GEOCHEMICAL MECHANICS FOR THE DISSOLUTION, TRANSPORT, AND DEPOSITION OF ALUMINUM IN THE ZONE OF WEATHERING

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Abstract – Organic acids in the 0·01M concentration range representing amino-, aliphatic, and aromatic types present in humus dissolve 70–85 ppm Al from Arkansas bauxite at room temperature, whereas 0·03 ppm is dissolved in water. The species of Al in aqueous solution, calculated from stability data, range from Al^{3+} at pH 3 and lower, through $Al_2(OH)_2^{4+}$ at a maximum concentration at pH 4·5, $Al(OH)^{2+}$ at a maximum at pH 4·7, $Al(OH)_2^+$ at a maximum at pH 6·0, to $Al(OH)_4^-$ at pH 8·5 and higher. In salicylic acid an $Al–Sal^+$ complex occurs between pH 1·5 and 8·5, and is at a maximum at pH 4·2. Solubility of Al obviously is pH dependent; also because of the vulnerability of organic acids to oxidation, the solubility and transport of Al is indirectly Eh dependent. Anions that combine with Al include OH^- to form bauxite, PO_4^{3-} to form lateritic phosphate such as the Bone Valley Formation, Fla., and SiO_4^{4-} to form allophane or kaolin as noted in the kaolin synthesis by Linares and Huartes. Spongelike, pisolitic or oolitic structures, and mineral veins in bauxites, lateritic phosphates, and some flint clays attest to mobilization of Al in solution. Lignites and humus zones associated with laterites are a logical geologic source of these complexing organic solvents. Although Al is inherently mobile, such commonly available precipitating anions render Al relatively immobile.

INTRODUCTION

ALUMINUM has long been categorized by geologists as one of the least soluble elements released from aluminous rocks and minerals during weathering. Because of its relative immobility it has been used as a reference "fixed-element" against which the loss and gain of the other elements have been compared in studies of rock alteration. Bauxite deposits correspondingly have been considered to be an end-product of weathering. Despite the seeming residual nature of deposits of bauxite, contradicting field, petrographic, and mineralogic evidence – such as crystals of gibbsite and boehmite in oolitic and pisolitic structures, and trails of those minerals in joints and channels through which solutions moved – indicates there has been transport of Al in solution. Unquestionably then, Al can be dissolved and moved in solution in the zone of weathering prior to deposition of Al minerals. In pedologic weathering aluminum may be mobilized by the process called "cheluviation" (Swindale and Jackson, 1956; Pedro *et al.* 1969). Earlier experiments by us (Huang and Keller, 1970, 1971), in which organic complexes of Al were dissolved from silicates of aluminum shaken in dilute organic acids led us to include Arkansas bauxite in a similar study. The results of these laboratory experiments have provided geochemical mechanisms for the dissolution, transport, and deposition of Al-minerals in the zone of weathering.

EXPERIMENTAL AND DISSOLUTION DATA

First-quality, gray pisolitic Arkansas bauxite was finely pulverized, and 2·0g aliquots were gently shaken in 350 ml of water and 0·01M citric, tartaric, and salicylic acids which are strongly complexing. After periodic intervals up to 102 days, 50 ml aliquots were withdrawn, centrifuged to clarity, so as to yield no Tyndall cone, and analyzed for Al by an improved flame emission technique (Pickett and Koirtyohann, 1968). Additional details of processing were previously described by us (Huang and Keller, 1970).

After 102 days reaction only about 20 parts per billion Al were dissolved from the bauxite in water at pH 5·81. In the 0·01M organic acid solvents, the concentration of Al dissolved was approximately 2000 to almost 3000 times as great: 68·4 ppm in citric at pH 3·14; 81·0 ppm in tartaric at pH 3·13; and 84·4 ppm in salicylic acid at pH 3·35.

These acids are representative of types of organic acids present in the relatively complex humic acid that is present in soils and lignite. Humic acid is not a single specific compound that can be characterized by chemical constants, but the acids used in this research permit calculations of the relative amounts of the several species of Al complexes dissolved in them.

