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Solution Activities of Aluminum and Silicon in Highly Weathered Soils that contain Gibbsite and Kaolinite[1]

R. M. WEAVER AND P. R. BLOOM[2]

ABSTRACT

Solution activities of aluminum (Al^{3+}) and monosilicic acid ($Si(OH)_4$) in dilute acid suspensions of six Brazilian Oxisols were measured over a period of 145 days. The steady state activity function of pH − ⅓pAl ranged from 1.86 to 2.69, while that of $pSi(OH)_4$ ranged from 3.69 to 4.22. Although all of the soils contained kaolinite and gibbsite, the observed solute activity functions of pH − ⅓pAl and $pSi(OH)_4$ deviated considerably from those expected for a thermodynamic equilibrium between gibbsite and kaolinite. It was found that the solution activities of Al and $Si(OH)_4$ in these soils appeared to result from the dissolution of a surface aluminosilicate component (R) of variable composition-$\{[Al(OH)_3]_{1-x}[SiO_2]_x\}_R$ rather than gibbsite and kaolinite.

Additional Index Words: **soil mineral dissolution, localized equilibrium.**

ONE OF THE PROBLEMS limiting crop production on highly weathered soils of the humid tropics is toxic levels of soluble Al that result from dissolution of soil minerals under acidic conditions. Commonly, the minerals apparently undergoing dissolution in highly weathered soils are gibbsite and kaolinite. Low temperature studies on the dissolution of well-characterized samples of gibbsite (Kittrick, 1966a) and kaolinite (Kittrick, 1966b) under carefully controlled conditions have provided reliable solute activity products that should allow a prediction of the soil solution activity values of Al^{3+} and $Si(OH)_4$ at a given pH when these minerals are present. However, the applicability of the latter to soils that contain gibbsite and kaolinite has not been extensively tested or demonstrated. Hence, the purpose of this investigation was to examine the solution activities of Al^{3+} and $Si(OH)_4$ that occur in acidified suspensions of some highly weathered soils that contain gibbsite and kaolinite.

MATERIALS AND METHODS

Samples of surface horizons (0-20 cm) of six soils, currently classified as Typic Haplustox, from the Central Plateau of Brazil were used in this investigation. Previous determinations (Weaver, 1975) have shown that gibbsite and kaolinite constitute a major portion of the clay fractions (<2 μm) of these soils (Table 1). Other constituents in the clay fractions consisted of iron oxides, 0.5*N* NaOH-extractable amorphous materials (Hashimoto and Jackson, 1960), traces of mica, Al-chlorite, and TiO_2 minerals. One interesting feature noted for the clay fractions (Table 1) was the presence of a surface reactive component, selectively extracted by 0.5*M* $CaCl_2$ of pH 1.5 (Tweneboah et al. 1967) that had a composition that differed substantially from the bulk of the clay fraction. The Si content of this surface reactive component appeared to have originated from a limited dissolution of quartz, the predominant mineral in the sand fractions, as there was an excellent relationship ($r^2 = 0.96$) between the reactive SiO_2 content of the clay fractions and the amount of sand-sized quartz. This apparent dissolution of quartz, however, did not occur to the extent such that gibbsite was resilicated to kaolinite as there was no relationship ($r^2 = 0.02$) between the quartz content and the kaolinite/gibbsite + kaolinite ratios of the clay fractions.

The solute activity studies on the soils were carried out under conditions designed to: (i) minimize the influence of exchangeable Al initially present; (ii) maintain a fairly constant ionic strength; and (iii) produce a steady-state pH value of < 5 so that the Al solution species would be limited to the hexaquo species, $Al(H_2O)_6^{3+}$ and its first hydrolysis product $Al(H_2O)_5(OH)^{2+}$. Accordingly, duplicate 10-g samples of the soils were placed into 250-ml polypropylene centrifuge bottles and washed three times with 0.5*N* $CaCl_2$ by centrifugation and decantation, followed by five washes with 0.01*N* $CaCl_2$. The samples were then suspended in 200 ml of 0.01*N* $CaCl_2$ that was also 0.005*N* with respect to HCl. Several drops of toluene were added to each bottle to inhibit microbial growth, and the bottles were placed in a constant temperature

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Table 1—Gibbsite, kaolinite, and reactive fraction (0.5M $CaCl_2$, pH 1.5) content of the clay fractions (< 2 μm) of Brazilian Oxisols.

