 1967), and uronic acids (Oades, 1978) and a series of amino acids including glutamine, proline, and methionine (Bokhari et al., 1979). Bruckert et al. (1971) identified citric, malic, oxalic, succinic, vanillic, p-hydroxybenzoic, and p-coumaric acids in rain washings of plant leaves. Gomah and Sakhar (1972) observed phenolic acids such as gallic acid among the substances released from plant leaves by leaching with water.

Plant cells contain a range of carboxylic acids, such as citric, quinic, and shikimic acids (Clément, 1977). The amounts present are related to the kind of plants and the soil type on which the plants are growing. These acids are released by autolysis of the death of the plant. As plant tissues decay, they are attacked by the microflorae that synthesize a similar range of metabolites. Therefore, the origin of these compounds in soils cannot be easily distinguished (McKeague et al., 1986). Bacteria flourishing on any

medium usually produce large quantities of simple volatile acids such as formic, acetic, propionic, and butyric, whereas the greater part of the acids formed by fungi resembles the range of aliphatic acids present in the tricarboxylic acid cycle that are predominant in the cells of higher plants. Some bacteria such as pseudomonades, able to grow in acid conditions, are also able to produce oxalic acid (Berthelin and Belgy, 1979).

Roots and leaves decomposing in soils generate relatively large amounts of acetic, propionic, and butyric acids (Lynch *et al.*, 1980). Organic acids formed during root decomposition include hexanoic, phenylacetic, succinic, cinnamic, 4-hydroxyphenyl propionic, *p*-coumaric, and 3,4-dihydroxyphenylpropionic acids. 2-Ketogluconic acid accounted for 20% of the products formed in the rhizosphere of wheat seedlings (*Triticum vulgare*) (Moghimi *et al.*, 1978) and was probably a bacterial product (Duff and Webley, 1959). A large proportion of the bacteria in newly formed soils on rock surfaces produce this acid, which is particularly effective in dissolving minerals (Duff *et al.*, 1963).

Long-chain fatty acids in the range C_{12}–C_{24} are also found in soils in the lipid fraction. Their nature can be related to the plant species that have been growing in the soils (McKeague *et al.*, 1986).

Phenolic acids in soils are considered to originate not only from plants but also from the decomposition of lignin and microbial synthesis (Flaig, 1982). The phenolic acids derived from lignin include *p*-hydroxybenzoic, vanillic, syringic, and ferulic acids. Water extracts of barley (*Hordeum vulgare*) and wheat straws have been found to contain *p*-hydroxybenzoic, ferulic, and *p*-coumaric acids (Stevenson, 1967). These phenolic acids are present in small amounts in soils. In the clay loam A horizon of an Alfisol, for example, *p*-hydroxybenzoic acid predominated in the soil solution (1.4 μM) with smaller amounts of vanillic acid (0.11 μM) and very much smaller amounts of *p*-coumaric and ferulic acids (Whitehead *et al.*, 1981).

Although low-molecular-weight organic acids are present in relatively low concentrations in the soil solution and normally have only a transitory existence in soil environments, they are constantly added to the soils through natural vegetation, farming, and microbial metabolism. Furthermore, since the time required for soil formation can extend over a period of centuries, the cumulative effect of these organic acids on the transformations of Al in soils and associated environments and the impact on soil-plant relationships, environmental quality, and human and animal health merit attention.

B. Influence of Organic Ligands on Hydrolytic Reactions of Aluminum

Organic components are an integral part of soils and associated environments. Organic acids that are present in soil solutions and natural waters form complexes with Al and thus influence the subsequent transformations. The extent of the influence depends on the nature and concentration of organic acids. The occupation of the coordination sites of Al by organic

Table 6. Percentage distribution of precipitated Al in suspensions at the initial Al concentration of 1.1×10^{-3} M and OH/Al molar ratio of 2.0 as influenced by selected complexing organic acids at the end of the 40-day aging period at room temperature

Organic acid	% Al precipitated ($> 0.025 \mu m$) organic acid concentration, M		
	0	10^{-6}	10^{-4}
p-Hydroxybenzoic acid	36.9	35.2	31.7
Aspartic acid	36.9	34.4	27.5
Tannic acid	36.9	32.0	24.4
Malic acid	36.9	30.6	20.5
Citric acid	36.9	12.4	11.0

Source: Kwong and Huang (1979a); reprinted by permission of Williams & Wilkins.

Table 7. Stability constants of the complexes formed between Al and p-hydroxy-benzoic, aspartic, tannic, malic, and citric acids at 25°C

Organic acid	Stability constants of the complexes	
	$\log K_1$	$\log K_2$
p-Hydroxybenzoic acid	1.66	—
Aspartic acid	2.60	—
Tannic acid	3.78	—
Malic acid	5.14	8.52
Citric acid	7.37	13.90

Source: Kwong and Huang (1979a); reprinted by permission of Williams & Wilkins.

ligands disrupts the hydroxyl bridging mechanism indispensable for the polymerization of Al ions (Kwong and Huang, 1975, 1977).

Kwong and Huang (1979a) reported that citric, malic, tannic, aspartic, and p-hydroxybenzoic acids hinder the precipitation of solid-phase hydrolytic products of Al (Table 6). Both the kinds and concentrations of organic acids are important in hampering the precipitation of Al. When organic acids are present at the same concentration, they hamper the precipitation of Al in the order citric acid > malic acid > tannic acid > aspartic acid > p-hydroxybenzoic acid. Among the five organic acids, citric acid gives rise to the most stable complexes with Al, and p-hydroxybenzoic acid has the least affinity for Al, as indicated by the stoichiometric stability constants (Table 7). The affinity of the organic acids for Al (Table 7) coincides with their ability, when present at the same concentration, to hamper the precipitation of Al (Table 6).

The positively charged edges of polynuclear Al ions, in the absence of organic acids, undergo hydrolysis as depicted below:
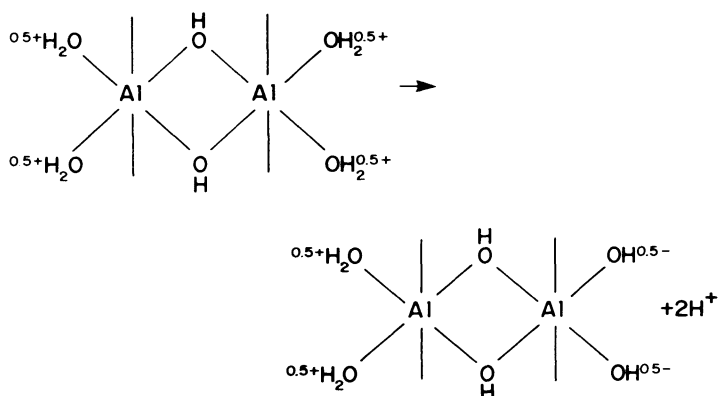
The hydrolysis of these positive edges in the absence of organic acids upon aging results in a decrease in pH (Kwong and Huang, 1979a).

If an organic acid such as citric acid is present in the aqueous solution of Al, the coordination sites of polynuclear Al are occupied by citrate instead of H_2O molecules, imposing a restraint on the hydrolysis of Al as shown below (Kwong and Huang, 1979a).

hydroxyl bridging mechanism of edge – Al is hampered by the citrate
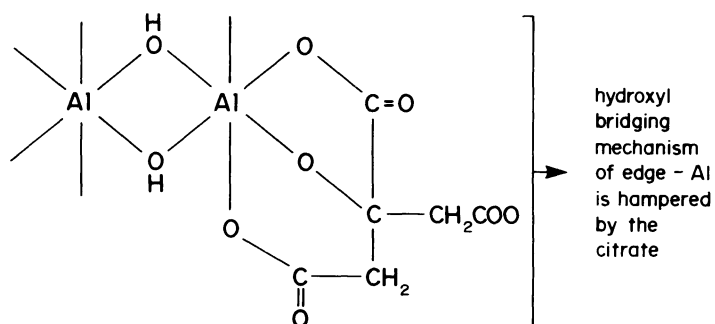
If more organic acids are present in the system, the greater would be the replacement of H_2O molecules and blocking of the coordination sites of Al, and the greater becomes the restraint on the subsequent hydrolysis of polynuclear Al ions. If the concentration of organic acids is held constant, the greater the affinity of the organic acids for Al, the more extensive would be their occupation of the coordination sites of Al, and the more efficient the restraint imposed on the hydrolysis of polynuclear Al ions. Therefore, the precipitation of Al decreases both with the increase of the concentration of organic acids present during the precipitation (Table 6) and with the increase of the stability constants of their complexes with Al (Table 7). The polymerization of Al could occur as interpreted from the broadening of NMR signals of aqueous solutions containing Al chelates of hydroxycarboxylic acids, such as citric and tartaric acids (Toy et al., 1973).

Some coordination sites of Al in Al chelate may be still occupied by hydroxyl groups or H_2O molecules which could undergo hydrolysis to some extent. The occupation of the coordination sites of Al by organic ligands blocks the sites that are indispensable for hydroxyl bridging in the polymerization of Al and its subsequent transformations.
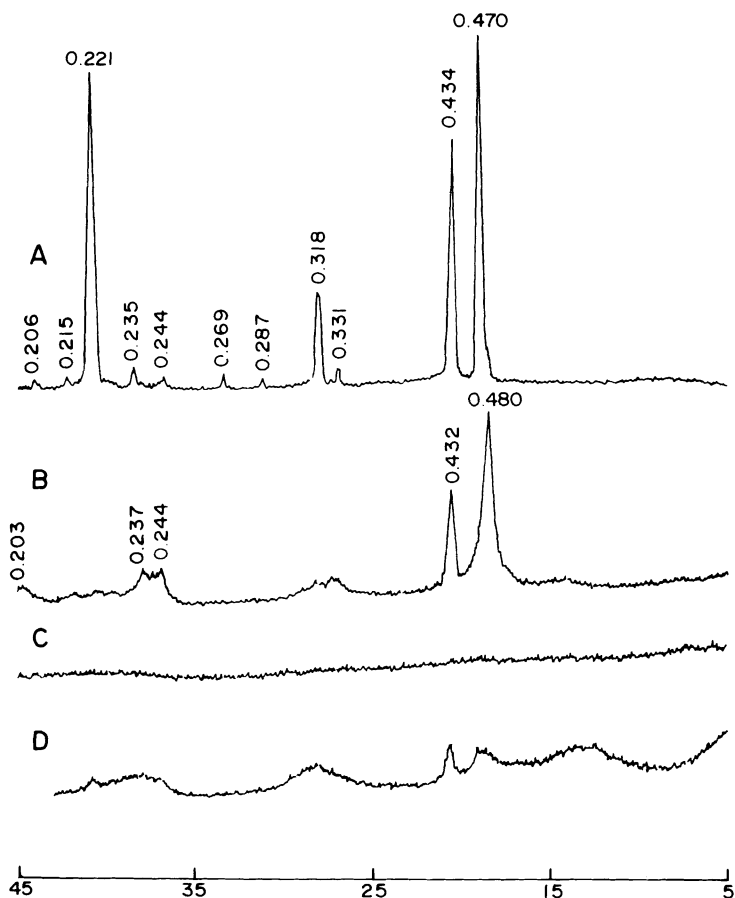
Figure 6. The X-ray diffraction patterns of precipitation products of Al at the initial OH/Al molar ratio of 3 and (A) Al concentration of 1.10×10^{-3} M in the absence of citric acid collected after the 40-day aging at room temperature; (B) Al concentration of 1.10×10^{-3} M in the presence of 10^{-6} M citric acid collected after the 40-day aging at room temperature; (C) Al concentration of 1.10×10^{-3} M in the presence of 10^{-4} M citric acid collected after the 40-day aging at room temperature followed by the 3-day aging at 80°C; and (D) Al concentration of 1.10×10^{-4} M in the presence of 10^{-6} M citric acid collected after the 40-day aging at room temperature (Kwong and Huang, 1975; reprinted with permission of Clay Minerals Society). d-Spacings are in nanometers.

C. Role of Organic Ligands in the Formation of Short-Range Ordered Precipitation Products of Aluminum

The persistence of organic acids in acid soils (Bruckert, 1970a) and the reported occurrence of noncrystalline hydrous oxides of Al under acidic conditions (Mitchell *et al.*, 1964) point toward a possible interference of organic acids in the crystallization of precipitation products of Al. Kwong and Huang (1975) reported that citric acid hampers the crystallization of aluminum hydroxides (Figure 6). The noncrystalline nature of the products is attributed to the occupation of the coordination sites of Al^{3+} ions by citric acid upon dissociation of proton, resulting in a distortion in the arrangement of the hexagonal ring units normally present in crystalline aluminum hydroxides. The structural water of the reaction products is lost more gradually when citric acid concentration is raised from 0 M to 1.4 $\times$ 10^{-4} M (Kwong and Huang, 1977), indicating that a greater structural disorder occurs within the products with increasing levels of citric acid in the systems. This inference from thermal analysis supports the reasoning that citric acid hampers the hydroxyl bridging mechanism in the hydrolytic reaction of Al.

Electron diffraction analyses reveal that the products formed from an initial Al concentration of 1.10 $\times$ 10^{-4} M and OH/Al molar ratio of 1 in the presence of 1.0 $\times$ 10^{-6} M citric acid after the 40-day aging, which are noncrystalline to X-rays, are in effect microcrystalline with reflections at d = 0.110 and 0.181 nm (Kwong and Huang, 1977). The reaction products collected after the 40-day aging from the system with an initial Al concentration of 1.0 $\times$ 10^{-4} M and OH/Al molar ratio of 3 in the presence of a citric acid concentration as high as 1.0 $\times$ 10^{-4} M are also microcrystalline and give reflections at d = 0.321, 0.275, 0.198, 0.166, and 0.142 nm. The microcrystalline nature of the products from the d-values obtained by electron diffraction analyses are still obscure. The electron diffraction data reveal that at the concentrations used, citric acid hampers the formation of even microcrystalline bayerite and gibbsite. They also indicate that the masking effect of noncrystalline products on crystalline cores is not the reason why the solid-phase reaction products formed in the presence of citric acid are noncrystalline to X-rays.