SPECIES OF Al IONS IN SOLUTION

The amphoteric properties of Al manifest themselves in a wide variety of ion species and com-

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plexes which may be present in varying proportions in an aqueous solution depending upon the pH. Apart from polymers, these include Al^{3+}, $Al(OH)_2^+$, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, and $Al(OH)_4^-$, all hydrated. The proportion of each complexed ion can be calculated as a function of pH in simple aqueous and organic acid solutions, based on some defensible assumption, as follows: Certain Al species must be determined or assumed to be present in the system, chemical equilibrium must be assumed, and the law of mass action taken as valid and applicable (Butler, 1964). Thermodynamic data are available for the complexed ions from Sillén and Martell (1964).

Equilibrium equations may then be used, as illustrated.

$$[H^+][OH^-] = 10^{-14.0}$$
$$[H^+]^4[Al(OH)_4^-] = 10^{-23.5}[Al^{3+}]$$
$$[H^+][Al(OH)^{2+}] = 10^{-4.89}[Al^{3+}]$$
$$[H^+]^2[Al(OH)_2^+] = 10^{-8.56}[Al^{3+}]$$
$$[H^+]^2[Al_2(OH)_2^{4+}] = 10^{-6.67}[Al^{3+}]^2$$
$$[Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_4^-] + 2[Al_2(OH)_2^{4+}] = C.$$

Ideally, the brackets in the above equation symbolize the activities of particular species enclosed. Since in natural geologic systems the solution is rather dilute, the equilibrium concentration may be used for calculation. The C in the above equation denotes the total analytical concentration of Al in the solution.

The number of equations needed to calculate the species in a system depends on the number of species present. When an organic acid solution is involved, e.g. salicylic acid, additional data on the acid are introduced so that at least the following generalizations enter into the calculations:

(1) total analytical concentration of Al in the
(2) initial acid strengths of organic acid solutions, solution,
(3) pH of the solution,
(4) dissolution constant of H_2O,
(5) acidity constant of salicylic acid,
(6) formation constants of hydrolysis of Al,
(7) formation constants of Al salicylic-acid complex,
(8) law of mass action.

Although curves depicting the concentration of species theoretically could be calculated as continuously changing functions, actually a smaller but adequate number of points were calculated (360/65 computer) and curves drawn as in Fig. 1.

In H_2O, Fig. 1, Al^{3+} is the dominant (94% or greater) Al species dissolved at pH less than 3·5, $Al(OH)^{2+}$ is dominant from pH 5 to 7, and Al$(OH)_4^-$ above pH 7·5. Minor concentrations of
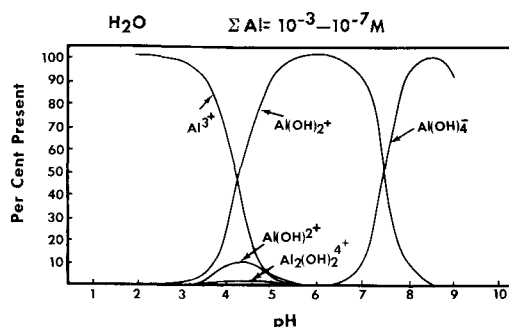

Fig. 1. Distribution of Al ionic species (all hydrated) in an aqueous solution of Al-hydrate mineral as a function of pH. $\Sigma Al = 10^{-3}$–10^{-7} M.

$Al(OH)^{2+}$, and $Al_2(OH)_2^{4+}$ are not to be ignored because oversaturation of them may result in precipitation of Al–hydrate minerals by way of them. Currently we do not know if there is a one-to-one genetic correlation between any single Al-ion species and a specific Al–hydrate mineral, such as bayerite, gibbsite, boehmite, or diaspore. Neither is it known whether any specific Al-ion species predisposes toward four-fold or six-fold coordinated Al in an aluminous mineral product. Although relationships such as these are speculative, if true they could be significant in understanding Al–hydrate genesis.

Hem (1968) and Hem and Roberson (1967) elegantly showed that, in aqueous solution, as the ratio of OH to Al increased above 1·0 the monomeric hydrated (6-fold) Al^{3+} polymerized to the dimer form, and thence toward 6-membered rings. Eventually the polymerized Al-hydroxide yielded gibbsite. McHardy and Thomson (1971) found under conditions of their experiments that a pseudoboehmite type of gel predominates in the absence of acids, is uncharged, and rapidly crystallizes to bayerite. In carboxylic acid solutions, the gel is positively charged and, in the absence of inorganic cations, crystallizes slowly to gibbsite. Hsu, for example with Bates (1964), has been reporting on polymerization of Al ionic species in solution since 1963.