Soil no.	Clay	Gibbsite	Kaolinite	Kaolinite/ Kaolinite + Gibb	Reactive Si	Reactive Al	Reactive Si/Al+Si
	%				mmole/100 g		
2	69	27	36	0.57	0.70	5.65	0.11
5	16	9	40	0.82	2.52	6.67	0.27
8	29	58	5	0.08	1.50	9.31	0.14
11	68	24	39	0.62	0.50	6.53	0.07
14	56	50	5	0.09	0.50	10.1	0.05
17	31	27	34	0.56	1.58	8.73	0.15

room (25°C ± 1). The bottles were shaken by hand daily. Periodically aliquots of the suspensions were taken and after centrifugation, the pH of the supernatants was determined with a Leeds and Northrup pH meter; aluminum by the Aluminon method of McLean (1965); $Si(OH)_4$ by the procedure of Weaver et al. (1968); and iron by the Orthophenanthroline method (Jackson, 1969). Activity coefficients of Al were calculated by using the extended Debye-Hückel equation (Butler, 1964, p. 423). The activities of Al were calculated from the analytical concentrations of Al by the method of Hem and Roberson (1967). The activity coefficient of $Si(OH)_4$ was assumed to be unity.

RESULTS AND DISCUSSION

The solute activity values (Table 2) were characterized by initial rapid increase in pH (decreasing H^+ activity), while Al^{3+} and $Si(OH)_4$ activities increased which is to be expected for dissolution of an aluminosilicate phase from undersaturated conditions. The amounts of Fe released (< 1 μg Fe/ml) were insignificant in comparison to Al and therefore, measurements of Fe were discontinued after the first two samplings. The variation among the soils in regard to aluminum activities was slight compared to those of pH and $Si(OH)_4$. There was little relationship between pH and Al activity as regression analysis gave pAl = 0.0164pH + 3.52 (r^2 = 0.08). Obviously, pH alone would not be a good indication of the expected Al activities of these soils.

Interpretation of the possible solid phase control on solute activities was initially made by plotting the observed values in a phase stability diagram (Fig. 1) that describes the stability of well-crystallized gibbsite and kaolinite in terms of the

Table 2—pH, pAl, and $pSi(OH)_4$ of soil suspensions of Brazilian Oxisols.

Soil no.	Time (days) 14	60	106	145
		pH		
2	3.05	3.56	3.70	3.70
5	2.50	2.90	3.00	3.05
8	2.75	3.41	3.60	3.60
11	2.90	3.44	3.58	3.60
14	3.10	3.68	3.82	3.85
17	2.60	3.25	3.40	3.45
		pAl		
2	3.59	3.55	3.56	3.53
5	3.81	3.59	3.53	3.51
8	3.51	3.45	3.43	3.43
11	3.47	3.42	3.41	3.41
14	3.47	3.48	3.48	3.49
17	3.54	3.46	3.45	3.43
		$pSi(OH)_4$		
2	4.19	4.02	4.00	3.96
5	4.14	3.80	3.74	3.69
8	4.22	4.03	4.00	3.96
11	4.36	4.21	4.18	5.17
14	4.39	4.27	4.25	4.22
17	4.31	4.07	4.01	3.98

