



0016-7037(95)00200-6

Dissolution behavior of kaolinitic tropical soils

JON CHOROVER* and GARRISON SPOSITO

Department of Environmental Science, Policy and Management, Division of Ecosystem Sciences,
University of California, Berkeley, CA 94720, USA*(Received June 15, 1994; accepted in revised
form May 3, 1995)*

Abstract—Batch experiments at controlled pH and ionic strength were conducted with representative kaolinitic soils from Brazil to investigate their short-time dissolution behavior. The release of Al and Fe from the soils showed similar pH dependence, exhibiting a minimum value (p.m.d.) just above the point of zero net charge for the soils. Both Al and Fe release rates below the p.m.d. were correlated positively with soluble organic C, proton concentration, and net proton surface charge, the last two relationships being power-law functions similar to those observed for the dissolution rates of specimen metal oxides and aluminosilicates. Below the p.m.d., release of Si from the soils exhibited a pH dependence very much like that observed for specimen kaolinites and the molar ratios, Si/Al and Fe/Al released, were smaller than 1.0, probably because of the rapid solubilization of organic Al forms. Above the p.m.d., colloidal dispersion occurred and Al, Si, and Fe were released in both dissolved and microparticulate forms.

1. INTRODUCTION

The chemistry of waters draining terrestrial environments in the humid tropics is a result of both geological source and erosional regime (Sioli, 1975; Stallard and Edmond, 1983; Furch, 1984). In transport-limited systems, characterized by small slopes and deeply weathered profiles, denudation rates depend on the rates of weathering of soils (Stallard, 1988). Tropical rivers often have low concentrations of suspended sediment (Hedges et al., 1986), high Si-to-base-cation ratios (Berner and Berner, 1987), and high amounts of humic substances (Leenheer, 1980; Ertel et al., 1986). The humic substances produce elevated concentrations of Fe and Al in the most dilute rivers by either complexation or colloidal stabilization mechanisms (Stallard, 1985). These observations apply particularly to geochemical reactions occurring in highly weathered tropical forest soils containing principally kaolinite, along with quartz, Fe and Al oxides, and organic matter (Kronberg et al., 1979; Juo, 1981; Hughes, 1981).

The dissolution reactions of specimen minerals that are related to the constituents of soils in the humid tropics have been studied intensively in the laboratory (Bloom, 1983; Stumm et al., 1983, 1985; Wollast and Chou, 1985; Furrer and Stumm, 1986; Zinder et al., 1986; Bennett and Siegel, 1987; Bloom and Erich, 1987; Carroll-Webb and Walther, 1988; Carroll and Walther, 1990; Chin and Mills, 1991; Schwertmann, 1991; Xie and Walther, 1992). These studies show that dissolution rates of oxides and silicates depend on the surface concentrations of protons, hydroxyls, and complexing ligands (Stumm, 1992). Discrepancies between laboratory and field dissolution behavior are often reported and attributed to differences in solid-solution contact (Pačes, 1983; Velbel, 1985; Schnoor, 1990).

However, natural soils exhibit unique chemical properties that distinguish them from simple mixtures of well-character-

ized specimen minerals. For example, Singh and Gilkes (1992) found that an Australian kaolinitic soil contained appreciable Fe within the kaolinite structure, and had larger surface area and cation exchange capacity than specimen kaolinite. They concluded that results obtained on mineral specimens may not be relevant to soil kaolinites. Even under identical laboratory conditions, soil particles may dissolve in a manner differing from that of their constituent minerals in specimen form because of the character of naturally weathered mineral surfaces and the presence of natural organic ligands (Heyes and Moore, 1992; Van Grinsven and Van Riemsdijk, 1992; Anbeek, 1993; Mulder and Stein, 1994).

Recent soil dissolution studies have shown that element release rates are initially much higher than those observed for specimen minerals and tend to decrease with the depletion of the most reactive solid-phase sources (Van Grinsven and Van Riemsdijk, 1992; Dahlgren and Walker, 1993). This short-time dissolution behavior is especially important to the geochemistry of natural waters because soil solution chemistry in forested ecosystems under high soil water fluxes is regulated by constituents exhibiting a fast response to changes in ambient conditions (Furrer et al., 1990; Reuss et al., 1990). The chemical reactions of these constituents serve to produce the temporal and spatial variations in drainage water chemistry that are observed immediately following precipitation events (Robarge and Johnson, 1992).

The contribution of individual constituents to elemental release from highly weathered tropical soils cannot be quantified unambiguously because of the intimate coexistence of numerous finely divided solid-phases (exchangeable, amorphous, crystalline, organic). Aluminum, Fe, and Si occur in various independent and associated forms in such systems. Strong surface associations among microcrystalline kaolinite, Fe and Al oxides, and humified aliphatic organic matter have been observed in magnetic separations and spectroscopic studies of selected Brazilian soils (Oades et al., 1988; Vitorello et al., 1989; Fontes, 1992). Transmission and scanning electron microscopic investigations (Cambier and Prost,

* Present Address: Department of Agronomy, Pennsylvania State University, University Park, PA 16802, USA.

TABLE 1. Selected physical and chemical data pertaining to five kaolinitic tropical soils. Standard deviations in parentheses. Data in columns 2-7 are from Motavalli et al. (1994, 1995).

Soil	Depth (cm)	Sand -----	Silt (g kg ⁻¹)	Clay -----	Org-C ¹	Surface Area ² (m ² g ⁻¹)	σ _o ³ (mmolc kg ⁻¹)	pH _{sp} ⁴	p.z.n.c. ⁵
MF1	0-8	235(9)	10(6)	750(17)	33(3)	64(5.7)	19(1)	4.2(0.1)	3.1(0.5)
MF2	8-20	220(18)	50(31)	730(37)	19(5)	60(4.9)	12.6(0.5)	4.2(0.1)	3.4(0.5)
MC	0-20	218(5)	36(8)	750(10)	17(3)	*	12.5(0.4)	5.3(0.3)	3.3(0.3)
OP	0-12	673(6)	180(8)	150(10)	12(2)	104(5)	8.3(0.6)	5.7(0.2)	2.3(0.3)
UNA	0-12	350(16)	71(14)	580(30)	32(5)	83(1.4)	15(2)	4.3(0.1)	3.4(0.3)
VAL	0-12	650(15)	120(11)	230(10)	22(4)	95.5(0.7)	12(2)	4.9(0.2)	3.3(0.5)

1) Organic carbon measured by CHN analyzer

2) Measured by ethylene-glycol-monoethyl ether adsorption (Heilman et al., 1965) for < 2 μm fraction

3) Cesium accessible structural charge density (Chorover and Sposito, 1995a)

4) pH of saturated soil paste in deionized H₂O

5) Point of zero net charge (Chorover and Sposito, 1995a)

*Data not available

1981; Santos et al., 1989) indicate a complex assemblage of poorly crystallized or microcrystalline minerals, and organic matter reflecting extensive humification and complexation of Fe. Variability in individual dissolution kinetics among different soil solid phases implies a time-dependent alteration of solid-phase composition with feedback effects on the composition of the solution phase and the surface concentrations of adsorbed species. Thus, for soil solid phases containing chemical elements subject to preferential dissolution, the assumption of a fixed surface composition is not valid over long dissolution times.