Our purposes in this paper are to present the broad concept of otherwise mobile Al being trapped by OH, PO_4, and SiO_4, apart from the valuable researches on the detailed mechanisms of precipation, and that organic-acid complexes of Al add another dimension to Al mobility besides that in pure water.

In a strongly complexing organic acid solution although in low concentration, for example, 0·001 M salicylic acid, dissolved Al is complexed as $AlSal^+$ in the wide range of pH 3–7·5, Fig. 2. Al^{3+} predominates at pH 2 and less, as it did in H_2O, but

H$_2$Sal=0.001M Σ Al=10^{-3} to 10^{-7} M

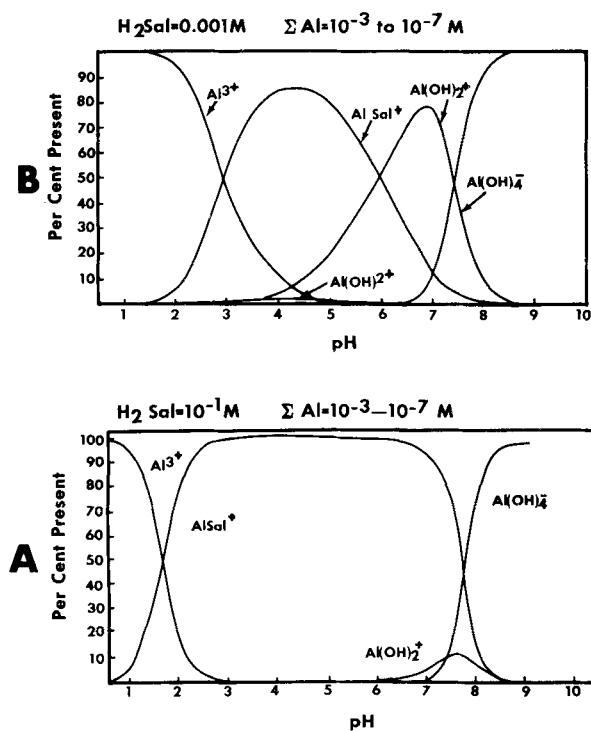H$_2$ Sal=10^{-1}M Σ Al=10^{-3}—10^{-7} M

Fig. 2. Distribution of Al ionic species (all hydrated) from an Al-hydrate mineral in (a) 0·1M and (b) 0·001M solutions of salicylic acid. ΣAl = $10^{-3} - 10^{-7}$M. ΣH$_2$Sal = [H$_2$Sal] + [H$_2$Sal$^-$] + Sal^{2-} + Al Sal$^+$.

from pH 3 to 6 the complexed AlSal$^+$ becomes dominant. Al(OH)$_2{}^+$ becomes a maximum at about pH 6·9, being notably decreased relative to its prominence in water. Al(OH)$_4{}^-$ is much the same as in water.

When the concentration of salicylic acid is increased to 0·1M, the species distribution differs vastly from that at 0·001M, Fig. 2. Note how Al^{3+} is suppressed, while AlSal$^+$ predominates from about pH 1·5–7·5. Al(OH)$^{2+}$ essentially vanishes, and Al(OH)$_2{}^+$ decreases markedly but maximizes at about pH 7·5.

These two examples showing the change in distribution with change in concentration of organic acid illustrate in a small way how variations can occur in dissolutions involving only one organic acid. In a multiple-component, humic-acid complex, inherent in lignites or decomposing plant residues, the variations may be several times greater. During geologic transport, additional environmental changes may modify the species distribution and cause deposition of Al minerals. For example, dilution by rain or mingling ground water; change in pH due to contact with reactive

minerals, such as calcite or oxidizing FeS$_2$, or with ground water; destruction of the organic ligand by bacterial metabolism (reminiscent of, but unlike Logan's 1919 theory, that "they [bacterial] seem to secrete kaolin"); or its oxidation with increase in pO$_2$, may cause sequential or alternating deposition of Al–hydrates. Noteworthy is that deposition of Al minerals is not only pH dependent, but also indirectly dependent on Eh — a contingency that has largely been omitted for Al. It is possible that one set of conditions might result in deposition of gibbsite, and other of boehmite (or other variety of Al mineral). These are speculations, and although we would prefer to have sound geochemical data to support them, lacking such data we can at least suggest mineral relationships to look for in field observations and give leverage to interrelate field and laboratory studies.