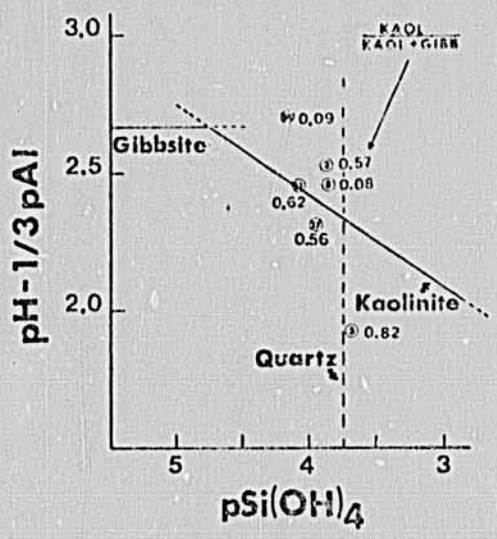

Fig. 1—Steady state solute activity functions of $pSi(OH)_4$ and pH-⅓ pAl of soil suspensions in relationship to those of well-crystallized gibbsite and kaolinite at 25°C and 1 at.

solute activity functions, pH − ⅓pAl and $pSi(OH)_4$. The diagram in Fig. 1 was constructed from the dissolution equations:

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O \quad [1]$$
(Gibbsite)

$$pH - 1/3pAl = -1/3pK_{Gibb} \quad [2]$$

$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2Si(OH)_4 + H_2O \quad [3]$$
(Kaolinite)

$$pH - 1/3pAl = -1/6pK_{Kaol} + 1/3pSi(OH)_4 \quad [4]$$

Values for pK_{Gibb}(−8.0) and pK_{Kaol} (−6.53) were determined using standard thermodynamic relationships and ΔG°_f values given in Table 3. Essentially, the diagram shows that gibbsite will be stable relative to kaolinite at pH − ⅓pAl = 2.67 or greater and $pSi(OH)_4$ = 4.8 or less. If both kaolinite and gibbsite are present, the solute activity values should cluster around a given point at pH − ⅓pAl = 2.67 and $pSi(OH)_4$ = 4.8. Included in the diagram is the stability line corresponding to the dissolution and precipitation of quartz ($pSi(OH)_4$ = 3.74, Siever, 1962). The position of the line indicates that quartz presence should cause $Si(OH)_4$ activities greater than that of gibbsite-kaolinite equilibrium and suggests that gibbsite would be unstable

Table 3—Standard free energy of formation† (ΔG_f) values used in development of the stability diagram.

Species	ΔG°_f	Source
	Kcalories/mole	
Al^{3+} aq	−116.0	Robie & Waldbaum, 1968
Gibbsite‡ $Al(OH)_3$	−275.2	Kittrick, 1966a
Kaolinite	−905.8	Kittrick, 1966b
$Si(OH)_4$	−313.0	Kittrick, 1969
H_2O	−56.7	Garrels & Christ, 1965

† 25°C, 1-atm.
‡ The ΔG°_f values for gibbsite and kaolinite, originally reported on the basis of ΔG°_f Al^{3+} = −115.0 Kcalories/mole, have been recalculated using the more recent value of −116.0 Kcalories/mole.

relative to kaolinite in the presence of quartz. However, as discussed by Kittrick (1969), the kinetics of quartz dissolution and precipitation are extremely slow at earth-surface temperatures and pressures and thus quartz may have negligible influence on gibbsite-kaolinite equilibrium.

The steady state solute activity functions[3] (Table 2), when plotted in the stability diagram, showed a considerable variation from that expected for gibbsite-kaolinite equilibrium. Generally speaking, the pH − ⅓pAl values were less (undersaturated) than that expected for gibbsite and the $pSi(OH)_4$ values are greater than that associated with gibbsite formation and/or stability. Furthermore, the relative amounts of gibbsite and kaolinite present in the clay fractions have only a very general relationship to the displacement of the solute activity functions towards either the gibbsite or kaolinite stability regions. The steady-state solute activities of $Si(OH)_4$ with the exception of soil no. 5 were all less than that of quartz. Although previous results (Weaver, 1975) have suggested that some dissolution of quartz has occurred in these soils during their development as reflected in the relationship between the sand-size quartz and the reactive SiO_2 content of the clay fractions, it is unlikely that the dissolution of quartz is of sufficient rate to make any significant contribution to the steady state activities of $Si(OH)_4$. In support of this, unpublished results obtained in this laboratory on some Brazilian Oxisols similar to the present ones have shown that the presence or absence of quartz (suspensions of soils vs. suspensions of quartz-free, separated clay fractions) had no influence on $Si(OH)_4$ solute activities over a 1-year period of time. Studies currently in progress, however, show that the presence of sand-size quartz can influence solution activities of soil suspensions through an abrasion effect if the soil suspensions are continously agitated.