The complexity of highly weathered soils precludes a precise molecular description of "reactive surface" contributing to the observed elemental release pattern. However, methods developed with the objective of characterizing surface reactivity, without invoking unwarranted assumptions regarding the molecular nature of the surfaces involved, can be used to identify those phases controlling surface behavior. For example, in an earlier study of kaolinitic tropical soils, the simultaneous measurement of net adsorbed proton charge density and background electrolyte adsorption provided strong evidence for the importance of permanent-charge clay minerals and organic matter to soil surface chemistry (Chorover and Sposito, 1995a). In a similar fashion, the simultaneous measurement of surface charge and short-time element release could elucidate the functional relationship between these two variables and, therefore, provide a useful basis for comparison with specimen mineral dissolution behavior.

Information regarding the short-time dissolution behavior of natural soil particles in transport-limited tropical systems is not widely available, but would contribute to understanding the processes that regulate water chemistry in these environments. Specimen mineral studies would be more useful as a guide to deciphering soil weathering mechanisms if a more quantitative understanding of soil dissolution behavior itself and the concurrent surface charge development were estab-

lished. The objective of the present study was to help fill this gap through an investigation of the short-time dissolution behavior of kaolinitic tropical soils under conditions of known solution and particle surface composition, and in light of the known variability of net proton surface charge. Of particular interest was the potential role of native humic substances in the release of dissolved and colloidal phases of Al, Fe, and Si.

2. MATERIALS AND METHODS

2.1. Soil Samples

Samples of the surface horizons of five kaolinitic soils in isohyperthermic regions of Brazil were provided by Dr. Cheryl Palm (Natural Resource Ecology Laboratory, Colorado State University) for use in the present study. Soil samples MF and MC were collected 50 km outside of Manaus (Amazonas) from sites in moist tropical rainforest or cultivated ecosystems, respectively. Soil sample OP, collected near Ouro Preto (Rondonia), and soil sample VAL, collected near Iheus (Bahia), were all obtained in moist tropical rainforest. Details of the soil sampling and characterization procedures are described by Motavalli et al. (1994, 1995). Selected chemical and physical data pertaining to the soils are presented in Tables 1-3 (Motavalli et al., 1995; Chorover and Sposito, 1995a). The clay mineralogy of the soils is dominated by kaolinite, but the soils also contain varying amounts of organic matter, Fe and Al oxides, 2:1 layer type clay minerals, and quartz (Tables 1, 2). The pH value of the saturated paste of the MC soil is higher than those for soils MF1 and MF2 (Table 1) as a result of lime addition.

2.2. Preparation of LiCl-Saturated Soil Paste

Each soil was first reacted repeatedly with LiCl, a 1-1 "background electrolyte," in a procedure designed to remove exchangeable lithogenic cations, including Al, and to facilitate the simultaneous measurement of dissolution reaction behavior and surface charge density. Although some rapidly dissolving constituents are liberated in this procedure, failure to generate a homoionic soil paste would otherwise hinder subsequent interpretation of dissolution and readorption data. Initial washes at pH 5.5 were of sufficiently high ionic strength to preclude any visible colloidal or organic matter disper-

TABLE 2. Minerals and approximate kaolinite and gibbsite contents of the < 2 μm fraction determined by x-ray diffraction (XRD) and differential thermal analysis (DTA). In column 2, capital letters indicate major components and lower case letters indicate minor components as inferred from XRD peak intensities and DTA. Components are listed in estimated order of abundance. Data courtesy of Dr. Paul C. Smithson, North Carolina State University.

Soil	Mineralogy (XRD) ¹	Differential Thermal Analysis (g kg ⁻¹ clay)	
		Kaolinite	Gibbsite
MF1	K, v	870	n.d. ²
MF2	K, v	840	n.d.
MC	K, v	*	*
OP	K, v, hiv, go	530	n.d.
UNA	K, Go, gi, hiv	390	trace
VAL	K, Gi, Go, hiv	540	10

- 1) k = kaolinite, v = vermiculite, hiv = hydroxyinterlayer vermiculite, go = goethite, gi = gibbsite
 2) Not detectable
 * Data not available

sion. All solutions were prepared on a mass basis and are presented in terms of molinity (moles per kilogram of solution).

Approximately 0.035 kg of field moist soil was transferred into a 250 mL polycarbonate centrifuge bottle. The soil was suspended in 0.2 kg of 0.5 mol kg⁻¹ LiCl adjusted to pH 5.5 with LiOH and mixed by gentle rotation at 7 rpm for 1 h. The suspension was then removed from the mixer and allowed to settle for 15 min. Forceps were used to remove light-fraction organic matter from the suspension surface. Suspensions were centrifuged at 13,000 relative centrifugal force (RCF) for 15 min. The supernatant solution was aspirated by Pasteur pipette into a filter flask and discarded. The soil was resuspended in 0.5 mol kg⁻¹ LiCl at pH 5.5 and the treatment was repeated. The soil was then resuspended in 0.2 kg of 0.1 mol kg⁻¹ LiCl, mixed by rotation for 30 min, and centrifuged at 13,000 RCF for 15 min. Following aspiration of the supernatant solution, reaction of the soil with 0.1 mol kg⁻¹ LiCl was repeated. The soil was reacted once again with 0.2 kg of 0.01 mol kg⁻¹ LiCl adjusted to pH 4.1 with 0.01 mol kg⁻¹ HCl, mixed by rotation for 30 min, and centrifuged at 13,000 RCF for 30 min.