GEOLOGIC INTERPRETATION

These laboratory observations show that significantly high concentrations of Al may be dissolved in weathering by action of dilute organic acids at room temperature. Transport of the dissolved Al undoubtedly continues until either the organo-complex was destroyed, or a strongly precipitating anion is encountered. Significant residual deposits of Al-rich minerals, such as hydroxides, phosphates, and silicates, indicate that OH$^-$, PO$_4{}^{3-}$, and SiO$_4{}^{4-}$ are strongly precipitating anions of Al under field conditions. Al, therefore, is an inherently "soluble" cation whose precipitating anions are exceedingly wide-spread and abundant.

Precipitation of Al by OH is exemplified geologically by the minerals of bauxite. An Al-containing system, upon encountering an excess of OH moves toward pH 6·7, the isoelectric point of Al in an aqueous system (Reesman, Pickett and Keller, 1969), whereupon bauxite-mineral deposition would follow. Obviously at such critical concentration of OH, it would override the effect of organic acids. The strikingly low solubilities of lateritic Al compounds are illustrated by the solubility products of amorphous aluminum hydroxide reported by Sillén and Martell (1964): $K_{s_0} = 10^{-32·69}$, $K_{s_1} = 10^{-22·88}$, $K_{s_2} = 10^{-13·29}$, $^*K_{s_4} = 10^{-12·26}$. Raupach (1963) used $10^{-12·45}$ as $^*K_{s_4}$ for fresh boehmite: but for the natural mineral boehmite, Reesman, Pickett, and Keller (1969) used $10^{-14·4}$ as K_{s_4}, and for diaspore, 10^{-12}–10^{-14} (pH 6·65–6·99).

Precipitation of Al by PO$_4$ is illustrated by large-scale deposits in the "leached, aluminum phosphate zone" occurring over many square miles in the Pliocene Bone Valley Formation of the phosphate deposits of Florida (Altschuler, Jaffee and Cuttita, 1956; Altschuler, Cathcart and Young, 1970), which were visited on the Clay Minerals Society

Field Trip, 1970. Altschuler, Cathcart, and Cuttita (1970, p. 32) provide an unexcelled description of these occurrences:

"*Lateritic weathering — the aluminum phosphate zone....*

The aluminum phosphate zone is the product of more intense leaching and alteration than normally prevails in the southeast. The zone is essentially lateritic. This is evident chemically in the appreciable vertical changes from a calcic and silicate-rich rock to one in which all bases and silicates other than quartz have been leached. It is seen texturally in the extremely porous and vesicular rock whose open spongelike texture is indurated, and maintained, by secondary minerals and cements, as in the classic laterite of India. At the same time the character of the aluminum phosphate zone is greatly influenced by the primary Bone Valley texture and petrography. Where graded-bedded pebbly rock of the lower Bone Valley is altered, coarse vesicularity, with relic graded texture results, and as these layers were rich in apatite, they become rich in calcium aluminum phosphates. Where the alteration is restricted to the upper, more clayey unit of the Bone Valley Formation, the pure aluminum phosphate, wavellite, dominates, and the rock is finely vesicular.

At the base of the zone, carbonate-fluorapatite and 'clay still occur, through both are incipiently leached and laterized. Higher in the section pebbles are gone and large cavities display the original pebbly texture. In the middle of the zone, bases and silicates are substantially diminished and the calcium aluminum phosphates crandallite, $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$, and millisite, $(Na, K) CaAl_6(PO_4)_4(OH)_8 \cdot 3H_2O$, prevail. The crandallite and millisite in the middle of the zone generally occur as a microcrystalline intergrowth within the clay bands they replace (Owens, Altschuler and Berman, 1959). At the top of the zone the rock is essentially quartz sand cemented by intergranular wavellite, $Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$. The wavellite has therefore replaced the former intergranular clay, as well as the secondary calcium phosphate which represented an earlier stage in the replacement process. The wavellite of this origin occurs as bands of cryptocrystalline fibrous material (Altschuler, Jaffee and Cuttitta, 1956). Wavellite also occurs as euhedral druses, vein fillings and large spherulites (Bergendahl, 1955)."

Aluminum–phosphate compounds, in general, are known to be scantily soluble but no solubility data are available for crandallite, millisite, or wavellite. The dissolution of these minerals in simple aqueous and organic-acid solutions, however, is under study in our laboratory. Hsu (1968) found that different products are formed, depending upon whether hydroxy–aluminum polymers or Al^{3+} react with phosphate. Furthermore, in solutions containing both polymers and Al^{3+}, each reacted separately because a rapid equilibrium between Al^{3+} and polymers does not exist.