Organic acids, which are common in soil solutions and natural waters, vary in their chemical composition, structure, nature of functional groups, size, and basicity. Therefore, they vary in their ability to perturb the hydrolytic reactions of Al (Kwong and Huang, 1979a). In systems at the initial Al concentration of 1.1 $\times$ 1.0^{-3} M, OH/Al molar ratio of 3 and citric acid concentration of 10^{-6} M, the complexation of Al by citrate, which has the strongest affinity for Al (Table 7), is sufficient to cause the hydrolytic precipitation products formed to be noncrystalline to X-rays after the 1-day aging (Figure 7E). *p*-Hydroxybenzoic, aspartic, and malic acids, which have weaker affinity for Al than citric acid (Table 7), do not complex Al
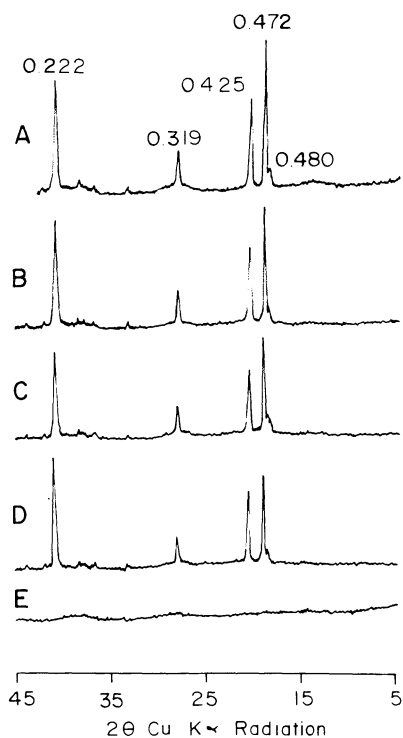
Figure 7. X-ray diffraction patterns of hydrolytic products of Al precipitated at the initial Al concentration of 1.1×10^{-3} M, OH/Al molar ratio of 3.0 and aged for 1 day at room temperature in the presence of (A) no organic acid, (B) 10^{-6} M p-hydroxybenzoic acid, (C) 10^{-6} M aspartic acid, (D) 10^{-6} M malic acid, and (E) 10^{-6} M citric acid (Kwong and Huang, 1979b; reprinted with permission of Elsevier Science Publishers B.V.). d-Spacings are in nanometers.

sufficiently to hamper the formation of bayerite after the 1-day aging (Figure 7B–D). When the concentration of citric, malic, and aspartic acids is raised to 10^{-4} M in the system, the hydrolytic products formed are noncrystalline to poorly crystalline to X-rays even after the 40-day aging (Figure 8B–D). p-Hydroxybenzoic acid, which formed the least stable complexes with Al (Table 7), does not inhibit the crystallization of hydrolytic precipitation products of Al (Figure 8A). The critical molar ratio of organic acid to Al in inhibiting the crystallization of Al hydroxides varies with the nature of organic acids (Kwong and Huang, 1979b). In the case of citric, malic, and aspartic acids, even at the molar ratio of organic acid to Al of 0.01, the crystallization of Al hydroxides is greatly retarded, and the presence of pseudoboehmite in the reaction products is indicated by the X-ray diffraction data.

Organic acids of higher molecular weight, such as tannic acid and fulvic acid, perturb the crystallization of precipitation products of Al. The noncrystalline to poorly crystalline hydrolytic precipitation products of Al, including pseudoboehmite, are formed in the presence of tannic acid (Kwong and Huang, 1981) and are shown to be fine, shapeless, hollow colloids that are deformed and aggregated (Figure 9). Kodama and Schnitzer (1980)
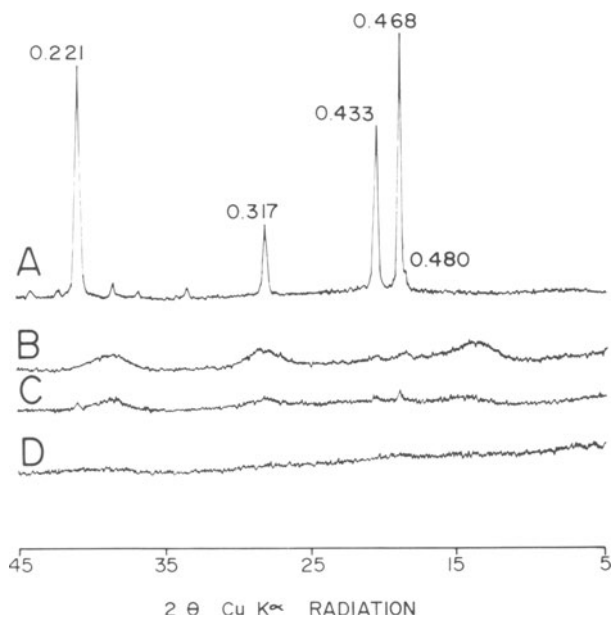
Figure 8. X-ray diffraction patterns of hydrolytic products of Al precipitated at the initial Al concentration of 1.10×10^{-3} M, OH/Al molar ratio of 3.0, and aged for 40 days at room temperature in the presence of 10^{-4} M: (A) p-hydroxybenzoic acid, (B) aspartic acid, (C) malic acid, and (D) citric acid (Kwong and Huang, 1979b; reprinted with permission of Elsevier Science Publishers B.V.). d-Spacings are in nanometers.

reported the significant effects of fulvic acid on the crystallization of Al hydroxides. In the absence of fulvic acid, gibbsite was formed at pH 6, a mixture of nordstrandite and bayerite was formed at pH 8, and bayerite crystallized at pH 10 (Table 8). At pH 6 and 8, the addition of increasing amounts of fulvic acid first delays and then inhibits the crystallization of these Al hydroxide polymorphs but favors the crystallization of pseudo-boehmite. As the ratio of fulvic acid to Al reaches 0.1, crystalline materials are no longer formed, and only amorphous precipitates are formed. At pH 10, the addition of fulvic acid totally inhibits precipitation and crystallization of hydrolytic products of Al.

Fulvic acid resembles low-molecular-weight aliphatic acids such as citric and malic acids in that it contains COOH and aliphatic OH groups. It also resembles quercetin and tannic acid, as it contains phenolic hydroxyl and ketonic C=O groups. The crystallization of Al hydroxides is delayed or inhibited by the presence of low-molecular-weight organic acids (Kwong and Huang, 1975, 1977, 1979b) and tannic acid (Kwong and Huang, 1981). The polymerization of Al hydroxides is inhibited by the presence of very
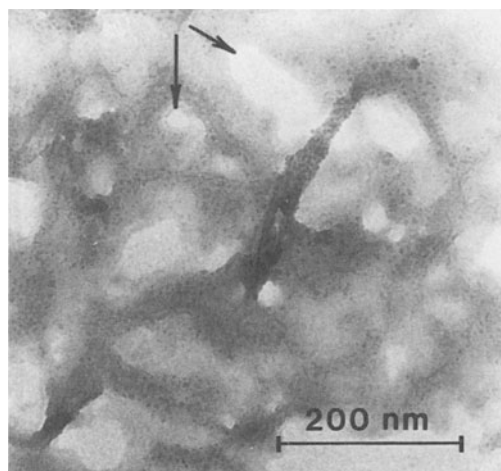
Figure 9. Transmission electron micrographs of the precipitation products of Al formed after the 40-day aging at room temperature at the initial concentration of 1.1×10^{-3} M Al, OH/Al molar ration of 3.0, and in the presence of 1.0×10^{-4} M tannic acid. Porous nature (see arrows) results from influence of tannic acid (Kwong and Huang, 1981; reprinted with permission of Elsevier Science Publishers B.V.).

small amounts of the flavone quercetin (Lind and Hem, 1975). Through these functional groups, fulvic acid can form stable complexes with Al and prevent the crystallization of $Al(OH)_3$ (Kodama and Schnitzer, 1980). The influence of fulvic acid on the crystallization of Al hydroxides also resembles that of salts (Hsu, 1967) in that fulvic acid appears to favor the formation of Al-O-Al (oxo) over that of

$$Al \underset{OH}{\overset{OH}{\diagup \diagdown}} Al$$
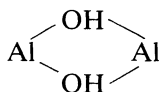
(Ol) linkages.

Pseudoboehmite formed at low temperatures and pressures in the absence of foreign anions is unstable and rapidly converted to $Al(OH)_3$ polymers (Souza Santos et al., 1953; Aldcroft et al., 1969; Vedder and Vermilyea, 1969; Yoldas, 1973; Serna et al., 1977). However, certain organic and inorganic ligands not only promote the formation of pseudoboehmite over Al hydroxides, but also stabilize it (Hsu, 1967; Kwong and Huang, 1979b; Violante and Jackson, 1979, 1981; Kodama and Schnitzer, 1980; Violante and Violante, 1980; Kwong and Huang, 1981). Pseudoboehmite samples formed in the presence of various organic and inorganic perturbing ligands that are common in soil environments differ significantly in their

Table 8. Summary of X-ray data for the effect of FA on the crystallization of aluminum hydroxides at 30°C[a]

FA(mg)/500 ml[b] pH	0	0.25	0.5	1.0	1.5	2.5	5.0	50.0
6	GIBBS	gibbs + "bm"	gibbs + "bm"	gb + "boehm"	/	"BOEHM"	"BOEHM"	/
8	NORD + bayer	nord + bayer+ "bm"	nord + bayer+ "boehm"	/	ns and/or by (?) + "BOEHM"	/	ns and/or by (?) + "BOEHM"	Am. ppt.
10	BAYER	/[c]	—[d]	/	/	—	—	—

Source: Kodama and Schnitzer (1980); reprinted with permission of Elsevier Science Publishers.

[a] Abbreviations used in this table:

	Semi-quantitative estimates		
	Major	Minor	Trace
Amorphous precipitate (Am. ppt.)			
Bayerite	BAYER	bayer	by
Gibbsite	GIBBS	gibbs	gb
Nordstrandite	NORD	nord	ns
Pseudoboehmite	"BOEHM"	"boehm"	bm

[b] Approximate FA/Al molar ratios ranged from 0 (0 mg FA) to 10^{-1} (50.0 mg FA).

[c] Not determined.

[d] No or very little precipitate.

Table 9. Comparison of X-ray diffraction data of standard boehmite and pseudoboehmite samples formed in the presence of optimum concentration range of perturbing organic and inorganic ligands at room temperature

Sample	d-Spacings (nm)						
	(020)	(120)	(140,031)	(051)	(200)	(231)	(251)
Boehmite (standard)[a]	0.611	0.316	0.235	0.186	0.185	0.145	0.131
Pseudoboehmite (citrate) R[b] = 0.01	0.665	0.318	0.235	0.190	0.186	0.144	0.134
	(β = 3.20)	(β = 2.35)	(β = 2.50)	b.v.[d]	(β = 2.00)	b.v.	b.v.
Pseudoboehmite (tartrate) R = 0.01	0.663	0.316	0.239	0.191	0.189	0.146	0.134
	(β = 3.00)	(β = 2.00)	(β = 2.40)	b.v.	(β = 1.80)	(β = n.d.)	b.v.
Pseudoboehmite (tannate) R = 0.01	0.707	0.319	0.235	0.190	0.185	0.152	0.136
	(β = 3.60)	(β = 2.40)	(β = 2.80)	b.v.	(β = 2.20)	(β = n.d.)	b.v.
Pseudoboehmite (tannate) R = 0.02	0.716	0.319	0.234	—	0.185	0.143	0.136
	(β = 3.65)	(β = 2.80)	(β = 3.00)	—	(β = 2.30)	(β = 2.00)	b.v.
Pseudoboehmite (chloride) R = 700	0.665	0.319	0.239	0.194	0.191	0.143	0.136
	(β = 3.55)	(β = 3.40)	(β = 2.80)	b.v.	(β = 2.30)	(β = 1.80)	b.v.
Pseudoboehmite (sulfate) R = 70	very broad	0.320	0.235	0.192	0.187	0.143	0.134
	(β = n.d.)[c]	(β = 4.00)	(β = 3.30)	(β = n.d.)	(β = n.d.)	(β = n.d.)	b.v.

Source: Violante and Huang (1984); reprinted with permission of the Soil Science Society of America.

[a] Only the d-spacings with a $I/I_1 \geq 15$ are reported (ASTM card no. 21-1307); β = breadth (2θ) measured at half-maximum intensity; β and 2θ position were measured according to the procedures described by Tettenhorst and Hofmann (1980).

[b] R is the initial ligand/Al molar ratio.

[c] Not determinable (the peak is visible, but the β value is difficult or impossible to determine).

[d] Barely visible (the peak is only barely visible).

Table 10. Order of effectiveness of organic ligands in promoting the formation of pseudoboehmite and X-ray noncrystalline precipitation products of Al after 5 months of aging at room temperature

Ligand	R^a	R^b
Phthalate $\cong$ succinate	7–14	15
Glutamate	0.4–3.0	4
Aspartate	0.1–2.0	2.5
Oxalate	n.c.p.^{c}	1
Salicylate $\cong$ malate	0.02–0.05	0.10
Tannate	0.01–0.03	0.04
Citrate	0.007–0.02	0.03
Tartrate	0.005–0.015	0.02

Source: Violante and Huang (1985); reprinted with permission of Clay Minerals Society.

^{a}R = the range of the initial ligand/Al molar ratios at which stable pseudoboehmite was formed at pH 8.2.

^{b}R = the lowest initial ligand/Al molar ratio at which X-ray noncrystalline materials were formed at pH 8.2.

^{c}No evidence for the crystallization of pure pseudoboehmite.

surface morphology and chemical composition (Violante and Huang, 1984). The pseudoboehmite samples that are synthesized at room temperature in the presence of selected organic and inorganic ligands show similar X-ray diffraction data (Table 9). The Al oxyhydroxides consist of fibrillar particles as well as many aggregates (> 5 nm) even after ultrasonification. These studies throw new light on the genesis of noncrystalline alumina of boehmite characteristics in certain tropical soils (De Villiers, 1969) and of some bauxites that consist of submicroscopic boehmitelike particles that are very similar to pseudoboehmite (Lippens and Steggerda, 1970).

The sequence of the relative effectiveness of certain perturbing organic ligands commonly present in nature in promoting the formation of pseudoboehmite over $Al(OH)_3$ polymorphs is as follows: phthalate $\cong$ succinate < glutamate < aspartate < salicylate $\cong$ malate < tannate < citrate < tartrate (Table 10). As the molar ratios of perturbing ligands to Al exceed the critical ratios for the formation of pseudoboehmite, organic ligands that are coprecipitated with Al inhibit the crystallization of Al hydroxides or oxyhydroxides and promote the formation of X-ray noncrystalline Al precipitation products. First of all, the hydrolysis of the positively charged sites of hydroxy-Al polymers is retarded because of the occupation of the coordination sites of Al by the perturbing ligands instead of H_2O molecules (Kwong and Huang, 1979a). Secondly, because of steric factors, the perturbing ligands occupying the coordination sites of Al distort the arrangement of the platelets (the *001* sheets) normally found in crystalline Al hydroxides (Figure 10).