Following aspiration of the supernatant solution, the wet soil was transferred to sterile polystyrene petri dishes and mixed to produce a uniform soil paste. Triplicate 500 mg subsamples of each paste were transferred to acid-washed, oven-dried, ceramic crucibles. The paste samples were then oven-dried to constant mass at 110°C to determine water content. The remaining paste was stored in sealed polystyrene containers at 4°C until use.

2.3. Batch Dissolution Experiments

An Orion-Ross model 8102 glass combination electrode was used with a Beckman ϕ 71 pH meter for the measurement of H⁺ concentration, [H⁺]. In each experiment, the output from the pH meter was calibrated to [H⁺] by Gran titration (Gran, 1952; Chorover and Spósito, 1993, 1995a) in the same ionic media as used in a given dissolution experiment. Standardized acid was used for the calibration titration and the calibration was checked against reference standards following measurements of sample proton concentrations.

All stock solutions and dilutions were prepared using distilled H₂O which had been passed through a Milli-Q[®] water purification unit. All batch systems, corresponding to a given soil, ionic strength (*I*),

and $-\log[\text{H}^+]$, were prepared in duplicate. A measured mass of soil paste was added to a weighed, acid-washed 35 mL polyallomer centrifuge tube. The paste was suspended in LiCl/HCl/LiOH solution at a solids concentration of 10 g kg⁻¹ and ionic strength of 0.001, 0.005, or 0.01 mol kg⁻¹. Mixtures of electrolyte, acid, and base solutions of equivalent ionic strength were prepared to reach equilibrium supernatant solution $-\log[\text{H}^+]$ values between 2 and 6.

The suspensions were mixed for 3 h by gentle rotation at 7 rpm and 25 \pm 2°C. The samples were then centrifuged at 27,000 RCF and 25 \pm 1°C for 20 min. The supernatant solution was aspirated by Pasteur pipette into an acid-washed, 60 mL high density polyethylene (HDPE) container and a subsample was taken for immediate measurement of emf (mV) calibrated to $-\log[\text{H}^+]$. Electrode/solution equilibration was considered complete when the emf reading changed less than 0.1 mV min⁻¹. The remaining supernatant solution in the HDPE container was acidified to pH 2 by addition of HNO₃, and stored at 4°C prior to chemical analysis.

The polyallomer tube containing the soil sample and entrained solution was weighed and the mass of entrained solution was determined. The sample was then reacted with 0.03 kg of 1.0 mol kg⁻¹ NH₄NO₃ solution for 30 min at low speed on a reciprocal shaker and centrifuged for 10 min at 27,000 RCF. The supernatant solution was aspirated by Pasteur pipette into an acid-washed, preweighed 60 mL HDPE container. The NH₄NO₃ exchange step was repeated. Both extraction solutions were quantitatively combined and the total mass of solution was recorded. The solution was acidified to pH 2 by addition of HNO₃ and stored at 4°C prior to chemical analysis.

2.4. Light Scattering Experiments

Dissolution experiments suggested that a pH-dependent release of colloidal or macromolecular materials into solution may occur with increasing pH. The hypothesis of a "dispersive dissolution" mechanism, i.e., that elemental release patterns were influenced by particle peptization and subsequent retention of microparticulates in supernatant solutions, was evaluated by performing the following light scattering experiments on four of the six soils studied.

A measured mass of soil paste containing approximately 175 mg of dry soil was added to an acid-washed, 35 mL polyallomer centrifuge tube. The paste was suspended in LiCl/HCl or LiCl/LiOH so-

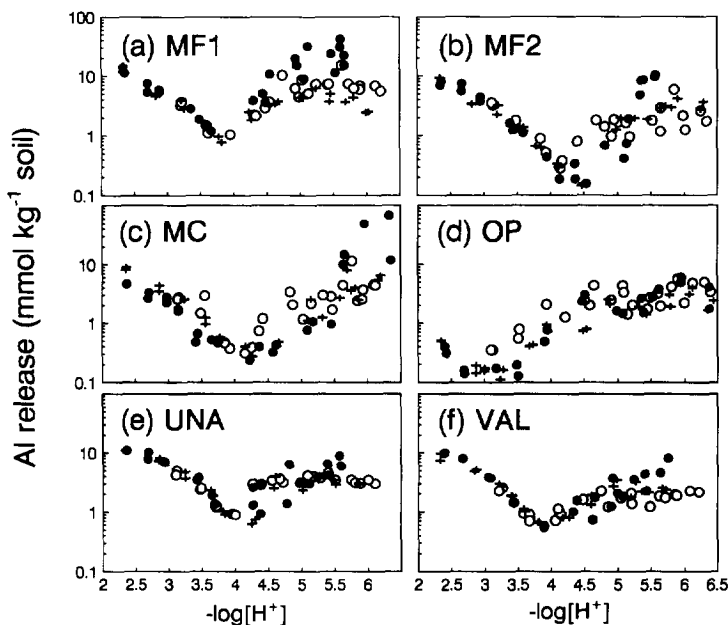


FIG. 1. Al release in LiCl solution as a function of "pH." Ionic strength: open circles—0.001 mol kg⁻¹; crosses—0.005 mol kg⁻¹; closed circles—0.01 mol kg⁻¹.

lution at $I = 0.001, 0.005, \text{ or } 0.01 \text{ mol kg}^{-1}$ to produce a total suspension mass of 0.035 kg. Mixtures of electrolyte, acid, and base of equivalent ionic strength were selected to reach nominal $-\log[\text{H}^+]$ values in the equilibrium supernatant solutions ranging from 2 to 6. The final solids concentration of the suspension was 5 g kg⁻¹.

The suspensions were mixed for 3 h by gentle rotation at 7 rpm and $25 \pm 2^\circ\text{C}$, then centrifuged at 27,000 RCF and at $25 \pm 1^\circ\text{C}$ for 20 min. Each supernatant solution was aspirated by Pasteur pipette into an acid washed, 60 mL HDPE container and subsamples were taken for immediate measurement of proton concentration.

An aliquot of the supernatant solution was transferred to a clean quartz cell (path length 1 cm) while avoiding the formation of air bubbles. Light scattering by colloidal particles in the supernatant solution was measured on a Perkin-Elmer Luminescence Spectrophotometer with the detector placed at 90° relative to the direction of the incoming beam. The excitation and emission wavelengths both were 320, 400, or 641 nm in successive readings of the time-integrated (10 s) scattering intensities. Light scattering by distilled-deionized H₂O was measured in the same way immediately following the sample measurements in order to express the data as the ratio of the scattering intensity of the sample to that H₂O (dimensionless relative intensity). The supernatant solutions at ionic strength 0.005 mol kg⁻¹ remaining in the HDPE container were acidified to pH 2 by addition of HNO₃ and stored at 4°C prior to chemical analysis.