The apparent failure of the solution activities to agree with what is expected from the crystalline clay minerals present is more the rule than the exception especially in regard to the activities of Al (Turner and Singh, 1971; Bache, 1974). Such discrepancies have usually been attributed to incomplete description of the Al species in solution and failure to reach equilibrium (Richburg and Adams, 1971; Misra et al., 1974). In the present case, uncertainty about the nature of the Al species in solution should hardly be a complicating factor. The steady state pH values were all <4 and the hxaaquo species $Al(H_2O)_6^{3+}$ should predominate and the small amount of the first hydrolysis product-$Al(H_2O)_5(OH)^{2+}$ can be readily calculated. The question in regard to equilibrium is more difficult to answer. Helegeson (1971) has presented an extensive theoretical treatment on the mass transfer reactions involved in aluminosilicate transformation, but actual data on the rates of precipitation and dissolution of gibbsite and kaolinite are lacking. However, judging from the results of Kittrick (1967) equilibration of gibbsite and kaolinite under acidic conditions for several months appears to result in a near equilibrium state.

Although reasonable uncertainty can exist about whether or not the steady-state values (Table 2) actually represent

[3]The solute activity functions at 145 days were taken to represent steady-state values that are presumably near or at an equilibrium state as there was little difference between the 106 day values and those at 145 days.

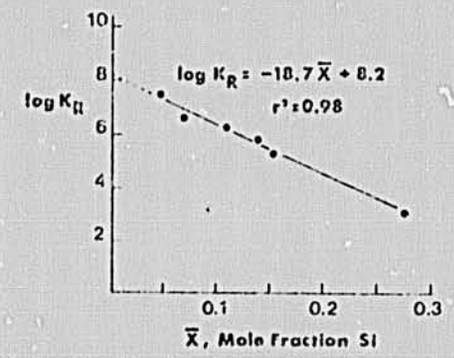

Fig. 2—Relationship of log K_R values to the molar fraction of $SiO_2(x)$ in the surface component.

equilibrium conditions, there is yet another factor that could have a significant influence on the observed solute activities. This would be the nature of the solid phase surface with which the solute activities are presumably in equilibrium. Surprisingly, this factor has received scant attention from soil scientists, but it has been pointed out by Helegeson (1968) that geochemical transformations such as kaolinite ⇌ gibbsite most likely occur through a series of partial equilibrium states, each reversible to the next, but all irreversibly related to the initial or final state of the system. These successive partial equilibrium states may result in a condition of localized equilibrium for the system, i.e., a situation in which weathering processes produce a surface coating or "reaction rim" on a crystalline mineral, of a different composition from that of the bulk mineral phase. Consequently, the solute activities are in equilibrium with the surface phase rather than the bulk mineral. Accordingly, even though it has been demonstrated that mixtures of gibbsite and kaolinite, under carefully controlled laboratory conditions, can attain the expected equilibrium state (Kittrick, 1967), it would seem not unlikely that soils which contain gibbsite and kaolinite could give solute activities of Al^{3+} and $Si(OH)_4$ that reflect an intermediate state or localized equilibrium rather than that of gibbsite ⇌ kaolinite. Along this line of reasoning, it has been shown (Paces, 1973) that solute activities of Al^{3+} and $Si(OH)_4$ in the ground waters of the Sierra Nevada were controlled by the solubility of an amorphous aluminosilicate of variable composition. To apply the latter interpretation to the Brazilian soils, a dissolution equation for an aluminosilicate intermediate phase (R) of variable composition was written as:

$$\{[Al(OH)_3]_{(1-x)}[SiO_2]_x\}_R + (3-3x)H^+ = (1-x)Al^{3+} + xSi(OH)_4 + (3-5x)H_2O \qquad [5]$$

where x represents the molar fraction of silica in the intermediate material. The equilibrium condition for the latter reaction can be written as:

$$\log K_R = (1-x)\log(Al^{3+}) + x\log(Si(OH)_4) - (3-3x)\log(H^+). \qquad [6]$$