The order of common organic ligands in promoting the formation of

Unit sheets (OOI) of
aluminum hydroxide

Organic ligands distorting
the orientation of unit sheets
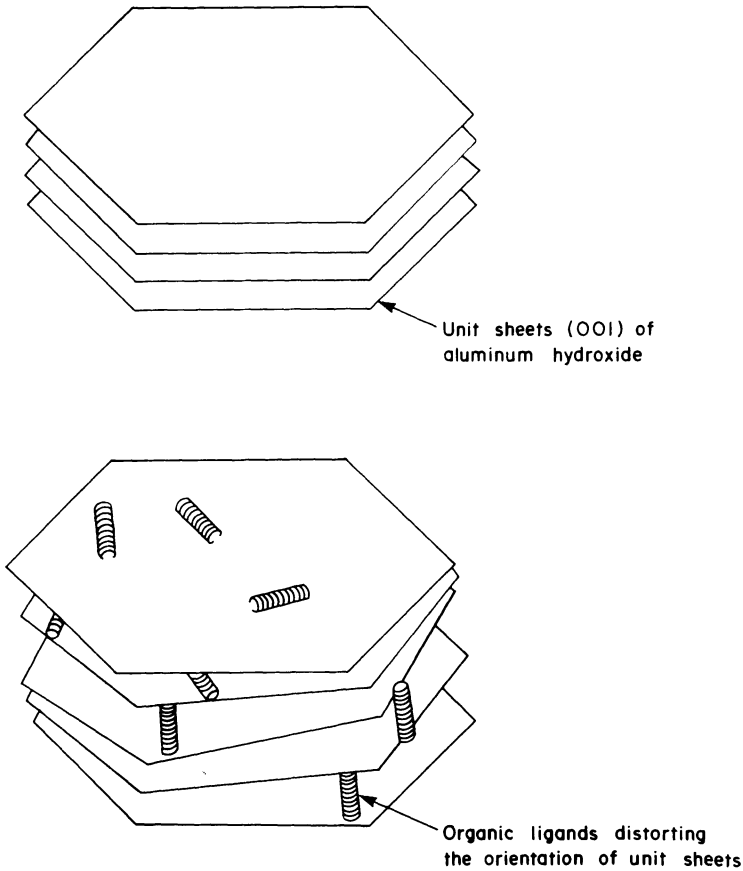
Figure 10. Structural models showing the distortion of the orientation of the platelets (the *001* sheets) of Al hydroxides by organic ligands which coprecipitate with Al and are incorporated into the sheets (modified from Kwong and Huang, 1979b; reprinted with permission of Elsevier Science Publishers B.V.).

noncrystalline Al precipitation products is as follows: phthalate $\cong$ succinate $<$ glutamate $<$ aspartate $<$ oxalate $<$ salicylate $\cong$ malate $<$ tannate $<$ citrate $<$ tartrate (Table 10). Many organic ligands such as tartrate, citrate, tannate, malate, and salicylate are much stronger than inorganic ligands such as silicate and phosphate in promoting the formation of precipitation products of Al that are noncrystaline to X-rays (Violante and Huang, 1985). The strength of the ligands promoting the formation of noncrystalline materials appears to vary with their nature, size, and affinity for Al. Ligands that form polydentate complexes generally have a stronger ability in causing the structural distortion of precipitation products of Al than those with fewer functional groups. The implications of these findings are

evident in the formation of short-range ordered organomineral complexes in soils (Mitchell *et al.*, 1964; Campbell *et al.*, 1977). Furthermore, these studies indicate that besides hydroxy-Al interlayering of expansible phyllo-silicates (Jackson, 1963b; Rich, 1968; Bertsch and Barnhisel, 1987), the formation of crystalline Al hydroxides in soils and sediments can be hampered through the complexation reactions of hydroxy Al with these organic acids, especially in environments where accumulation of organic acids tends to occur. Substantial concentrations of crystalline Al hydroxides are thus absent in organic matter–rich soils in the temperate regions.

D. Formation of Aluminum Hydroxide Polymorphs as Influenced by Organic Ligands

The nature and concentration of organic acids and the associated pH are related to the formation of Al hydroxide polymorphs (Table 11). At a given pH and organic acid/Al ratio, there is a change in the final aluminous products formed from bayerite to nordstrandite and/or gibbsite and finally to pseudoboehmite and noncrystalline materials, approximately according to the increasing chelating power of the organic acids. The same order of formation of the various aluminous precipitation products follows at a given pH by increasing the concentration of some of the organic acids.

Succinic acid weakly complexes Al ions (Murmann, 1964) by forming unstable seven-membered rings, so its presence has a relatively minor influence on the crystallization rate, particularly at pH > 8.0 (Table 11). Data for phthalic acid show the same trend as for succinic acid (not reported in Table 11).

Glycine (aminoethanoic acid), a bidentate agent, like phthalic and succinic acids, complexes Al ions by forming a more stable five-membered ring. Consequently, in glycine systems, particularly at the highest glycine/Al ratio and at pH 8.0 and 9.0, the rate of Al $(OH)_3$ crystallization is slower than in succinate or phthalate systems (Violante and Violante, 1980), and the formation of gibbsite (at pH 8) and nordstrandite (at pH 9.0) is favored (Table 11).

With more effective retarding agents, such as glutamic and aspartic acids, gibbsite, nordstrandite, and pseudoboehmite form easily at pH 8.0 and commonly at pH 9.0 (Table 11). Aspartic and glutamic acids are both tridentate, but in the presence of the former, the crystallization rates of hydrolytic products of aluminum are slower than in the presence of the latter. In samples where aspartic acid is present, gibbsite, nordstrandite, and pseudoboehmite form more easily than bayerite. Aspartic acid, in fact, acts as a stronger retarding agent, probably because the COOH group at the end of the aliphatic side chain and the $-NH_2$ group might stabilize the complex by chelating Al ions with two stable five- and six-membered rings. On the contrary, glutamic acid might complex Al ions more weakly by forming a stable five-membered ring and an unstable seven-membered

Table 11. Aluminum hydroxides and oxyhydroxides formed in the presence of complexing organic acids after 60 days at 20°C

Organic acid/Al molar ratio	Acid								
	Succinic	Glycine	Glutamic	Aspartic	Oxalic	Malic	Salicylic	Citric	Tartaric
Samples aged at pH 8.0									
0.014	B, (G)	B, (G)	—	G	G, (P)	G, P	—	P	P
0.029	B, (G)	B, (G)	G, N, (B)	P, G, (N)	G, P or P	P	P	A	A
0.050	B, (G)	B, G	G, N	P, (G)	P	P	P	A	A
0.167	G, N, B	G	P	A	A	A	A	A	A
Samples aged at pH 9.0									
0.029	B	B, (N)	B, N	N	N, B	N, P	N, P	P	P
0.050	B	B, N	N	G, N, P	N, (P, B)	P, (N, G)	P, N, (G)	P	A
0.167	B, N	N, (P)	G, N, P	G, P	G, P or P	P	P, (N, G)	A	A
Samples aged at pH 10.0									
0.050	B	B	B	B	B, (P)	B, N	N, (B)	N	P
0.167	B	B	B, (P)	B, P	N, B, (P)	N, P	N, P, (G)	P	A

Source: Violante and Violante (1980); reprinted with permission of Clay Minerals Society.

A = amorphous Al hydroxides; P = pseudoboehmite; B = bayerite; G = gibbsite; N = nordstrandite; ( ) small amounts; — = no Al hydroxides or oxyhydroxides detected.

ring. According to Das Sarma (1956), glutamate, aspartate, and other α-amino acid ligands do not always easily form a tridentate ligand to a single ion, and other structures have been suggested as alternatives where these ligands behave as either tridentate or bidentate ligands. However, the above reasoning easily explains the greater influence of aspartic acid over glutamic acid on the crystallization of $Al(OH)_3$ polymorphs (Table 11).

Gibbsite is commonly favored over nordstrandite when the crystallization rate is particularly slow, even at high pH values. At pH 9.0 and at a glutamic acid/Al ratio of 0.1, almost pure nordstrandite has been synthesized, whereas in the presence of aspartate, gibbsite and nordstrandite are formed (Violante and Violante, 1980). In addition, a concentration increase of a complexing organic ligand results in a progressive increase in the ratio of gibbsite to nordstrandite (Table 11).

In the optimal concentration range, oxalic acid has a greater influence than malonic, succinic, and glutaric acids (in the order listed) in favoring the formation of gibbsite, nordstrandite and/or pseudoboehmite (Violante and Violante, 1980). This may be explained by considering that chelates of five- or six-membered rings are more stable than larger ones. The closer the carboxyl groups, the more active is the bicarboxylate anion. The carboxylate group in glutarate, and probably in higher homologues, are too far apart; hence these ligands behave like monocarboxylates—e.g., acetate (Violante and Violante, 1978).

Strong chelating organic acids significantly retard the crystallization process, so that gibbsite is favored as the precipitation product even at high pH (Violante and Violante, 1980). Intermediate conditions created by moderately strong chelating anions do not retard the rate of crystallization significantly to favor gibbsite but rather favor nordstrandite, particularly at pH > 8.0. In the absence of organic acids or in the presence of weakly complexing organic acids, the rapid crystallization processes lead to the formation of bayerite. The data indicate that organic acids affect the kinetics of the crystallization of hydrolytic products of Al and thus influence the kinds of Al hydroxide polymorphs formed. In alkaline soils, the presence of clays and organic matter with its carboxylic and amino groups would inhibit the crystallization of bayerite by favoring the formation of gibbsite or nordstrandite. These results provide the interpretation that nordstrandite and gibbsite, rather than bayerite, are common in some alkaline soils. Furthermore, it is logical that bayerite is virtually absent in soils and natural environments (Schoen and Roberson, 1970; Milton et al., 1975).

E. Formation of Hydroxy-Aluminum-Organics-Clay Complexes

Soils are a complex mixture of organic and inorganic components that interact with each other (Greenland, 1965a,b; Schnitzer and Kodama, 1977). The stability of the chloritelike complexes in montmorillonite in the alkaline range of pH is influenced by the presence of citric acid (Violante and Violante, 1978; Violante and Jackson, 1979, 1981).

Table 12. Total Al sorbed from solution, KCl-exchangeable Al, HCl-extractable Al, and CEC of montmorillonite after equilibration with hydroxy Al and citric acid

Sample No.	NaOH/Al	Citrate/Al	pH Initial	pH Final	Al[a] sorbed	Sorbed Al[b] exch. by 1 M KCl	Sorbed Al[c] ext. by 0.2 M HCl	CEC[d] before extraction by 0.2 M HCl	CEC[d] after extraction by 0.2 M HCl
						— g · kg^{-1} —		— cmol (1/2 Ca^{2+}) · kg^{-1} —	
1	In water		7.4	7.4	ND[e]	ND	ND	96	95
2	In AlCl$_3$		4.0	3.9	7.54	5.48	7.35	78	83
3	0[f]	0.1	3.5	3.6	6.35	5.71	5.95	92	88
4	0	0.5	3.0	3.0	6.07	6.06	6.31	84	86
5	0	1.0	2.8	3.0	5.65	5.34	5.77	89	85
6	2.5	0	4.5	4.1	49.95	1.22	10.49	31	43
7	2.5	0.1	4.6	4.7	48.43	0.82	1.85	34	47
8	2.5	0.5	4.3	4.6	28.18	5.55	8.35	61	76
9	2.5	1.0	3.6	3.7	14.96	6.33	6.76	82	83

Source: Goh and Haung (1984); reprinted with permission of the Agricultural Institute of Canada.

[a] Mean error of duplicates = ± 0.43 g Al · kg^{-1}.

[b] Mean error of duplicates = ± 0.21 g Al · kg^{-1}.

[c] Mean error of duplicates = ± 0.70 g Al · kg^{-1}.

[d] Mean error of duplicates = ± 3 cmol (1/2 Ca^{2+}) · kg^{-1}.

[e] ND, not detectable.

[f] At NaOH/Al = 0, no NaOH was added to the montmorillonite suspension in the AlCl$_3$ solution.

More recent research data show that the formation of hydroxy-Al-montmorillonite complexes in the acidic pH range that is most conducive to chloritization (Rich, 1968) is significantly perturbed by low-molecular-weight organic acids such as citric and tannic acids (Goh and Huang, 1984, 1986). Once hydroxy Al ions interact with organic acids to form hydroxy Al-organic acid complexes, the adsorption of these complexes by the interlayer spaces of montmorillonite can take place only if the net attractive forces between the positively charged sites of the complexes and negatively charged clay surfaces can overcome the repulsive forces between the anionic ligands of the complexes and clay surfaces and any steric hindrances that may be present. Table 12 shows that the citrate/Al molar ratio has an important influence on the formation of hydroxy Al interlayers. At the citrate/Al molar ratio of 0.1 or less, the mutual repulsion between negatively charged sites is apparently not strong enough to prevent the formation of hydroxy Al interlayers in smectite. Between the citric acid/Al molar ratios of 0.3–0.5, a smaller but substantial amount of Al can still be adsorbed by smectite. If the citric acid/Al molar ratio is 0.7 or higher, very little is adsorbed by smectite. The formation of hydroxy-Al-smectite complexes appears to be critically perturbed if the citrate/Al molar ratio exceeds 0.5.