2.5. Chemical Analysis

The concentrations of Li, Ca, Mg, Mn, Al, Fe, and Si in the LiCl supernatant solution and the NH₄NO₃ extractant were measured by inductively coupled plasma atomic emission spectroscopy (ICPAES). Both Na and K in the supernatant and extractant solutions were found to be negligible by atomic absorption spectroscopy. Calibration standards were prepared on a mass basis from ICPAES reference standards (AMEX Inc.) in the LiCl and NH₄NO₃ matrices used in the dissolution experiment. Chloride concentrations in the LiCl supernatant solution and the NH₄NO₃ extractants were measured by Ag⁺ titration with a Buchler digital chloridometer. Dissolved organic carbon (DOC) concentrations in the LiCl supernatant solutions were measured by persulfate oxidation and infrared detection of CO₂ using a Dohrmann DC-80 carbon analyzer.

2.6. Data Analysis

Net proton surface charge density was calculated according to the methods described in Chorover and Sposito (1993, 1995a). The surface excess, q_i , of ion i , in moles of charge per kilogram of dry adsorbent, following the 3 h equilibration period was calculated with the equation (Sposito, 1989):

$$q_i = |z_i| n_{i,\text{NH}_4\text{NO}_3} - M_{\text{ent}} |z_i| m_i \quad (1)$$

where z_i is the valence of ion i , $n_{i,\text{NH}_4\text{NO}_3}$ is the number of moles of ion i per unit dry adsorbent mass extracted by NH₄NO₃ following a dissolution experiment, M_{ent} is the mass of entrained LiCl solution per unit dry adsorbent mass, and m_i is the molality of species i in the supernatant solution. Surface charge excesses were calculated in this way for Li⁺, Ca²⁺, Mg²⁺, Mn²⁺, and Cl⁻, and their sum was utilized in the present study only to provide a measure of surface charge components (see Discussion). The surface excess of Al calculated according to Eqn. 1 includes the NH₄NO₃ extractable Al that was released and then adsorbed to particle surfaces during the dissolution period. (Recall that LiCl exchangeable Al had been removed previously.) The surface excess of Al was calculated as the moles of total Al per unit mass of solid. The speciation of Al, Fe, and Si in the presence of organic ligands was not determined.

Studies of "background electrolyte" (LiCl) adsorption by the soils are presented and discussed in detail by Chorover and Sposito (1995a). Their data were used in the present paper only to calculate the net proton surface charge density, σ_{H} .

3. RESULTS

Figure 1 shows the dependence on $-\log[\text{H}^+]$ (hereafter termed "pH" for convenience) of the millimoles of Al released per kilogram of dry soil after a 3 h batch equilibration at an ionic strength of 0.001, 0.005, or 0.01 mol kg⁻¹. Each graph exhibits a sharp minimum at "pH" > p.z.n.c. (Table 1) that is essentially independent of ionic strength. For all but soil OP, this point of minimum dissolution (p.m.d.) is near "pH" ≈ 4 , whereas for soil OP, which also has a significant content of Mn oxides (Chorover and Sposito, 1995a) and a

p.z.n.c. much lower than the other soils (Table 1), p.m.d. ≈ 2.6 .

Preliminary experiments (data not shown) indicated that supernatant solution "pH" became constant (variation of less than 0.2 "pH" units) within 0.3 h for the batch suspensions. Therefore, constant $[H^+]$ will be assumed throughout the duration of a batch reaction, a necessary prerequisite for any estimation of dissolution rates as a function of "pH." No claim is made that the release rates determined in the present study were for the steady state. Short-time Al release rates from soils are known to be higher than steady-state rates, possibly from the release of adsorbed or organically complexed Al (Schnoor, 1990; Dahlgren and Walker, 1993). The soils used in the present study were washed several times to generate homoionic pastes. This procedure removed LiCl exchangeable Al that otherwise would be an additional source of rapidly mobilized Al.

At "pH" < 4 , the batch suspensions were highly undersaturated with respect to the gibbsite solubility "window" (Fig. 2a; Sposito, 1989, pp. 98–99), as well as aluminosilicate constituents (Lindsay, 1979). Aluminum precipitation thus may be assumed negligible, and apparent dissolution rates, equal numerically to the total Al released divided by 3 h, may be calculated from the low "pH" data in Fig. 1. As there was also no detectable effect of ionic strength on Al release at "pH" < 4 (Fig. 1), data at all ionic strengths were combined. The log "rate of Al dissolution" ($\log R_H$, R_H in moles of Al released per kilogram of dry soil per hour) for all but soil OP is plotted against "pH" < 4 in Fig. 2b. Linear regression of $\log R_H$ on "pH" for each soil is summarized in Table 4 (left side).

The trends in Fe release were similar to those for Al, but the magnitude of metal release at low pH and the p.m.d. were generally lower (Fig. 3). There was little difference in Fe release irrespective of whether soils were high (UNA and VAL) or low (MF1, MF2) in crystalline Fe oxides (Table 3, col. 3), suggesting that this solid phase pool may not be a primary source of rapidly released Fe. All four soils contained similar quantities of oxalate-extractable Fe (Table 3, col. 5) and the total Fe released at "pH" < 4 was less than the amount of oxalate-extractable Fe. However, as a result of the LiCl saturation procedure, unknown quantities of Al, Fe, and Si were removed from these extractable "pools" prior to the dissolution experiments.

Some of the aqueous Fe concentrations encountered below the p.m.d. exceeded the solubility of strictly inorganic systems containing well-crystallized Fe oxides (Schwertmann, 1991). However, the solubility of soil Fe oxides can be several orders of magnitude higher than for well-crystallized goethite or hematite. This increased solubility is accompanied by an increased dissolution rate that has been attributed to the presence of high-surface-area Fe precipitates in soils resulting from both structural and particle size properties (Schwertmann, 1991). The initial dissolution rate of Fe in the soils is, therefore, likely to be governed by small, poorly crystalline particles.