Silica as a precipitating anion with Al is illustrated by the familar clay minerals. Linares and Huartes (1971) synthesized kaolinite from solutions of monomeric silica and aluminum–fulvic acid, the latter interpreted as yielding a six-fold coordinated aluminum ion which was essential in the synthesis. Other kaolin synthesis in which organic acids were used further illustrate the mutual precipitating effect of dissolved aluminum and silica (Eberl, 1970; De Kimpe, Gastuche and Brindley, 1961).

We hasten to disavow that all kaolins are formed by pouring together solutions of aluminum and silica, but nevertheless intermediate solution-phases may be present in many argillic weathering systems, even including pseudomorphic replacement of feldspar by kaolinite. Well-crystallized kaolinite is very scantily soluble in pure water — its $*K_{s_4}$ being in the order of 10^{-38}–10^{-40} at pH 6·8 (Reesman and Keller, 1968). Some occurrences of kaolinite which appear texturally to have crystallized from solution are so large they require impossibly large volumes of water to have transported them to location. Possibly organo-complexed solutions were involved.

Stability interrelations between bauxite minerals, Al–phosphate minerals, and clay minerals (Al silicates) from both the field and laboratory standpoints are incompletely known. Geologic observation has shown that kaolinite may be desilicated to form bauxite, and that bauxite may be resilicated to kaolinite. Clay minerals in the Florida phosphate region have undergone alteration in the presence of PO_4 to form Al–phosphate minerals. Presumably plant metabolism can weather Al–phosphates such that Al–silicates and/or Al–hydrate minerals can form. Speculatively, bauxites may become Al–phosphate under field conditions where the activity of PO_4 was high. If this occurs, the hydrates, phosphates, and silicates of Al may be converted, cyclically each one to the other, depending upon the chemical energies available. Geologists should expect to find mineral evidence of these interactions, and geochemists, having determined the thermodynamic constants for the minerals, ought to be able to predict specific conditions under which these reactions occur.

In summary, Al may be viewed as an inherently soluble ion in organic acids, but its distance of transport is typically short because of the abundant and wide-spread occurrence of competing anions, such as OH^-, PO_4^{3-}, and SiO_4^{4-}, which can precipitate it.

Far afield from laterization and argillation, in the area of silicosis therapy is another possible application of these geochemical factors. Silicosis is thought to occur partly from dissolution of silica from quartz or cristobalite by organic body fluids. One type of therapy involves the inhalation of finely powdered Al metal by a silicosis patient. Perhaps the deleterious reaction of silica within the patient is deterred due to dissolution of Al by body fluids

and subsequent reaction with the dissolved silica to yield a form of Al–silicate which can be expelled, or which is less toxic.

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Résumé– Des acides organiques d'une concentration voisine de 0,01 M et représentant les types aminés, aliphatiques et aromatiques présents dans l'humus, dissolvent, à température ambiante, de la bauxite de l'Arkansas, 70–85 ppm d'Al, alors que l'eau n'en dissout que 0,03 ppm. Les espèces ioniques sous lesquelles Al se trouve en solution aqueuse, calculées à partir des données de stabilité, sont Al^{3+} à pH 3 et au dessous, $Al_2(OH)_2^{4+}$ en concentration maximum à pH 4,5, $Al(OH)^{2+}$ en concentration maximum à pH 4,7, $Al(OH)_2^+$ en concentration maximum à pH 6,0 et $Al(OH)_4^-$ à pH 8,5 et au dessus.

Dans l'acide salicylique, un complexe Al-Sal$^+$ existe entre pH 1,5 et 8,5, et il est à une concentration maximum à pH 4,2. La solubilité de Al dépend d'une façon évidente du pH; de même, à cause de la vulnérabilité des acides organiques à l'oxydation, la solubilité et le transport de Al dépendent indirectement de E h. Les anions qui se combinent avec Al comprennent OH^- pour former la bauxite, PO_4^{3-} pour former un phosphate latéritique tel que la formation de Bone Valley, Fla., et SiO_4^{4-} pour former l'allophane ou le kaolin comme l'ont noté Linares et Huartes dans la synthèse du Kaolin. Des structures spongieuses, pisolithiques ou oolithiques, et des veines minérales dans les bauxites, les phosphates latéritiques et certains flint-clays, attestent de la mobilisation de Al en solution. Les lignites et les zones humifères associées aux latérites constituent une source géologique rationnelle pour ces agents de dissolution organiques et complexants. Quoique Al soit naturellement mobile, de tels anions précipitants communément rencontrés rendent Al relativement immobile.