The polynuclear Al ion of double ring structure (Hsu, 1977) can be chelated by citrate (Kwong and Huang, 1979a), and its structure can be depicted below:
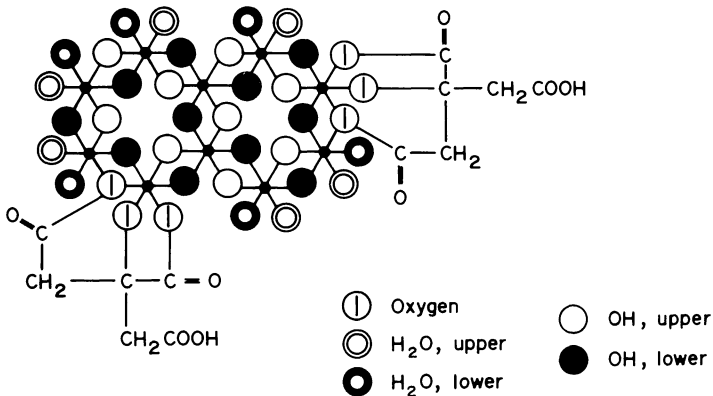
In view of the structure of a hydroxy-Al-citrate as illustrated above and the data obtained by using cation and anion exchange resins (Goh and Huang, 1986), hydroxy-Al-citrate chelates can be sorbed on the interlayer spaces of smectite. The adsorption of hydroxy-Al-citrate by smectite causes structural distortion from within the interlayer spaces of the clay as indicated by the broadening of the (001) peak in X-ray diffractograms (Figure
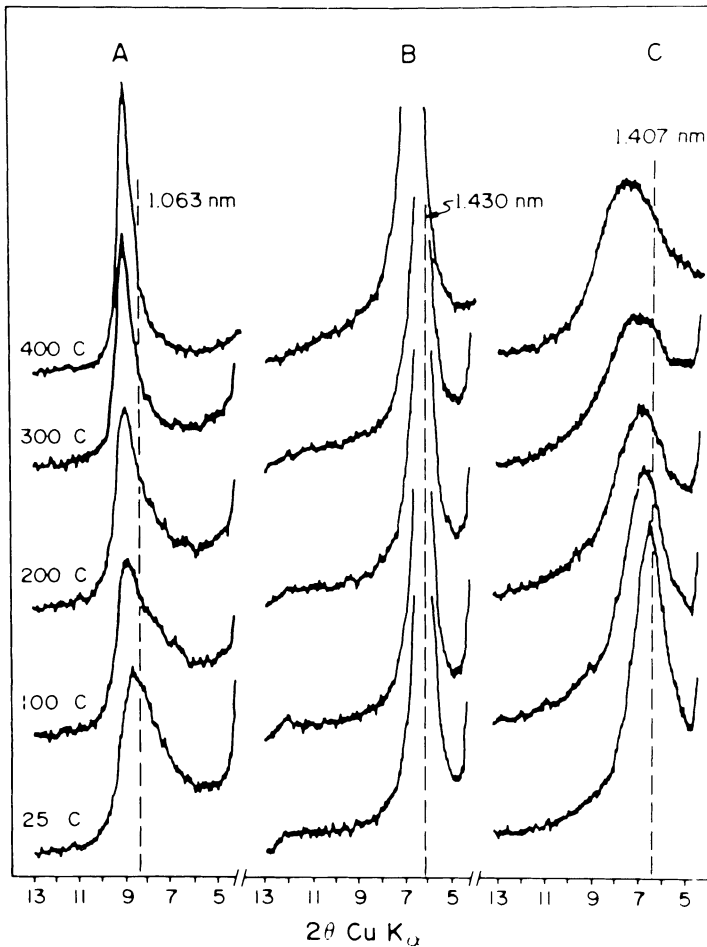
Figure 11. The X-ray diffractograms of the first-order reflection of selected solid-phase reaction products (room temperature) after heating at various temperatures: (A) Na-montmorillonite; (B) hydroxy-aluminum-montmorillonite, NaOH/Al molar ratio of 2.5; and (C) hydroxy-aluminum-citrate-montmorillonite, NaOH/Al molar ratio of 2.5, citrate/Al molar ratio of 0.5 (Goh and Huang, 1984; reprinted with permission of the Agricultural Institute of Canada).

11C) and the obscuring of the IR absorption bands at 3695 and 3570cm^{-1} (Figure 12C) representing the presence of hydroxy Al interlayers. In addition, the dehydroxylation endotherm is spread over a wide range of temperatures ranging from 430°C to about 520°C as the citrate/Al ratio is increased from 0.1 to 0.5 (Goh and Huang, 1985). Obviously, the perturbation to the interlayer hydroxy-Al caused by citric acid has the effect of causing the interlayers to lose their structural water more slowly. The com-

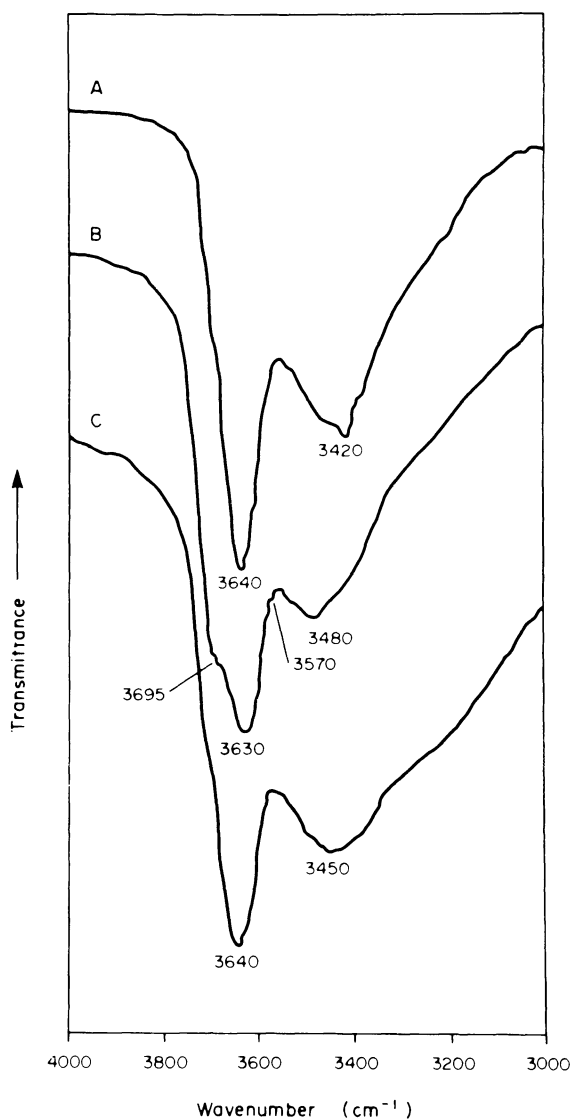**Figure 12.** Infrared spectra of selected solid-phase reaction products (room temperature): (A) Na-montmorillonite aged 3 months in water; (B) hydroxy-aluminum-montmorillonite aged at initial pH of 5.0; and (C) hydroxy-aluminum-citrate-montmorillonite aged at initial pH of 5.0 and citrate/Al molar ratio of 0.5 (Goh and Huang, 1984; reprinted with permission of the Agricultural Institute of Canada).

plexation between tannic acid and Al is deemed to occur more favorably when the pH of the suspension is increased, since the reaction generates protons (Goh and Huang, 1986). The protons are not likely generated by the simple dissociation of phenolic hydroxyls as the initial pH of aging suspension ranges from 5 to 6 and thus well below the reported pKa of phenolic groups, which is about 9.0 (Weast, 1978). The formation of a five-membered ring in the complex is more stable than a monodentate complex that has Al being coordinated to the carboxylate, COO^- group (Cotton and Wilkinson, 1980). Further growth of the hydroxy-Al-tannate complex to a large hydroxy-Al-tannate complex polymer may be possible (Goh and Huang, 1986). The high molecular weight of tannic acid apparently causes the hydroxy-Al-tannate complexes to precipitate as a discrete phase which acts as cementing agents between clay particles. The forces of physical adsorption are additive in high-molecular-weight organic compounds (Greenland, 1965a; Kwong and Huang, 1981). The aggregation of hydroxy-Al-clay particles is thus promoted by tannic acid.

The finding on the perturbation of Al interlayering of expansible phyllosilicates by organic acids also provides an interpretation to the observation that the accumulation of hydroxy Al interlayers is more pronounced under well-drained conditions than in imperfectly drained soils (Jackson, 1963b; Rich, 1968; Huang and Lee, 1969), since the latter environment is more conducive to the accumulation of organic acids (Stevenson, 1967).

More recent studies show that the formation of hydroxy-Al-montmorillonite complexes is significantly perturbed by HAs (Singer and Huang, 1986). The observation of Rich (1968) that Al interlayering of clays is not favorable in soils that are high in organic matter is thus explained.

F. Pedogenic Significance of Organic Ligands in the Formation of Short-Range Ordered Aluminosilicates

Frequency distribution of allophanes and imogolite in soils and sediments has been reported (Wada, 1977, 1980; Tait *et al.*, 1978; Ross and Kodama, 1979; McKeague and Kodama, 1981; Farmer *et al.*, 1980; Anderson *et al.*, 1982). These short-range ordered aluminosilicates have large specific surface and high chemical reactivity (Wada, 1981). They have a significant effect on the physical, chemical, and biological properties of soils and sediments. Little is known of the effect of low-molecular-weight organic acids on the formation of these short-range ordered aluminosilicates (Farmer, 1981). Very recently, Inoue and Huang (1984a, 1985) reported that citric acid (molar ratio of citric acid to Al at ≤ 0.1) greatly perturbs the interactions of hydroxy Al ions with orthosilicic acid and thus hinders the formation of imogolite and allophanes.

In the presence of citric acid and at a Si/Al ratio of 0.5 and an OH/Al ratio of 1.0–2.0, protoimogolite is found in the soluble products that pass through the 0.01-μm pore-size membrane filter and are recovered by

freeze-drying the filtrates (Inoue and Huang, 1985). Protoimogolite has positive charges in the acidic condition (Farmer, 1981); therefore, protoimogolite, which is composed of < 10-nm size particles (Inoue and Huang, 1984a), apparently forms complexes with citric acid. Thus, the complexed citric acid impedes the conversion of protoimogolite to imogolite.

The SiO_2/Al_2O_3 molar ratio of the precipitates formed is greatly influenced by citric acid and decreases markedly with increasing the citric acid/Al molar ratio (Inoue and Huang, 1985). Inverseley, the organic C content, which is a measure of the amount of citrate in the precipitate, increases with an increase in the citric acid/Al molar ratio. The results clearly show that citric acid coprecipitates with aluminosilicates during their formation.

The XRD pattern of the precipitates formed in the absence of citric acid indicates that imogolite (d = 2.16, 1.51, 0.87, and 0.64 nm) (Farmer and Fraser, 1979; Wada et al., 1979) and small amounts of boehmite (d = 0.61 nm) and bayerite (d = 0.47 nm) (Hsu, 1977) are dominant in the products (Figure 13). The intensity of the XRD peaks of imogolite, however, is significantly reduced with increasing citric acid/Al ratios.

The IR spectra of the precipitates formed in the absence of citric acid (Figures 14a,d, 15a) resemble those obtained from natural imogolite. The characteristic absorption bands of imogolite at 995, 936, 700, 565, 504, 422, and 345 cm^{-1} (Wada and Harward, 1974; Wada, 1977, 1980; Farmer et al., 1977, 1979; Farmer and Fraser, 1979) are distorted or weakened with increasing citric acid/Al ratios of the parent solution (Figures 14a–c, 14d–h, 15a–c).

The IR spectra of the precipitate formed at the Si/Al molar ratio of 1.0, OH/Al molar ratio of 1.0 and citric acid/Al molar ratio of 0.02 (Figure 14c) show absorption bands at 965, 563, 424, and 342 cm^{-1}, which are very similar to those of protoimogolite (Farmer et al., 1978, 1979; Farmer and Fraser, 1979; Inoue and Huang, 1984a). Protoimogolite is, however, known to be water-soluble. Therefore, these precipitates may be termed ill-defined aluminosilicate complexes.

The IR spectra of the precipitates formed in the Si/Al molar ratio of 1.0 and the OH/Al molar ratio of 3.0 show a broad absorption maximum at 990 cm^{-1} (Figure 15d), which is a feature common to allophanic clay separated from Ando soils (Wada and Harward, 1974; Wada, 1977, 1980). With increasing citric acid/Al ratio of the parent solution from 0.01 to 0.03, however, the IR spectra of the precipitates show a gradual shift of the Si-O stretching maximum from 985 to 965 cm^{-1} (Figure 15e–h). Especially at citric acid/Al ratios of 0.1–0.3 (Figure 15g,h), highly disordered products are formed, which are obviously different from allophane precipitated from the solution in the absence of citric acid. The disordered products show a sharp absorption maximum at 965 cm^{-1} and other absorption bands at 576, 424, and 345 cm^{-1} (Figure 15g,h), which are similar to those of

Figure 13. X-ray power diffractograms of the precipitates formed from solutions containing hydroxy Al ions, orthosilicic acid, and citric acid at Si/Al molar ratio of 0.5, OH/Al molar ratio of 2.0, and citric acid/Al molar ratios of 0–0.03 (Inoue and Huang, 1985; reprinted with permission of Clay Minerals Society).