Dissolution of organic C occurred over the "pH" range of the experiments, with a weak p.m.d. between 3.5 and 4 (Fig. 4). Although a correlation between dissolved organic C (DOC) and Al or Fe is apparent, DOC exhibits less "pH"

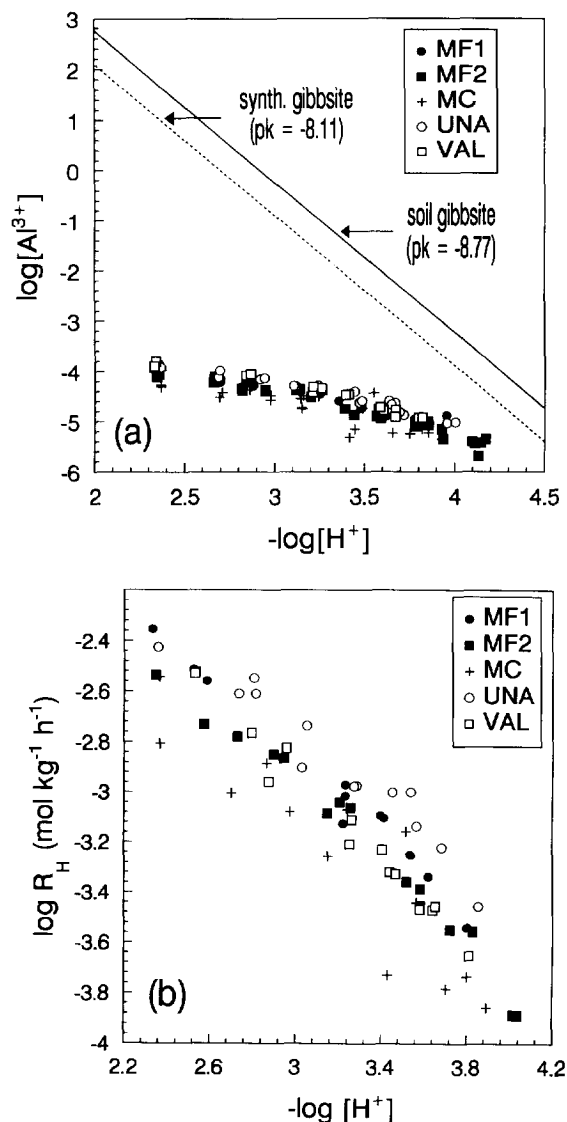


FIG. 2. (a) Al concentration (mol kg^{-1}) vs. "pH" in relation to the solubilities of synthetic and soil gibbsite (the gibbsite "window"). (b) Log apparent rate of Al dissolution (R_H , $\text{mol kg}^{-1} \text{h}^{-1}$) vs. "pH" for five soils.

dependence than Al or Fe release. Even when normalized by DOC, the element release patterns for Al and Fe still exhibit strong "pH" dependence (Chorover, 1993).

The dissolution behavior of Si (Fig. 5) did not exhibit a pattern closely similar to Al and Fe, although, at "pH" < 4 , it was similar to that for steady-state Si release from specimen kaolinite (Carroll and Walther, 1990). Silicon dissolution from both specimen kaolinite (Carroll-Webb and Walther, 1988; Carroll and Walther, 1990) and the kaolinitic soils decreases slightly with increasing pH between "pH" 2 and "pH" 4. However, unlike specimen kaolinite, the soils exhibit an increase in Si release beginning at "pH" > 4 and, in this case, p.m.d. \approx p.z.n.c. (Table 1).

Figure 6 is a plot of the released-Si/Al molar ratio (log scale) against "pH." At low "pH," except for soil OP, there was greater release of Al; near the p.z.n.c. there was a transition over

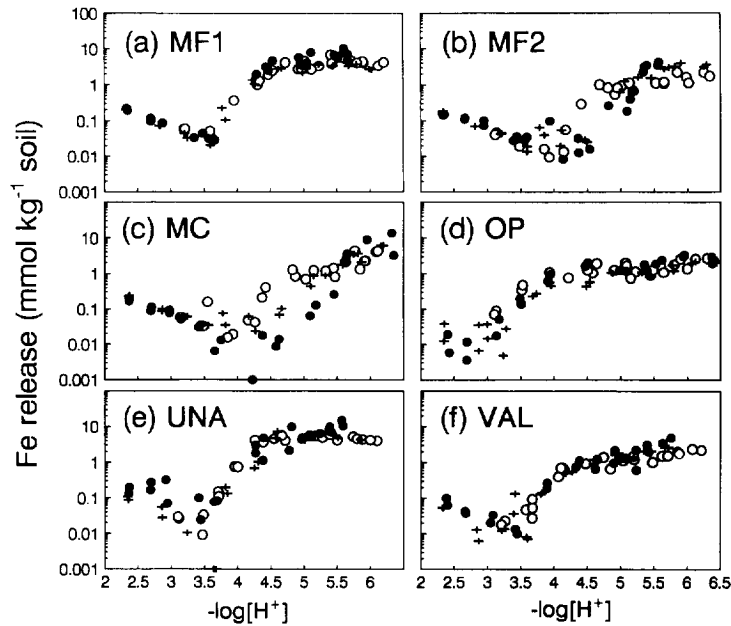


FIG. 3. Fe release in LiCl solution as a function of "pH." Ionic strength: open circles—0.001 mol kg⁻¹; crosses—0.005 mol kg⁻¹; closed circles—0.001 mol kg⁻¹.

0.5 "pH" units to a constant value near 1.0 (the ratio in kaolinite) for soils MF1, MF2, MC, OP, and VAL, but only to 0.2 for soil UNA. This trend is similar to that observed by Carroll-Webb and Walther (1988) for specimen kaolinite, which Xie and Walther (1992) explained by greater protonation of Al sites than Si sites. Other authors have reported preferential release of Si over Al from kaolinite (Chin and Mills, 1991; Wieland and Stumm, 1992) and from forested soils (Schnoor, 1990) at pH < 4. For the OP soil, there appeared to be a maximum [Si]/[Al] > near "pH" 3 (Fig. 6d), after which [Si]/[Al] approached 1.0. Comparable plots of the released-Fe/Al molar ratio (log scale) vs.

"pH" are presented in Fig. 7. These data exhibit a "pH" dependence that is similar to that observed for the Si/Al molar release ratio (Fig. 6). Aluminum is preferentially released at low "pH," but the contribution of Fe to the dissolved load increases with "pH" with a transition to near equimolar dissolved concentrations near the p.z.n.c. For soils UNA and VAL, which are high in crystalline Fe oxides, the transition in "pH" over the p.z.n.c. induces a thousandfold increase in the Fe/Al molar ratio (Fig. 7e,f).