Kurzreferat– Organische Säuren im 0,1 M Konzentrationsbereich, welche die im Humus vorhanden aliphatischen und aromatischen Typen von Aminosäuren darstellen, lösen 70–85 ppm Al aus Arkansas Bauxit bei Zimmertemperatur, während in Wasser 0,03 gelöst werden. Die Sorten von Al in wässriger Lösung, berechnet aus Stabilitätsdaten erstrecken sich von Al^{3+} bei pH 3 und darunter, über

$Al_2(OH)_2^{4+}$ in einer Maximalkonzentration bei pH 4,5, $Al(OH)^{2+}$ mit einem Maximum bei pH 4,7, $Al(OH)_2^+$ mit einem Maximum bei pH 6,0 bis $Al(OH)_4^-$ bei pH 8,5 und darüber. In Salizylsäure entsteht ein Al-Sal$^+$ Komplex zwischen pH 1,5 und 8,5, und erreicht einen Maximalwert by pH 4,2. Die Löslichkeit des Al hängt eindeutig vom pH ab; infolge der Empfindlichkeit der organischen Säuren gegenüber Oxydation, sind die Löslichkeit und der Transport des Al ebenfalls mittelbar Eh-abhängig. Unter den sich mit Al verbinden Anionen befindet sich OH^- zur Bildung von Bauxit, PO_4^{2-} zur Bildung von lateritischem Phosphat wie etwa die Bone Valley Formation, Fla., und SiO_4^{4-} zur Bildung von Allophan oder Kaolin wie etwa in der Kaolin Synthese von Linares und Huartes. Schwammartige, pisolithartige oder oolithartige Gefüge, und Mineraladern in Bauxiten, lateritischen Phosphaten, sowie gewisse Flinttone bezeugen die Beweglichkeit von Al in Lösung. Lignite und Humuszonen, die mit Lateriten in Verbindung stehen, sind eine logische geologische Quelle dieser komplexbildenden organischen Lösungsmittel. Obwohl Al naturgemäss beweglich ist, machen diese allgemein vorhandenen, niederschlagbildenden, Anionen das Al verhältnismässig unbeweglich.

Резюме — Органические кислоты концентрации 0,01 М (амино-, алифатические и ароматические типы), содержащиеся в гумусе, растворяют при комнатной температуре 70–85 ч.н.м. (частей на миллион) Al из боксита Арканзаса, тогда как в воде растворяется лишь 0,03 ч.н.м. Al. Состояние Al в водном растворе, определенное путем подсчета характеристик устойчивости: Al^{3+} при рН з и ниже; $Al_2(OH)_2^{4+}$ с максимальной концентрацией при РН 4,5; $Al(OH)^{2+}$ с максимальной концентрацией при рН 4,7; $Al(OH)_2^+$ с максимальной концентрацией при рН 6,0; $Al(OH)_4^-$ при рН 8,5 и выше. В салициловой кислоте между рН 1,5 и 8,5 образуется ион Al–салицил$^+$ с максимальной концентрацией при рН 4,2. Растворимость Al, очевидно, зависит от величины рН; кроме того, вследствие чувствительности органических кислот к окислению, растворимость и перенос Al косвенно связаны с величиной Eh. Анионы, комбинирующиеся с Al, включают OH^- (образование боксита), PO_4^{3-} (образование латеритовых фосфатов, подобных обнаруженным в формации Бон Вэли) и SiO_4^{4-} (образование аллофана или каолина), как установлено при синтезе каолина Линаресом и Уэртасом. Губчатые, пизолитовые или оолитовые структуры и жилы в бокситах, латеритовых фосфатах и некоторых сухарных глинах говорят о перемещении Al растворами. Лигнитовые и гумусовые зоны, ассоциирующиеся с латеритами, являются логическим геологическим источником комплексных органических растворителей. Хотя Al и присуща подвижность, указанные обычно встречающиеся осаждающие анионы делают его относительно неподвижным.