protoimogolite allophane (Farmer *et al.*, 1980; Parfitt and Henmi, 1980). "Protoimogolite" allophane samples isolated from soils and pumices in New Zealand show IR spectra similar to that of protoimogolite, but their unit particles appear to be hollow spherules or polyhedra 3.5–5.0 nm in diameter with the SiO_2/Al_2O_3 ratio close to 1.0 (Parfitt and Henmi, 1980).
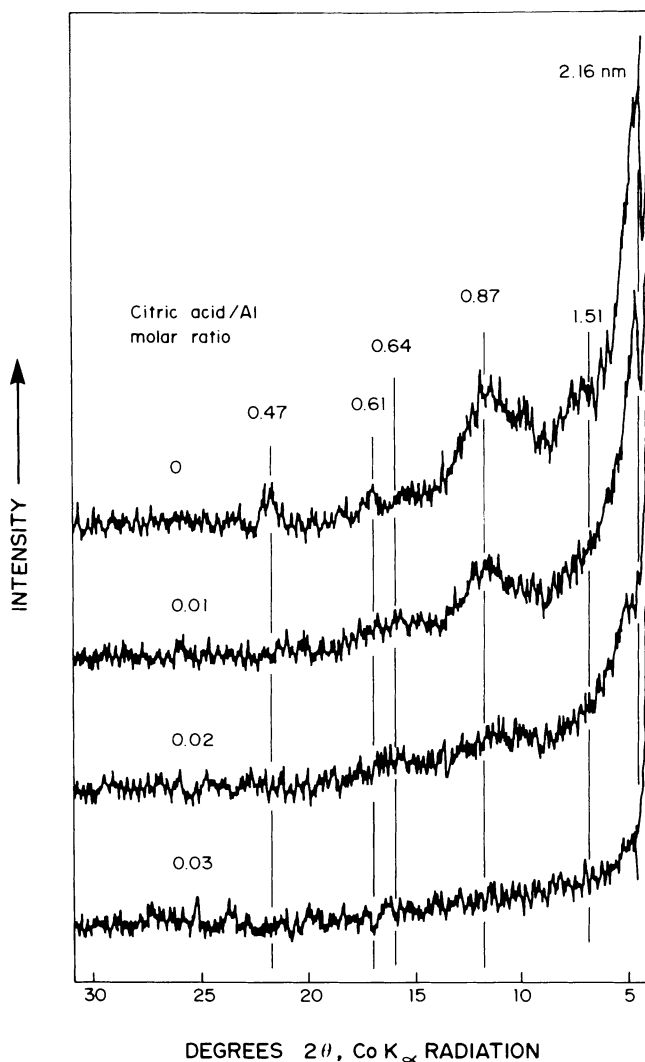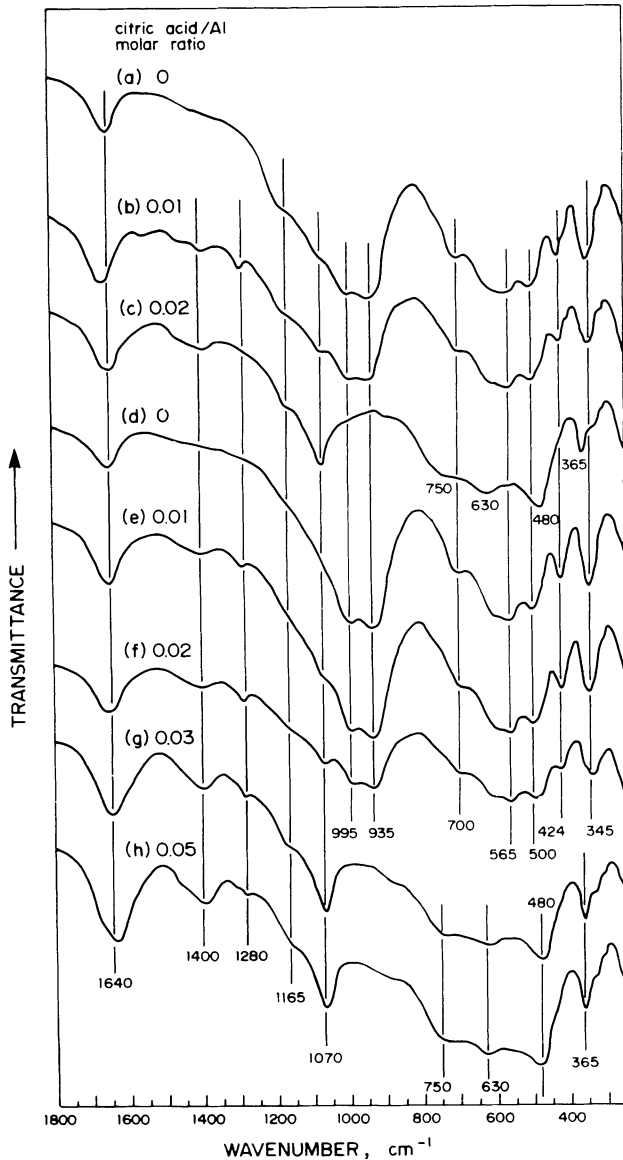
Figure 14. IR spectra of precipitates formed from solutions containing hydroxy Al ions, orthosilicic acid, and citric acid at citric acid/Al molar ratios of 0–0.05. (a–c) Si/Al molar ratio of 1.0 and OH/Al molar ratio of 1.0. (d–h) Si/Al molar ratio of 0.5 and OH/Al molar ratio of 2.0 (Inoue and Huang, 1985; reprinted with permission of Clay Minerals Society).
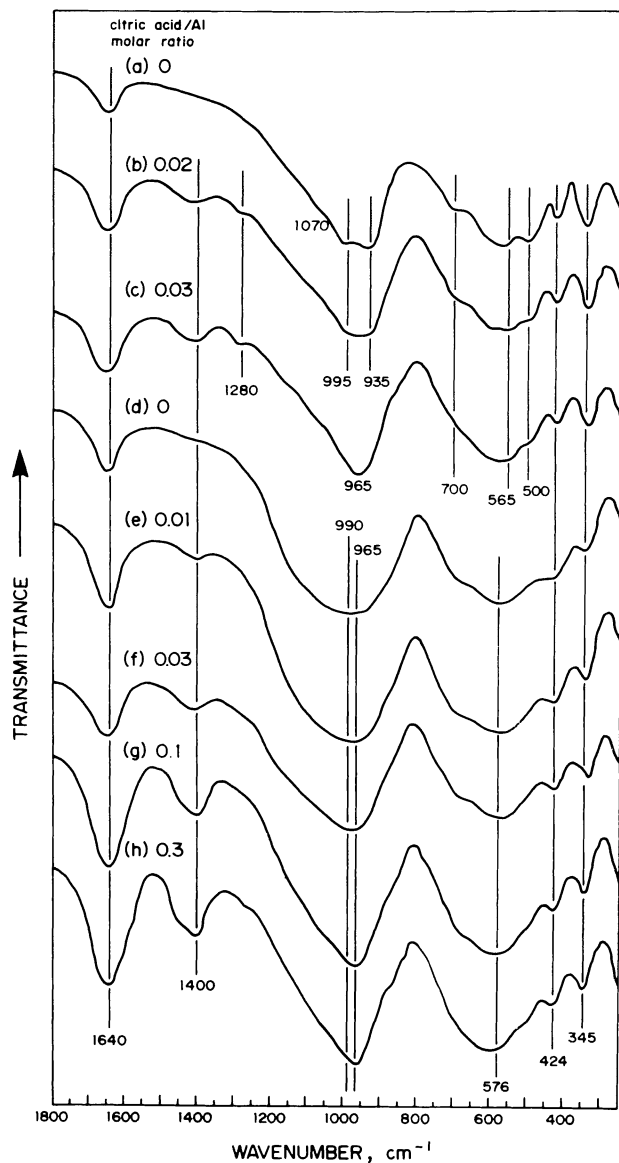
Figure 15. IR spectra of precipitates formed by reaction of hydroxy Al ions with orthosilicic acid both in the absence and presence of citric acid. (a–c) Si/Al molar ratio of 0.5 and OH/Al molar ratio of 2.8. (d–h) Si/Al molar ratio of 1.0 and OH/Al molar ratio of 3.0 (Inoue and Huang, 1985; reprinted with permission of Clay Minerals Society).

The precipitates formed by the reaction of hydroxy Al with orthosilicic acid in the presence of citric acid (Si/Al molar ratio of 1.0, OH/Al molar ratio of 2.8, citric acid/Al molar ratio of 0.1 or 0.3) are also very similar to protoimogolite in their IR spectra (Figure 15g,h). They are Al complexes of mixed ligands containing hydroxyl, citrate, and orthosilicate. The decrease of the SiO_2/Al_2O_3 ratio of the precipitates (Inoue and Huang, 1985) and the gradual shift of IR absorption maximum from 990 to 965 cm^{-1} (Figure 15g,h) seem to increase with the increase in the degree of complexation of hydroxyaluminosilicates with citrate ligands. This type of precipitates may be tentatively classified as ill-defined aluminosilicate complexes. Such groups of aluminosilicates seem to resemble the so-called allophanelike material (Wada and Greenland, 1970; Wada and Harward, 1974) and the ill-defined fraction of the allophane-imogolite complex (Farmer et al., 1983).

In the absence of citric acid, smooth and curved imogolite threads appear to be of micrometer length with the diameter of 2.0–50.0 nm (Figure 16a). A high-magnification TEM of the precipitates (Figure 16d) shows that the threads consist of fine tube units with inner and external diameters of about 1.0 and 2.0 nm, respectively. Irregular-shaped particles with different morphological characteristics and their aggregates are, however, observed in the precipitates formed at the Si/Al molar ratio of 0.5, OH/Al molar ratio of 2.0, and citric acid/Al molar ratio of 0.03 (Figure 16b), which are characterized by the predominance of disordered products with low SiO_2/Al_2O_3 ratios and pseudoboehmite.

A TEM of the precipitates formed at the OH/Al molar ratio of 2.8, Si/Al molar ratio of 0.5, and citric acid/Al molar ratio of 0.03 shows the presence of a gellike material (Figure 16c). The precipitates formed at the OH/Al molar ratio of 2.8, Si/Al molar ratio of 1.0, and citric acid/Al molar ratio of 0.02 are composed of gellike materials, very distorted imogolite tubes, and hollow spherules (Figure 16e).

Figure 17a shows a high-magnification TEM of noncrystalline precipitates formed at the OH/Al molar ratio of 3.0 and Si/Al molar ratio of 1.0 in the absence of citric acid. The presence of hollow spheres with diameters of 3.5–5.0 nm in the TEM (Figure 17a) and IR spectra of the products (Figure 15d) reveal that the noncrystalline aggregates observed in the TEM mainly consist of allophane. High-magnification TEM has shown that natural allophane in soils (Wada and Harward, 1974; Wada, 1977) and river sediments (Wells et al., 1977; Inoue et al., 1980) and synthetic allophane (Wada et al., 1979) consist of hollow spheres 3.5–5.0 nm in external diameter with walls 0.7–1.0 nm thick (Wada, 1979). The morphology of the hollow spheres is, however, markedly distorted by the presence of citric acid during their formation; only a few hollow spherules with diameters of 3.5–5.0 nm are present in the irregular aggregates (Figure 17b,c).

Organic ligands of different chelating power have varying effects on the formation of allophane and imogolite and the nature of precipitation

Figure 16. Transmission electron micrographs of precipitates formed by reaction of hydroxy Al ions with orthosilicic acid at citric acid/Al molar ratios of 0–0.03. (a) OH/Al molar ratio of 2.0, Si/Al molar ratio of 0.5, citric acid/Al molar ratio of 0. (b) OH/Al molar ratio of 2.0, Si/Al molar ratio of 0.5, citric acid/Al molar ratio of 0.03. (c) OH/Al molar ratio of 2.8, Si/Al molar ratio of 0.5, citric acid/Al molar ratio of 0.03. (d) OH/Al molar ratio of 2.0, Si/Al molar ratio of 1.0, citric acid/Al molar ratio of 0 (high magnification). (e) OH/Al molar ratio of 2.8, Si/Al molar ratio of 1.0, and citric acid/Al molar ratio of 0.02 (high magnification). Scale bar = 1μm (a–c), 50 nm (d,e) (Inoue and Huang, 1985; reprinted with permission of Clay Minerals Society).
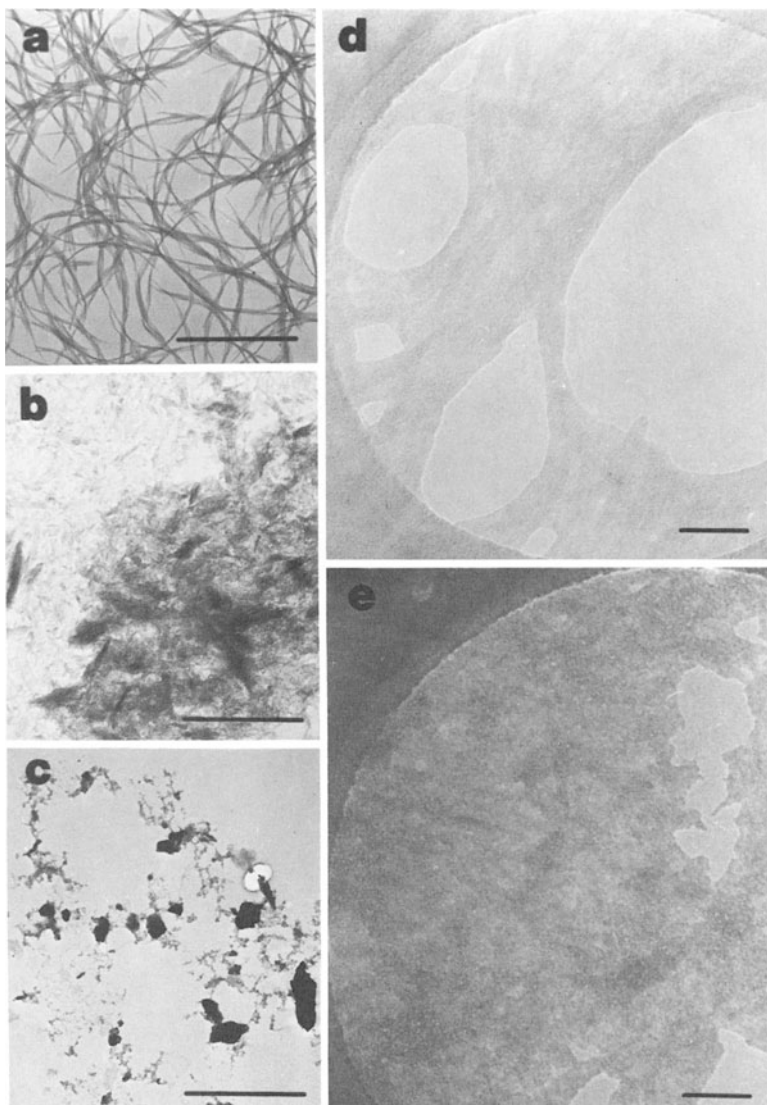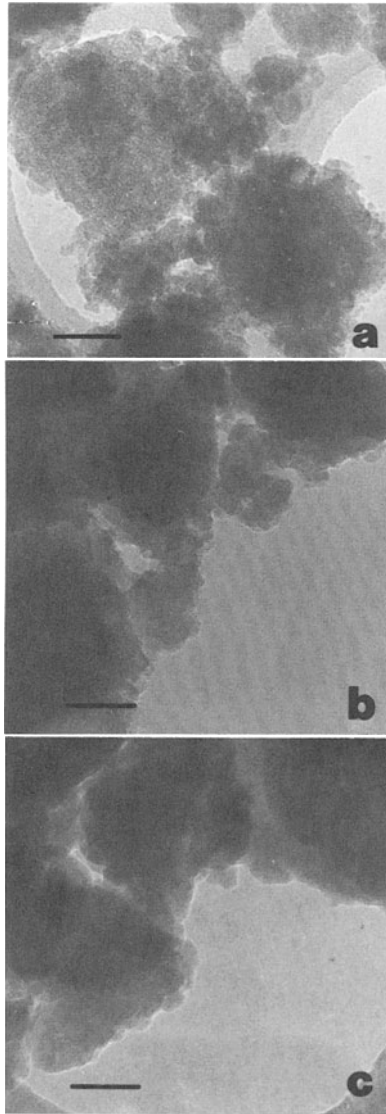
Figure 17. Transmission electron micrographs of precipitates formed by the reaction of hydroxy Al ions with orthosilicic acid at Si/Al molar ratio of 1.0 and OH/Al molar ratio of 3.0 in both the absence and presence of citric acid. (a) OH/Al molar ratio of 3.0, Si/Al molar ratio of 1.0, citric acid/Al molar ratio of 0. (b) OH/Al molar ratio of 3.0, Si/Al molar ratio of 1.0, citric acid/Al molar ratio of 0.1. (c) OH/Al molar ratio of 3.0, Si/Al molar ratio of 1.0, citric acid/Al molar ratio of 0.3. Scale bar = 50 nm (Inoue and Huang, 1985; reprinted with permission of Clay Minerals Society).