The relative intensity of light scattered by the supernatant solutions separated from the soil suspensions using high-

TABLE 3. Quantities of Al, Fe and Si extracted from soils with citrate-dithionite-bicarbonate (CDB) and ammonium oxalate (Motavalli et al., 1994, 1995). Standard deviations in parentheses.

Soil	CDB ¹		Oxalate ²		
	(mmol kg ⁻¹)				
	Al	Fe	Al	Fe	Si
MF1	181 (4)	278 (3)	60.4 (0.8)	31.6 (0.3)	3.4 (0.2)
MF2	181 (9)	279 (7)	57 (1.6)	31.6 (0.3)	3.2 (0.2)
MC	*	*	*	*	*
OP	409 (3)	2260 (25)	55 (1.8)	93 (3.0)	6.5 (0.1)
UNA	1750 (22)	3580 (42)	50.9 (0.8)	33.8 (0.3)	2.2 (0.3)
VAL	800 (3)	1650 (11)	97 (1.3)	39.2 (0.4)	5.6 (0.1)

1) Citrate-dithionite-bicarbonate extraction method of Jackson et al. (1986)

2) Acid-ammonium-oxalate extraction method of Jackson et al. (1986)

* Data Not Available

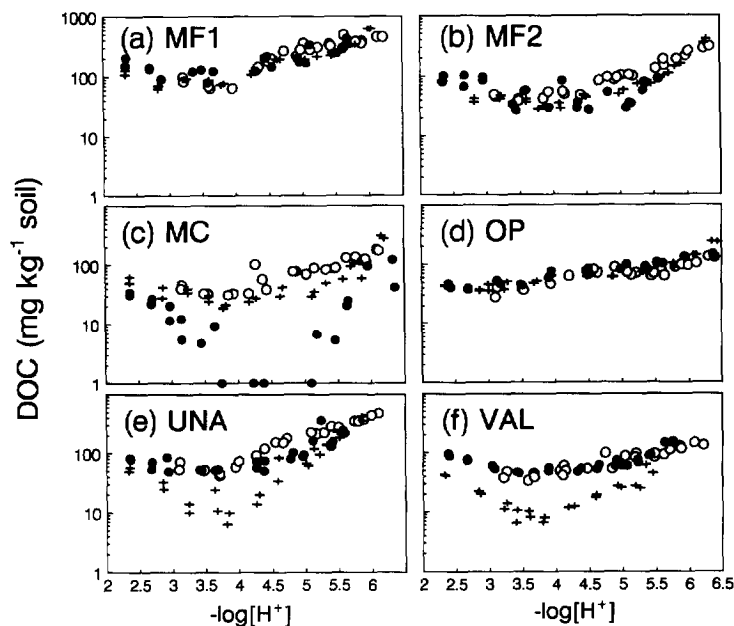


FIG. 4. Organic C release (DOC) in LiCl solution as a function of "pH." Ionic strength: open circles—0.001 mol kg⁻¹; crosses—0.005 mol kg⁻¹; closed circles—0.01 mol kg⁻¹.

speed centrifugation exhibits a roughly exponential increase with "pH" above the p.z.n.c. (Fig. 8). Scattering intensities were very similar at incident wavelengths 320, 400, and 640 nm, so only the $\lambda = 400$ nm results for the four soils investigated are shown in Fig. 8. Evidently, colloidal material was released which cannot be captured by centrifugation for 20 min at 27,000 RCF. These particles, which are <80 nm equivalent Stokes diameter for an assumed particle density of 2.5 Mg m⁻³, contribute to "soluble" Al, Fe, or Si measured by IC-

PAES. Indeed, relative intensity exhibits a pH dependence which correlates well with dissolution data in the high pH ranges (Figs. 1, 3–5) and increases above the p.z.n.c. for each soil. Figure 9 shows relative scattering intensity plotted against the sum of Al, Fe, and Si concentrations determined by ICPAES at "pH" > p.z.n.c. A positive correlation is apparent and consistent with the plateaux at Si/Al = Fe/Al = 1.0 in Figs. 6–7, which may simply reflect the release of kaolinitic and oxidic colloids into the aqueous phase as in-

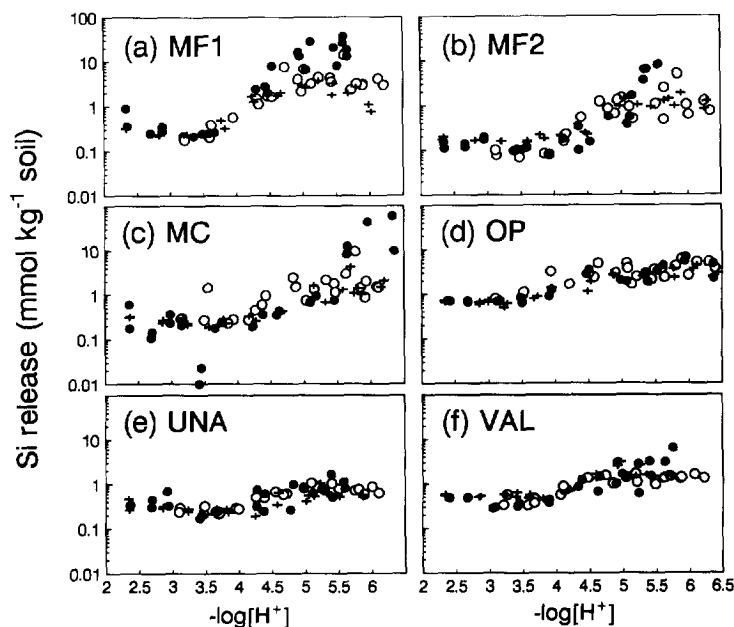


FIG. 5. Si release in LiCl solution as a function of "pH." Ionic strength: open circles—0.001 mol kg⁻¹; crosses—0.005 mol kg⁻¹; closed circles—0.01 mol kg⁻¹.