It was assumed that the acid-extractable reactive fraction (Table 1) could be used to approximate the value of x for each soil. Values of log K_R were than calculated by substitution of the values of x and the steady-state solute activities

(Table 2) into Eq. [6]. A plot of log K_R as a function of x (Fig. 2) gave log $K_R = 18.7x - 8.2$ ($r^2 = 0.98$) and indeed, it does appear that the activities of Al^{3+} and $Si(OH)_4$ in the suspensions of these Brazilian soils can be described by the dissolution of an aluminosilicate of variable composition. The relationship in Fig. 2 shows that at $x = 0$ or when the composition of the surface component would correspond to $Al(OH)_3$, log K_R = log $(Al^{3+}) - 3$ log $(H^+) = 8.2$. This value is remarkably close to what would be expected for these soils. It is greater (more soluble) than that of well-crystallized gibbsite (log $Al^{3+} - 3$ log $H^+ = 8.0$, Kittrick, 1966a), but much lower (less soluble) than that of amorphous $Al(OH)_3$ (9.7, Sillen, 1964). On the other hand, at $x = 1.0$ or a composition of SiO_2, the relationship in Fig. 2 gives Log $K_R = -10.4$. This value is much less (lower solubility) than that of amorphous SiO_2 (log $Si(OH)_4 = -2.7$, Krauskopf, 1956) and for that matter any reported value for SiO_2 minerals. However, the observed surface compositions (Table 1) were predominantly aluminous, and apparently the relationship in Fig. 2 cannot be extended to a hypothetical SiO_2 composition which would be an unlikely occurrence in these highly weathered soils. It does follow though, from Eq. [6] and Fig. 2, that with increasing amounts of SiO_2 in the surface component, at least within the range $x = 0.05$ to 0.25, the solution activity of Al becomes less than that expected from the stoichiometric and thermodynamic dissolution of an $Al(OH)_3$ mineral. Apparently, a small amount of SiO_2 when associated with the predominantly aluminous surface component, can markedly reduce the solubility of the aluminous phase. It has been noted (Hem et. al., 1973) that the solubility of microcrystalline gibbsite is reduced when in the presence of $Si(OH)_4$. Iler (1973) showed that the adsorption of small amounts of Al^{3+} onto amorphous silica surfaces markedly reduced the solubility of the silica phase. It does not seem unlikely that in an analogous manner that the precipitation of $Si(OH)_4$ onto $Al(OH)_3$ surfaces, which has apparently occurred during the development of these Brazilian soils, would reduce the solubility of the $Al(OH)_3$. Such a phenomenon would go far in explaining the often noted variation in $(Al^{3+})(OH^-)^3$ ion activity products among soils with apparently similar mineralogical compositions.

While dissolution of an alaminosilicate surface component appears to describe the observed solution activities of Al^{3+} and $Si(OH)_4$ of these highly weathered Brazilian soils, it should be pointed out that this may be at least in part a consequence of kinetic factors. That is, gibbsite and kaolinite may themodynamically be the ultimately stable clay-sized constituents in these soils. However, because of the greater accessibility to weathering solutions and a more rapid rate of reaction the solution activities of Al^{3+} and $Si(OH)_4$ will appear to be controlled by surface components rather than the ultimately more stable, but kinetically less active minerals. Investigations are currently being carried out on these Brazilian soils in order to elucidate the kinetics of $Si(OH)_4$ and Al^{3+} release over long periods of time.

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