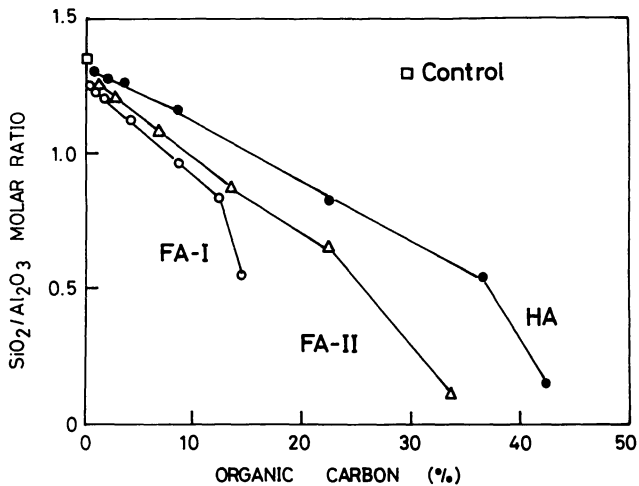**Figure 18.** Relationship between SiO_2/Al_2O_3 molar ratios and organic carbon content of precipitates formed from solutions containing hydroxy Al ions, orthosilicic acid, and humic substances (Inoue and Huang, 1987; reprinted with permission of Clay Minerals Society).

(> 0.01 μm) and soluble (< 0.01 μm) products (Inoue and Huang, 1986). Chemical composition, size, number, and nature of the functional groups and concentration of organic ligands have a bearing on the perturbation of the formation of short-range ordered aluminosilicates. The order of effectiveness of organic ligands studied is tannic $\gg$ DL-tartaric $>$ citric $>$ DL-malic $\gg$ salicylic $>$ DL-aspartic $\geq$ p-hydroxybenzoic. Organic acids with a strong affinity for Al greatly perturb the interaction of hydroxy-Al ions with orthosilicic acid and thus retard or even inhibit the subsequent formation of allophane and imogolite.

More recent studies (Inoue and Huang, 1984b, 1987) show that FAs and HAs can also greatly perturb the genesis of allophane and imogolite. The SiO_2/Al_2O_3 ratio of the precipitates decreases with increasing organic C carbon (Figure 18). The strong competition of such humic substances with orthosilicic acid for the coordination sites of Al is considered to account for the marked impedance of the humic substances on the formation of allophane. The IR spectrum of the precipitates formed in the absence of humic substances (Figure 19a) gave strong absorption maxima at 1633, 988, and 570 cm^{-1} and weak absorption bands at 424 and 345 cm^{-1}. These bands are common to soil allophane (Wada and Harward, 1974; Wada, 1977, 1980). At increasing concentrations of humic substances, however, the absorption maxima of the Si-O stretching band at 900–1000 cm^{-1} shifted gradually from 988 to 944 cm^{-1} (Figure 19b–d) and from 983 to 964 cm^{-1} (Figure 19f–i), and their intensities all weakened (Figure 19). The IR bands (972–944, 569–554, 424, and 345 cm^{-1}) of the precipitates formed in
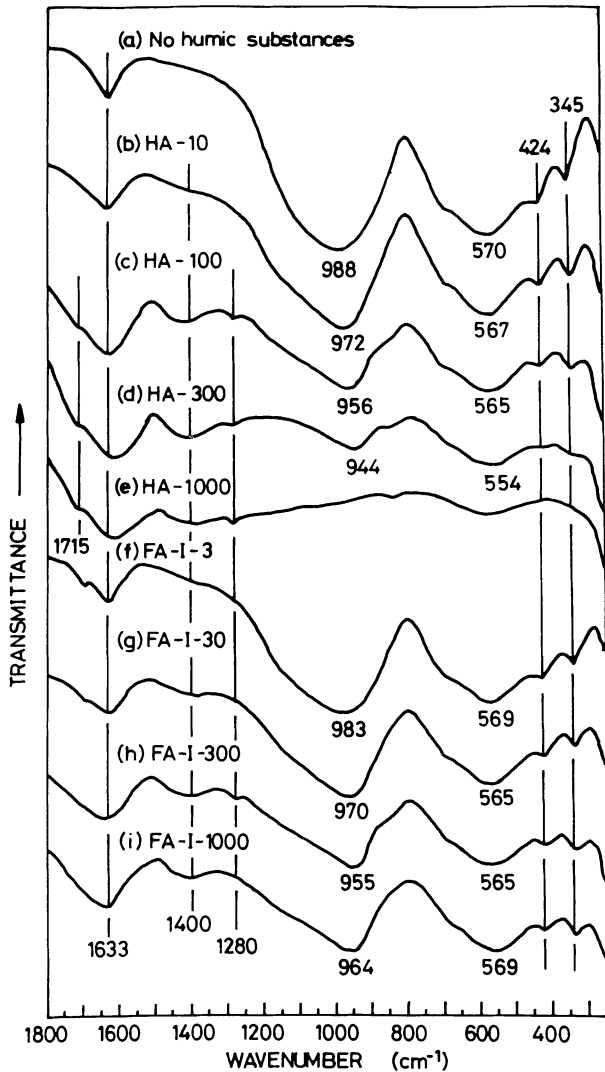
Figure 19. Infrared spectra of precipitation products (> 0.01 μm) formed by reaction of hydroxy Al ions with orthosilicic acid in both the absence and presence of humic substances: (a) no humic substances; (b) humic acid, 10 mg/L; (c) humic acid, 100 mg/L; (d) humic acid, 300 mg/L, (e) humic acid, 1000 mg/L; (f) fulvic acid-I, 3 mg/L; (g) fulvic acid-I, 30 mg/L; (h) fulvic acid-I, 300 mg/L; and (i) fulvic acid-I, 1000 mg/L (Inoue and Huang, 1987; reprinted with permission of Clay Minerals Society).

the presence of humic substances (Figure 19) were similar to those of the "allophanelike constituents" of Wada and Harward (1974) and Wada (1977, 1980) and to the "protoimogolite" allophane of Parfitt and Henmi (1980) and Farmer et al. (1980). HA at a concentration of 1000 mg/L almost completely inhibited the formation of allophanes or even of "allophane-like" materials or "protoimogolite" allophane and resulted in the formation of hydroxy-Al-humate complexes (Figure 19e). FA-I at a concentration of 1000 mg/L did not completely perturb the interaction of hydroxy Al ions with orthosilicic acid, but led to the formation of "protoimogolite" allophane (Figure 19i) complexed with FA. FA-II at the same concentration inhibited the formation of even "protoimogolite" allophane (not shown).

The accumulation of humus in the Dystrandept A_1 horizon may favor the formation of opaline silica, if the supply of silica is plentiful, and may retard the formation of "allophanelike" constituents, allophane, and imogolite, particularly the last two (Shoji and Masui, 1972; Tokashiki and Wada, 1975; Wada and Higashi, 1976; Higashi and Wada, 1977). The formation of imogolite from the solutions containing hydroxy Al ions and orthosilicic acid was strongly perturbed by humic substances (Inoue and Huang, 1984b). The data obtained by Inoue and Huang (1987) show that humic substances inhibit the formation of allophane, leading to the formation of hydroxy-Al-humic substances complexes and/or "protoimogolite" allophane. Al released from parent volcanic ash by weathering is strongly bound to humic substances, which limits the coprecipitation of Si and Al (Wada and Higiashi, 1976; Higashi and Wada, 1977) The findings of Inoue and Huang (1984a,b, 1985, 1987) substantiate the hypothesis that the accumulation of humus in the Dystrandepts A_1 and Spodosol A_2 and B_h horizons favors the formation of hydroxy-Al-humus complexes, "allophanelike" constituents, and/or opaline silica and may retard the formation of allophane and imogolite, which are formed in the Dystrandept B and (B) and Spodosol B_s horizons (Wada and Higashi, 1976; Higashi and Wada, 1977; Farmer et al., 1980, 1983; Farmer, 1981, 1984; Anderson et al., 1982).

VII. Impact of Aluminum Transformations on Soil and Environmental Sciences

Aluminum transformations have an enormous impact on soil and environmental sciences and human health, as summarized in Figure 20 and discussed below.

A. Weathering Reactions of Soil Minerals

Aluminum released to soil solution through chemical weathering of minerals can be adsorbed by interlayers of 2:1 expansible clay minerals (Jackson,
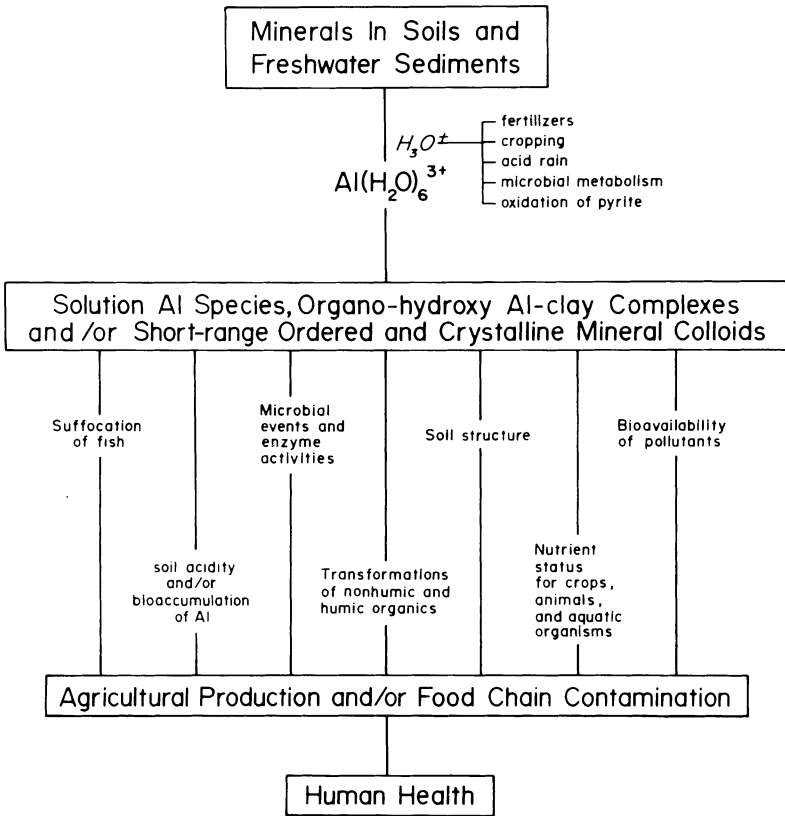
Figure 20. Impact of environmental Al chemistry on human health (Huang, 1987b; reprinted with permission of Soil Science Society of America).

1963b; Rich, 1968) or external surfaces of phyllosilicates (Huang and Kozak, 1970) or transformed to aluminum hydroxide polymorphs (Hsu, 1977) and short-range ordered precipitation products of aluminum (Huang and Violante, 1986). Among the three polymorphs of aluminum hydroxides, only gibbsite is common in soils (Hsu, 1977), and nordstrandite was found in some soils (Wall *et al.*, 1962).

Hydroxy-interlayered smectite and vermiculite occur in soils as a product of weathering reactions. These minerals may result from degradation of chlorite or deposition of hydroxy materials in the interlayers of expansible phyllosilicates. Pearson and Ensminger (1949), MacEwan (1950), Brown (1953), and Rich and Obenshain (1955) reported the presence of a 1.4-nm soil mineral that has properties similar to chlorite at room temperature. However, the 1.4-nm peak shifted toward a diffuse 1.0-nm d-spacing when the mineral was heated. Therefore, hydroxy-interlayered minerals

do not fit the properties of either chlorite or vermiculite and smectite. Geographical distribution of this type of minerals is wide. They may occur in the soils of several soil taxonomic orders (Soil Survey Staff, 1975). The frequency of their occurrence is greatest in the Ultisols and the Alfisols. Hydroxy Al interlayering is frequently greatest in the surface horizon and decreases with depth. Frequency distribution and occurrence of Al-interlayered minerals in soils and sediments throughout the world have been reviewed by Rich (1968), Barnhisel (1977), and Bertsch and Barnhisel (1987).

B. Soil Physical Properties

Polynuclear Al species are known to exert important influences on soil physical properties. The swelling of Na montmorillonite is reduced by the formation of hydroxy Al and Fe interlayers (El Rayah and Rowell, 1973). Swelling is reduced to a greater extent with polynuclear Al species than with polynuclear Fe species. The removal of hydroxy interlayer materials has resulted in increased swelling of clays (Tamura, 1957). The tensile strength, liquid limit, shear-stress, and shrinking-swelling properties of montmorillonite clay systems may be significantly altered by hydroxy inter-layering and the accompanying changes in cation saturation (Dowdy and Larson, 1971; Gray and Schlocker, 1969; Davey and Low, 1971; Kidder and Reed, 1972).