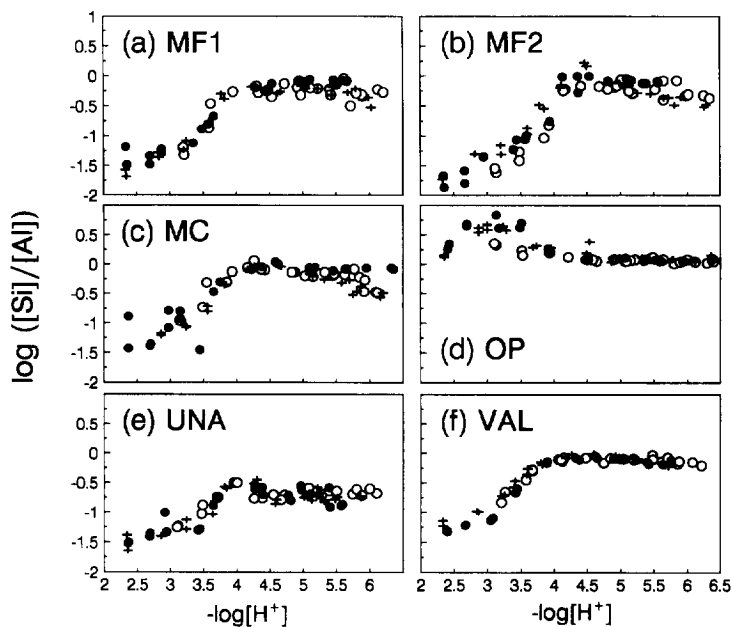


FIG. 6. Log Si/Al released vs. "pH." Ionic strength: open circles—0.001 mol kg⁻¹; crosses—0.005 mol kg⁻¹; closed circles—0.01 mol kg⁻¹.

duced by an overall negative surface charge at "pH" > p.z.n.c.

4. DISCUSSION

The fractional-order dependence of R_{II} on $[H^+]$ found in the present study (Table 4) is consistent with a surface-controlled dissolution reaction (Stumm and Wollast, 1990). The fractional-order dependence of 0.66–0.85 indicated in Table 4 is

much higher than that observed for specimen kaolinite [$n = 0.24$, Wieland and Stumm (1992)], a difference possibly correlated with organic C content (Table 1). For example, the soils highest in organic C (MF1 and UNA) show the highest Al release at a given "pH," whereas the soils lowest in organic C (MC and OP) exhibit low Al release (Figs. 1, 2b). Microcrystalline source phases may also contribute to the higher fractional-order dependence observed. In a study of gibbsite dissolution kinetics, Bloom and Erich (1987) re-

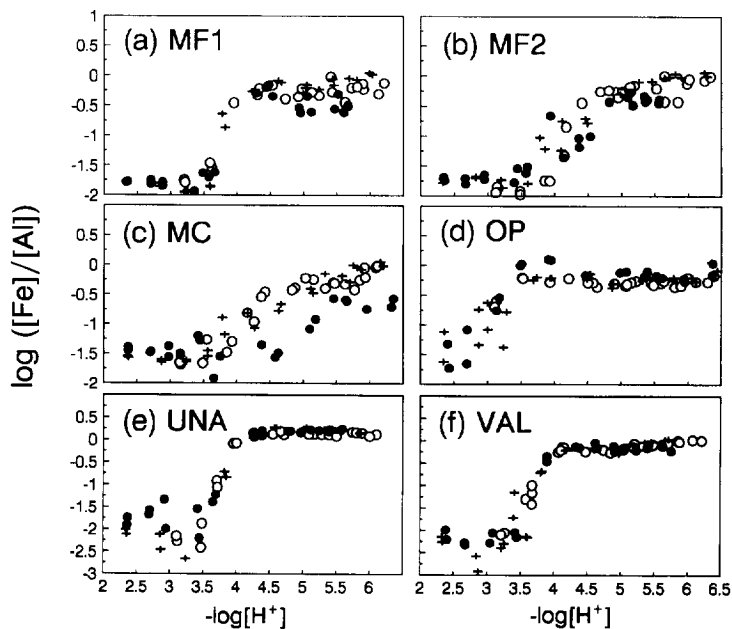


FIG. 7. Log Fe/Al released vs. "pH." Ionic strength: open circles—0.001 mol kg⁻¹; crosses—0.005 mol kg⁻¹; closed circles—0.01 mol kg⁻¹.

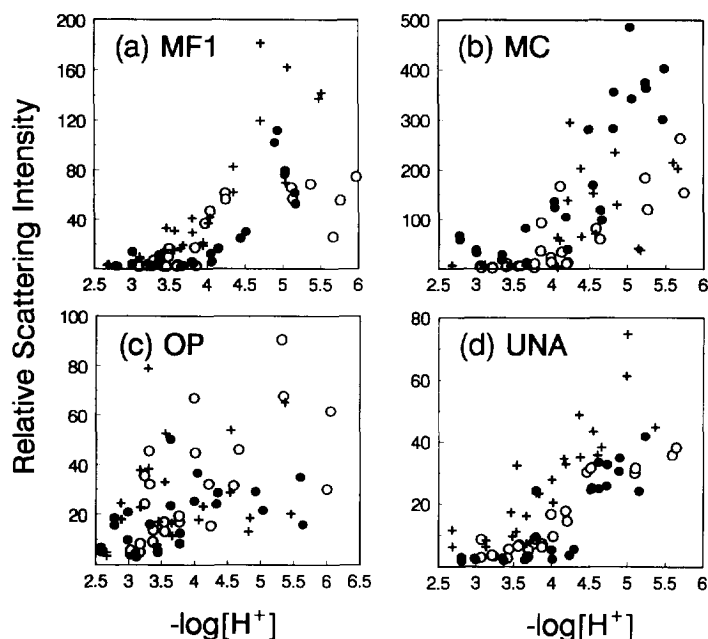


FIG. 8. Relative scattering intensity of supernatant solutions separated from soil suspensions by high speed centrifugation. Ionic strength: open circles—0.001 mol kg⁻¹; crosses—0.005 mol kg⁻¹; closed circles—0.01 mol kg⁻¹.

ported a pH dependence of Al release rate in HNO₃ solution that was similar to those found for the soils studied here. Regardless of the source phases, if the dissolution mechanism(s) is (are) proton promoted and surface reaction limited, correlation of Al release rate with net proton surface charge, σ_H , is expected (Stumm, 1992). The dissolution rates of soils have not been related previously to σ_H as a "master variable." To examine the correlation of Al release rate with σ_H , this latter parameter was calculated with the surface charge data of Choro-ver and Sposito (1995a) according to the following equation:

$$\sigma_H = -[(q_+ - q_-) + \sigma_O], \quad (2)$$

where q_+ is the surface excess of cation charge, q_- is the surface excess of anion charge, and σ_O is the net structural charge density as measured by Cs⁺ adsorption (Table 1). The logarithm of R_H is plotted against $\log \sigma_H$ in Fig. 10. Linear regression results for each soil (over all ionic strengths) are presented in Table 4 (right side). Significant variability in the data is reflected in the R^2 values and slope confidence limits given in Table 4. The increased variability in the $\log R_H - \log \sigma_H$ plots, relative to $\log R_H - \log[H^+]$ plots, primarily reflects variability in the Li⁺ and Cl⁻ adsorption data (Choro-ver and Sposito, 1995a).