   The amount of sesquioxides extracted from a well-aggregated fraction of several prairie soils was considerably greater than that extracted from the poorly aggregated fraction (Weldon and Hide, 1942). Stable aggregates are heavily coated with aluminum and iron oxides, and the removal of these oxides destroys the aggregates (Kroth and Page, 1947). Saini et al. (1966) reported that the partial regression coefficient relating aluminum "oxides" with aggregation is 1.84 times as large as that for iron oxides. Jones and Uehara (1973) showed the presence of amorphous gel hull linkage between clay particles. Such amorphous gel hull is bound to include short-range ordered precipitation products of aluminum. El Swaify and Emerson (1975) reported the presence of aluminum hydroxide as a thin layer around illite particles. It is evident that sesquioxides act as cementing agents in the formation of aggregates. Aluminum hydroxides are more effective than iron oxides in maintaining the stability of soil aggregates except in fre-quently alternating oxidized and reduced soils. Well-crystallized alumi-num hydroxide may also act as a cementing agent in acidic conditions, but it may be negligible in its magnitude compared with short-range ordered precipitation products of aluminum. It has been suggested that organic matter may promote soil aggregation through the following linkage: clay–(Al, Fe)–organic matter–(Al, Fe)–clay (Edwards and Bremmer, 1967). Figure 21 shows an ultrathin section of a surface aggregate from a clay soil, cut next to a grass root (Emerson et al., 1986). The pores between the
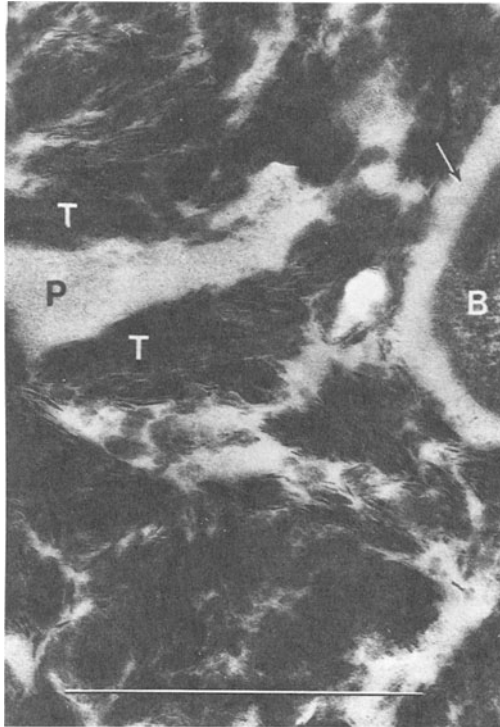
Figure 21. Ultrathin section of a surface soil treated with gluteraldehyde-La(OH)$_3$/O$_s$O$_4$ from a Wiesenboden (pellustert), a clay soil. Tactoids (T) are clearly visible with the intervening pores filled with acidic polysaccharides (P). A bacterium (B) is surrounded by extracellular polysaccharides (ECP) (arrow). Bar = 1μm (Emerson *et al.*, 1986; reprinted with permission of Soil Science Society of America).

tactoids are completely filled with a gel that consists of carbohydrate containing uronic acid groups. Aluminum ions may bridge uronic acid groups in the bonding polysaccharides.

C. Soil Acidity and Liming

Aluminum is released from soil minerals by chemical and biochemical weathering reactions. The hydrolysis and polymerization of Al release protons, leading to acidification of the environment. Released protons attack Al-bearing minerals, resulting in the dissolution of Al. The dissolved Al undergoes hydrolytic reactions and releases protons to soil solutions and natural waters. Therefore, generation of protons is perpetuated. Furthermore, this proton generation process can be accelerated by the presence of silica relics (pK$_1$ of Si(OH)$_4$ is 9.8) of silicates as a "proton sink." Con-

sequently, the weathering of Al-bearing minerals, which can be enhanced by leaching, natural vegetation, farming, and other anthropogenic activities, would lead to acidification of soils and the associated environments. The hydroxy Al polymers adsorbed on the surfaces of soil minerals are important sources of soil acidity and are termed "third buffer range" acidity (Schwertmann and Jackson, 1963), pH-dependent, or titratable acidity (Clark, 1964; Colemen and Thomas, 1964; De Villiers and Jackson, 1967b). More recent data show that besides hydroxy Al polymers, organic acids that are chelated with the adsorbed Al in interlayers of clays can very substantially contribute to the total and titratable acidity (Goh and Huang, 1985). Furthermore, Al released from soil minerals may complex with a series of inorganic ligands, low-molecular-weight organic acids, and humic substances and form discrete colloidal precipitates in a wide range of particle size fractions of soils (Huang, 1980).

The interaction of the Al released into the soil solution with a series of organic components greatly modifies the nature of soil acidity. An increase in the contents of organic matter of soils results in a decrease in the levels of exchangeable Al and exchangeable acidity (McLean et al., 1965; Poinke and Corey, 1967; Thomas, 1975; Hoyt and Turner, 1975; Hoyt, 1977; Hargrove and Thomas, 1981). On the other hand, the contents of soil organic matter are positively correlated with the levels of titratable Al and acidity (Hoyt, 1977; Curtin et al., 1984). Aluminum is hydrolyzed to a great extent at low pH in the presence of organic matter, because the hydrolytic products react with carboxyl groups more intensively than with clays, and because the organic matter serves as a sink for H^+ ions produced by hydrolysis (Thomas and Hargrove, 1984).

Salt addition to sesquioxide-coated 2:1 expansible minerals appears to increase the hydrolysis of nonexchangeable Al (or Fe), resulting in an increase in H^+ ion concentration of the solution and to lower the pH (Coleman et al., 1964). Extensive hydrolysis of nonexchangeable Al occurred during the extraction of soils with neutral unbuffered salts (Kissel et al., 1971). Furthermore, the proportion of hydroxy Al that hydrolyzed was related to the stability of the hydroxy Al interlayers.

Titratable acidity arises from dissociation of weak-acid functional groups of soil organic matter (Hoyt, 1977) and deprotonation from hydroxy Al polymers associated with the internal (De Villiers and Jackson, 1967b) and external (Huang and Kozak, 1970) surfaces of phyllosilicate minerals, from short-range ordered aluminosilicate (allophanic) materials (Wada, 1977), and from ruptured surfaces of oxides and silicates (Huang, 1980). As liming programs are commonly designed to raise pH to 6.5–6.8 (Shoemaker et al., 1961), both the exchangeable and titratable components of acidity must be taken into account in assessing the lime needs of soils. Curtin et al. (1984) reported that KCl-exchangeable acidity was very low (0.3–2.2 mmol(+) · kg^{-1}) in a group of 20 Saskatchewan soils (pH 5.0–5.8). Titratable acidity ranged from 9 to 191 mmol(+) · kg^{-1} and constituted about

99% of the total acidity in the soils examined. Titratable acidity was highly correlated with organic carbon (r = 0.83) and with Al extracted using citrate-dithionite-bicarbonate (r = 0.95), potassium pyrophosphate (r = 0.92), and pH 4.8 ammonium acetate (r = 0.79). The combination of organic carbon and citrate-dithionite-bicarbonate extractable Al accounted for 96% of the variation in titratable acidity.

D. Formation of Humic Substances, Dynamics of Natural Organics and Enzymes, and Microbial Events

Alumina has catalytic effects on the formation of humic substances. In a respirometer experiment with clay minerals, the amounts of Al in the citrate-bicarbonate-dithionite extracts are proportional to the reduction of O_2 uptake after the treatment (Wang et al., 1978). The yields of humic substances formed from the catechol are significantly greater in the presence of aluminum oxides than in the blank (Wang et al., 1986). The Al on edges of kaolinite and short-range ordered aluminum oxides has the ability to catalyze the formation of humic substances from hydroquinone or pyrogallol (Wang and Huang, 1986, 1987).

The humic colloids in allophanic soils are believed to be stabilized by complexing with active Al groups or aluminum and iron oxides associated with allophane surfaces (Wada and Higashi, 1976). The greater stabilization of organic matter is related to a stronger interaction of active functional groups of organic colloids with allophane surfaces. The interaction may be direct adsorption to positive sites of allophanes or, more likely, to the formation of humus-Al, Fe, or Al, and Fe-allophane complexes.

The rate of the loss of C as CO_2 is slower from allophanic soils than from nonallophanic soils (Broadbent et al., 1964; Ino and Monsi, 1964; Jackman, 1964; Martin and Haider, 1986). Martin et al. (1982) followed the release of C as CO_2 over a 1-year period from a number of allophanic soils of southern Chile and the release from normal soils of California and Chile. Losses of C range from 143 to 243 mg/100 g^{-1} soil from nonallophanic soils containing about 16–26 g/kg^{-1} organic matter. Comparable losses from allophanic soils containing about 88–161 g/kg^{-1} organic matter range from 92 to 191 mg.

The C loss from a wide variety of ^{14}C-labeled readily degradable organic substrates in normal agricultural soils of California and Chile and allophanic soils of southern Chile was studied by Zunino et al. (1982). Over a 16-week incubation period, the presence of allophane in the soil or the addition of 50–160 g/kg^{-1} allophane to a very sandy soil reduced C losses by 16–73%. The least reduction occurred with glucose and the greatest with a bacterial polysaccharide in allophanic subsoil (Table 13). The losses of C from additions of more resistant polymer substrates such as plant lignins and fungal melanins are reduced to a much greater extent in the allophanic soils than losses in the normal agricultural soils. Influence of

Table 13. Decomposition of some ^{14}C-labeled organic substrates in the presence and absence of allophane clay

	Percentage of added ^{14}C evolved as ^{14}CO$_2$ in 16 weeks						
Soil	Glucose	Polysaccharides	Wheat straw	*Chloella* protein	*Mucor* cells	Corn stalk lignin	*Aspergillus glaucus* melanin
Nonallophanic soils	77	75	60	67	55	17	5
Sandy loam + 16% allophane	58	56	37	41	36	—	—
Allophanic topsoils	56	44	34	38	39	4	2
Allophanic subsoil	56	21	25	26	34	—	—

Source: Compiled by Martin and Haider (1986) from the data of Martin *et al*. (1982) and Zunino *et al*. (1982).

aluminum-bearing minerals on the transformations of soil organic components through abiotic and biotic processes merits close attention.

The study of the interaction of enzymes with soil inorganic constituents has been mainly concerned with crystalline clay minerals (Burns, 1986). Ross (1983) reported that the original activities of α-amylase, β-amylase, and invertase were decreased by the presence of allophane to 57%, 12%, and 20%, respectively. The role of short-range ordered Al-bearing mineral colloids in influencing enzyme activities should receive more attention.

More recent evidence indicates that the utilization of organics by microbes seems to be modified when bound on metal oxide–coated clays, compared with clays homoionic to nonpolymeric cations (Stotzky, 1986). As the surface properties of these metal oxides vary with pH and ionic factors, the release of such bound organics may occur as the pH and ionic environments of natural microhabitats fluctuate. Once the organics have been released from the hydrous metal oxide–mineral complexes, they could be either degraded by soil microbes or complexed by mineral colloids. The role of short-range ordered Al hydrous oxides in the dynamics of transformations of organic compounds and in the ecology of microbes thus deserves increasing attention.

E. Transformations of Nutrients and Toxic Pollutants

Aluminum-bearing components in terrestrial and aquatic environments play a vital role in the transformations of nutrients and toxic substances, as stated below.

1. Nitrogen

a. Nitrate

Nitrate is weakly adsorbed on aluminum hydroxides by electrostatic attraction. Therefore nitrate can only be adsorbed by positively charged surfaces and is loosely held in the diffuse layer except in completely dehydrated systems. In most cases, nitrate is leached quite readily from soils and is held more weakly than chloride (Parfitt, 1978). Leached nitrate can be transported to aquatic environment. Soils such as volcanic ash soils that have positive sites on allophane retain nitrate more strongly than other soils and are thus able to prevent rapid leaching of nitrate.

b. Ammonium

Ammonium ions can be adsorbed on the negatively charged surfaces of Al components of soils and sediments. Furthermore, the adsorption of NH_4^+ ions by expansible phyllosilicates could also be affected by the deposition of hydroxy Al polymers on the interlamellar surfaces of the minerals (Huang, 1980).

c. Organic Nitrogen Compounds

Nitrogenous organic compounds (e.g., aspartic acid) can be adsorbed or coprecipitated with hydroxy Al compounds (Kwong and Huang, 1981). Such reactions could affect the transformations of nitrogen in the environment.

2. Phosphorus

Most research data show that phosphate adsorption is better associated with extractable Al than with iron (Parfitt, 1978). The affinity of phosphate for Al ions is strong enough to remove OH from an edge $Al \cdot OH$. This type of reaction is referred to as a ligand exchange reaction. Phosphate can be adsorbed at the point of zero change (PZC) or on its alkaline side (Hsu, 1977). Ligand exchange reactions occur rapidly between exposed $Al \cdot OH$ groups and phosphate in solution. During the processes of weathering reactions, fresh aluminum hydroxide is continuously added to the system. The adsorbed phosphate may be occluded and become unavailable to plants if it is coated with another layer of aluminum hydroxides.

In the immediate vicinity of phosphate fertilizer particles, there are local conditions of low pH and high phosphate concentration, which may cause dissolution of clays and precipitation of aluminum phosphate. Basic aluminum phosphates may form in acid soils even at low phosphate concentrations. Formation of taranakite was observed by reaction of Al hydroxide with concentrated K^+ or NH_4^+ phosphate solution, but these compounds hydrolyzed to noncrystalline aluminum phosphate upon dilution and are slow-releasing phosphate sources rather than products of fixation.

Organic acids promote the formation and stability of short-range ordered precipitation products of Al with an accompanying high specific surface and thus help to maintain their high phosphate retention capacities (Kwong and Huang, 1979c). Nevertheless, organic acids above certain concentrations also promote aggregation of the precipitates (Kwong and Huang, 1979c; Violante and Huang, 1984). The relative influence of the exposure of surfaces as a result of structural distortion of precipitation products of Al and their aggregation caused by organic acids on the adsorption of anions merits further attention.

3. Potassium

Potassium ions can be specifically adsorbed by vermiculitic minerals, because the K^+ ion has a crystalline radius compatible to the size of adsorption sites. The selectivity of K^+ ions by vermiculite is increased by the deposition of hydroxy Al polymers on the interlamellar surfaces of the minerals. The mechanisms of the effect of hydroxy Al interlayer on the K/Ca exchange selectivity may proceed through (1) propping effect, (2) preferential occupation of Ca adsorbing sites, and (3) retarding effect on the entry of the more hydrated Ca ions (Figure 22). Propping effect would
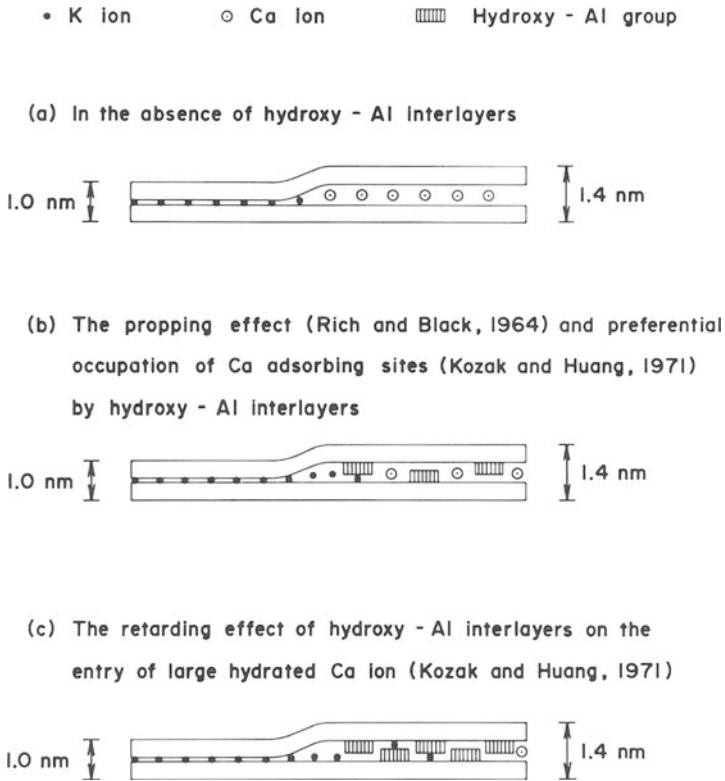
• K ion   ○ Ca Ion   ▥ Hydroxy - Al group

(a) In the absence of hydroxy - Al interlayers

1.0 nm   1.4 nm

(b) The propping effect (Rich and Black, 1964) and preferential

occupation of Ca adsorbing sites (Kozak and Huang, 1971)

by hydroxy - Al interlayers

1.0 nm   1.4 nm

(c) The retarding effect of hydroxy - Al interlayers on the

entry of large hydrated Ca ion (Kozak and Huang, 1971)

1.0 nm   1.4 nm

Figure 22. Structural models of the mechanisms of the effects of hydroxy Al inter-layers on the K/Ca exchange selectivity of 2:1 phyllosilicates which have wedge zones and rather limited interlayer expansibility (Huang, 1987a; reprinted with permission of Pergamon Books Ltd.).

prevent K fixation and increase K selectivity by permitting its entry to ver-miculite and weathered mica. Potassium ions are thus selected at wedge sites, whereas large hydrated ions such as Ca and Mg are excluded. The preferential occupation by hydroxy Al on exchange sites that normally would adsorb the more hydrated Ca ion would result in the concentration of K-retaining sites in interlayers. The hydroxy interlayers also create a retarding effect on the entry of the more hydrated Ca ions, thus effectively increasing the selectivity of the minerals toward the less hydrated K ions. The formation of hydroxy Al–clay complexes would thus affect the trans-formations of K^+ ions in the environment.

4. Sulfur

Soils with large amounts of hydrous oxides of Al and Fe retain substantial amounts of sulfate (Parfitt, 1978). Therefore, tropical soils and volcanic

ash soils strongly adsorbed sulfate. Sulfate adsorption has been shown to be correlated with extractable Al rather than Fe, although both hydrous Al and Fe oxides strongly adsorb sulfate.

Aluminum is more important than Fe in sulfate adsorption near to the saturation level. Loesses of sulfate by leaching are more significant in soils that are low in hydrous oxides of Al and Fe.

The mechanism of ligand exchange of $Al \cdot OH_2$ or $Al \cdot OH$ groups by sulfate ions can take place only on the acidic side of PZC (Hsu, 1977). The adsorption of sulfate by Al hydroxides greatly increases with decreasing pH.

5. Alkaline Earth and Heavy Metals

Alkaline earth (Ca, Mg, Ba) and heavy metals (Cu, Zn, Mn, Fe, Ni, Cr, Hg, Cd, Pb, Sn, U, V, Co, Ag) either are essential elements to plant growth and animal and human nutrition or are toxic environmental pollutants (Underwood, 1977).

Hydrous oxides of Al specifically adsorb alkaline earth metals such as Ba, Ca, Sr, and Mg and heavy metals such as Cu, Zn, Mn, and Hg (Huang, 1980; Kinniburgh and Jackson, 1981). Compared with aged oxides, fresh oxides have a much higher adsorptive capacity for Zn. Generally, Zn adsorption capacity is directly related to cation exchange capacity of clays and hydrous oxides. The surface reactivity of hydrous oxides of Al toward Ca is greatly enhanced by the presence of low-molecular-weight organic acids commonly present in soils during the formation of these oxides (Kwong and Huang, 1979c). Many organic acids prevalent in terrestrial and aquatic environments are very effective in perturbing the hydrolytic reaction of Al and promoting the formation of short-range ordered Al oxides. The influence of these organic acids on the surface reactivity of Al oxides toward alkaline earth and heavy metals warrants further studies.

6. Arsenic

Arsenic (V) is probably the dominant oxidation state of As in soils (Davies, 1980) and sediments. The adsorption of arsenate by soils and sediments is controlled largely by the hydrous oxides of Al and Fe. Arsenate could be desorbed from soils by leaching with phosphate, indicating that arsenate, like phosphate, is adsorbed on hydrous oxides by a ligand exchange mechanism.

7. Selenium

Selenites represent the most important form of Se in many soils (Davies, 1980). Selenite is immobilized by sesquioxides in acid soils, and its leaching is increased by additions of sulfate. This indicates that both selenite and sulfate are adsorbed on the same sites.

8. Boron

Much adsorption of B is attributed to hydroxy Al and Fe compounds present as coatings on surfaces of clays (Barber, 1984). Boron retention by Al compounds is far greater than that effected by analogous iron structures. Maximum adsorption of B by soils is observed at pH 9, which is close to the pK value of the formation of $B(OH)_4^-$ from $B(OH)_3$.

9. Molybdenum

Molybdate is adsorbed on surfaces of Al and Fe oxides by a ligand exchange reaction with exposed $Al \cdot OH$ and $Fe \cdot OH$ groups (Parfitt, 1978). The adsorption of molybdate increases from low pH values to a maximum at pH 4. Molybdate adsorption on different soils paralleled phosphate and sulfate adsorption.

10. Fluorine, Chlorine, Iodine

The reaction of fluoride with Al oxides and Al-bearing clay minerals involves the release of OH to solution. At low concentrations, the mechanism appears to involve exchange with the OH of Al hydroxides. At high concentrations, the complexation and release of Al is the mechanism of the reaction (Huang and Jackson, 1965).

Iodide is adsorbed by Al and Fe hydroxides. Sorption of I^- on sesquioxides is important only at pH < 6.

Chloride is adsorbed by electrostatic attraction to $Al \cdot OH_2^{0.5+}$ sites that occur at low pH (Parfitt, 1978). Adsorbed Cl^- is exchangeable with NO_3^- and could be desorbed by leaching with water.

11. Pesticides

Hydrous oxides of Al and noncrystalline aluminosilicates, allophane, have large surface areas. These materials carry both positive and negative charges on their surfaces. The interaction of cationic and anionic pesticides with such materials (Green, 1974) merits further study. Besides ionic pesticides, nonionic compounds that are organic bases such as *s*-triazine, when protonated, can be adsorbed by soil colloids. The proton-donating capability of clay surfaces is significantly enhanced when Al^{3+} is the saturating cation. The role of Al and its oxides in the adsorption and persistence of *s*-triazine herbicides such as atrazine (Huang *et al.*, 1984) has been demonstrated. Short-range ordered oxides of Al and Fe present in a series of particle size fractions of soils deserve close attention in defining soil components governing the degree of adsorptivity of pesticides by soils.

F. Ecological and Health Effects

The extent of the release of Al from minerals through acidification of the environment has increased with time, population growth, intensification of

agriculture, and industrialization. The Al^{3+} ion of soils damages the roots of some common crops such as barley and corn (*Zea mays*). The sensitivity of wheat to Al is conditioned by a single recessive gene. The effects of Al are a result of an interference in DNA replication in cell division, and the uptake by plants is usually excluded metabolically (Clarkson, 1969). With some crop plants, the accumulation of Al is mainly kept in the roots, with relatively little transported to the above-ground portions. Some plants develop resistance to Al intake and toxicity through Al chelation, precipitation, and other adaptations, and thus Al is forwarded upward into the food chain. Aluminum accumulator food plants include tea (*Thea sinensis* L.), spices such as oregano, and asparagus (*Asparagus officinalis*). It appears important to lower plant-available Al^{3+} in agricultural soils by the addition of ground limestone, with the provision of adequate supplies of Mg. Aluminum availability to some plants is repressed as the soil pH is raised up to pH 6.5 in some regions. This practice affords some protection of plants and animals from the toxicity of excess Al. Adequately liming acid soils thus provides an ecology of health on land.

Acid rains increase Al^{3+} levels in lake waters through the interaction of protons with Al-bearing minerals in suspended and bottom sediments. The enhanced Al^{3+} levels in lake waters cause Al gel accumulation in the neutral gills of fish, and suffocation results (Cronan and Schofield, 1979). Information concerning the toxicity of Al compounds of freshwater fish can be summarized in three categories: (1) lethal concentrations and causes of mortality, (2) subchronic concentrations and their effects, and (3) genotoxic or embryotoxic concentrations and their effects. The ecological effects of Al compounds on freshwater fish were thoroughly reviewed by Burrows (1977).

The human body burden is normally only 30 mg of Al (Alfrey, 1980). Yet the daily intake and excretion varies from 20 to 40 mg of Al in different countries (Underwood, 1977). Effective mechanisms for exclusion of Al and its potential toxicity from the normal human body evidently exist.

Acid soil–related diseases of the central nervous systems, however, have been identified in Guam and Japan (Yase, 1980). High levels of acid soil Al^{3+} and food Al^{3+} together with low Mg/Ca ratios are associated with amyotrophic lateral sclerosis (ALS) and Parkinsonism dementia (PD), with Al-enriched hydroxyapatite deposits in the spinal nerve region and brain of ALS/PD cases. The Al^{3+} of acid soils is particularly damaging in the food chain if Mg is not adequate in supply to maintain its function in animal hexokinase or "ATPase" necessary for glucose energy release. The Al-induced metabolic aberrations interfere with phosphorylation of sugars and impair P translocation (Underwood, 1977). Replacement of Mg^{2+} from hexokinase by Al^{3+} may cause potentially lethal "grass tetany" in cattle.

Water that receives Al treatment to lower its F content, when used in kidney dialysis, induced encephalopathology. Nondispersive X-ray

spectroscopic analysis of the amyloid plaques of the hippocampus portion of brain associated with human senile dementia of the Alzheimer type reveals a high Al concentration with some Si and Mg.

Aluminum ions react with various inorganic and organic constituents common in soils and the associated environments (Huang and Violante, 1986). However, insufficient information is available with respect to Al speciation relative to absorption, transport, distribution, storage, excretion, and metabolic interaction in any living system. Problems involving identification of a variety of aluminum species and characterization of their chemical and biological effects merit further research.

VIII. Summary and Conclusions

Aluminum is released from Al-bearing minerals to soil solutions and natural waters through the action of protons and complexing ions during chemical and biochemical weathering processes. The release of Al from mineral structure to soil solutions and natural waters leads to the hydrolysis and/or polymerization of Al and the subsequent formation of a series of solution Al species, organohydroxy Al–clay complexes, Al hydroxides and oxyhydroxides, and ill-defined short-range ordered mineral colloids.

Clay minerals can be considered as solid-state ions, and their particle size and structural and surface properties have an enormous influence on Al transformations. The ability of 2:1 expansible clays to fix polynuclear Al has been proposed as a reason for the absence of gibbsite in temperate soils. In addition to the formation of Al interlayered clays displaying a stable 1.4-nm d-spacing, direct magic-angle spinning NMR evidence indicates that Al_{13} polynuclear can be deposited in the interlayer space of the 2:1 clay minerals with a stable 1.8-nm d-spacing. However, the clay properties that affect the formation of Al_{13} interlayers remain obscure. Little is known about the mechanisms of the polymerization reactions of Al at the mineral water interface and their importance to the formation of polynuclear species in soils.

The nature and concentrations of inorganic ligands play an important role in influencing the hydrolysis and polymerization of Al. With anions that do not have strong affinity for Al, polynuclear Al ions continue to hydrolyze and polymerize unless a high concentration of the counteranion is present. In the presence of inorganic ligands that have strong affinity for Al, the further hydrolysis of polynuclear Al species is prevented or at least retarded. These counterpolyvalent anions tend to link polynuclear Al species together but in distorted arrangements for steric reasons. Most of such precipitation products are thus short-range ordered mineral colloids and different from Al hydroxide polymorphs. These ligands, with strong affinity for Al, can also promote physical flocculation, resulting from reduction in electrostatic repulsion between polynuclear Al ions.

Organic components are an integral part of soils and the associated environments. Low-molecular-weight biochemicals such as organic acids are being constantly introduced to the environment through natural vegetation and through farming and other anthropogenic activities. FAs and HAs account for the bulk of organic components of soils and sediments. Therefore, transformations of Al in soils and aquatic sediments take place in the presence of organics. These organic ligands disrupt the hydroxyl bridging mechanism which is indispensable for the formation of crystalline Al hydroxides. Because of steric factors, these perturbing organic ligands that occupy the coordination sites of Al also distort the arrangement of the platelets normally found in crystalline Al hydroxides, leading to the formation of short-range ordered precipitation products of Al. Consequently, it is logical that substantial concentrations of crystalline Al hydroxides are absent in temperate soils rich in organic matter. The research data also indicate that organic acids can perturb the formation of hydroxy-Al-montmorillonite complexes even in the acidic pH condition, which is most conducive to Al interlayering.

Organic acids can also influence the formation of Al hydroxide polymorphs through modification of the kinetics of the crystallization of precipitation products of Al. The organo-aluminopolymer associations also perturb the interaction of hydroxy Al ions with silicic acid and inhibit the formation of imogolite and allophane, leading to the accumulation of ill-defined aluminosilicates that have low SiO_2/Al_2O_3 ratios and contain considerable amounts of organic ligands.

Certain organic and inorganic ligands not only promote the formation of pseudoboehmites over Al hydroxides but also stabilize them. These results provide the interpretations for the genesis of noncrystalline alumina of boehmite characteristics in certain tropical soils and of some bauxites that consist of submicroscopic boehmitelike particles very similar to pseudoboehmites.

Complexation of Al by a series of organic and inorganic ligands may have a significant influence on the chemistry of Al in soil solutions and natural waters. The ecological significance of these Al species and the impact on human health merit close attention.

Besides affecting soil acidity, microbial events, enzyme activities, transformations of organic matter, soil structure, and the status of nutrients for plant and animal production, the transformation of Al can also affect the bioavailability of environmental pollutants such as heavy metals and biocides, and the subsequent food chain contamination in terrestrial systems. The hydrolytic products of Al can also influence the transformations, pathways, accumulation, and ecological effects of pollutants in freshwater environments. Therefore, the research on the mineralogy and environmental chemistry of Al is essential in the pursuits of environmental toxicology and in the studies pertaining to human health.

Acknowledgments

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