Wieland and Stumm (1992) concluded that the rate of proton-promoted dissolution at pH < 4 for specimen kaolinite was limited by the detachment of an Al center, followed by rapid hydrolysis of a Si atom. Given a surface-control model of proton-promoted dissolution from both edge and gibbsite surface sites of kaolinite, the dependence of $\log R_H$ on $\log \sigma_H$ is expected to be linear, with a slope between 1 and 3 (Wieland and Stumm, 1992). This predicted dependence is consistent with the results in Table 4, although the slopes of the regression lines may be >3 for soils higher in organic matter and metal oxides (MF1, UNA, and VAL). The regression results for soils UNA and VAL, with higher Al oxide content (Tables 2, 3), are more consistent with experimental data on synthetic hydrous oxides (Furrer and Stumm, 1986).

However, slopes between 1 and 3 in log-log plots of R_H vs. σ_H also would be expected for dissolution processes that liberate Al from the combination of coordination environments that exist in soil, each with its own range of kinetic parameters (e.g., 2:1 clay minerals, hydroxy interlayers, Al-humus complexes). For example, organic and amorphous solid phases can account for most of the Al released from spodic soil horizons within the first few hours of dissolution at low pH

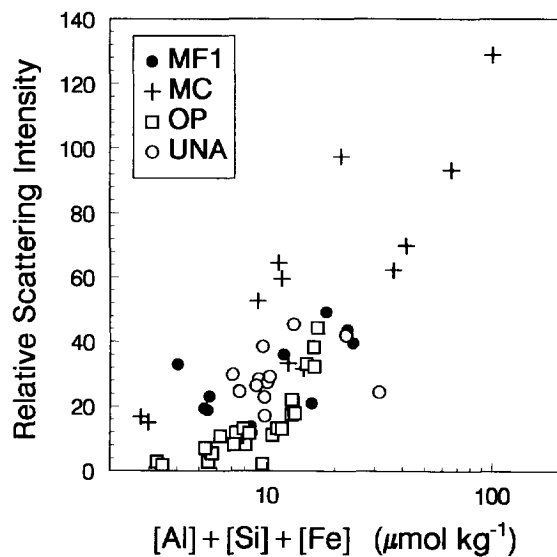


FIG. 9. Relative scattering intensity plotted against the sum of Al, Fe, and Si concentrations in supernatant solutions ($I = 0.005$ mol kg⁻¹) separated from soil suspensions by high-speed centrifugation.

TABLE 4. Linear regression of log "Al dissolution rate" (R_H , mmol kg⁻¹ hr⁻¹) on "pH" or log σ_H . Regression slope confidence intervals (95%) are indicated in parentheses.

Soil	Regression Equation	R ²	Regression Equation	R ²
MF1	log R_H = -0.60 - 0.75 (0.08) "pH"	0.98 a \ddagger	log R_H = 2.41 + 3.1 (1.04) log σ_H	0.62 b \ddagger
MF2	log R_H = -0.60 - 0.79 (0.08) "pH"	0.96 a	log R_H = -0.23 + 1.5 (0.53) log σ_H	0.53 a
MC	log R_H = -0.88 - 0.74 (0.20) "pH"	0.83 a	log R_H = -0.12 + 1.6 (0.45) log σ_H	0.66 a
UNA	log R_H = -0.80 - 0.66 (0.11) "pH"	0.94 a	log R_H = 3.71 + 3.7 (0.68) log σ_H	0.84 c
VAL	log R_H = -0.40 - 0.85 (0.07) "pH"	0.98 a	log R_H = 4.25 + 3.8 (0.96) log σ_H	0.73

\ddagger Level of significance (a) $p < 0.0001$, (b) $p < 0.001$, (c) $p < 0.01$

(Dahlgren and Walker, 1993). The maximum quantities of Al released per unit mass of soil in the present study (Fig. 1) are equal to or less than the oxalate-extractable Al for each soil (Table 3), suggesting that Al released in a 3 h period was derived from this strictly operationally defined pool. Large differences in CDB-extractable Al (Table 3) do not produce large differences in dissolution rate (Fig. 2b), indicating that this operational pool does not provide a predictive index of rapidly mobilized Al.

The sharp decline in Al release with increasing "pH" between 2 and 4 (Fig. 1) may be related to the readsorption of Al. The surface excess of Al ("exchangeable Al") following the 3 h reaction time for three soils is plotted against "pH" in Fig. 11. An increase in NH₄NO₃ exchangeable Al with "pH" was observed for all but soil OP. For all three soils, maximum adsorption was reached near the p.z.n.c. (arrows in Fig. 1). Adsorption of Al by organic matter is expected to increase with "pH" because of Al hydrolysis and increases in the negative charge (ionization) of organic matter (Zelazny

and Jardine, 1989). At "pH" > 4, hydroxy-Al species may form (Bertsch, 1989) which are more readily complexed by organic matter than Al³⁺ because of their lower charge and solvation and their larger size (Zelazny and Jardine, 1989). Moreover, even small quantities of Al in solution can precipitate on the surface of kaolinite (Jardine et al., 1985; Zelazny and Jardine, 1989).

The release of Si from the soils may be caused by the dissolution of amorphous silica, disordered aluminosilicates, kaolinite, or quartz. Unlike Al or Fe, Si does not form surface complexes with solid-phase organic matter, and this fact may be relevant to the close correspondence between Si release from the soils and that reported for specimen kaolinite. Below the p.m.d., Si release was even quantitatively consistent with the reported dissolution behavior of specimen kaolinite, decreasing slightly with increasing "pH" for each soil (Fig. 5). Adsorption of Si by the soil was negligible (Chorover, 1993). Similar behavior is well documented for kaolinite (Carroll-Webb and Walther, 1988; Carroll and Walther, 1990; Wieland and Stumm, 1992).

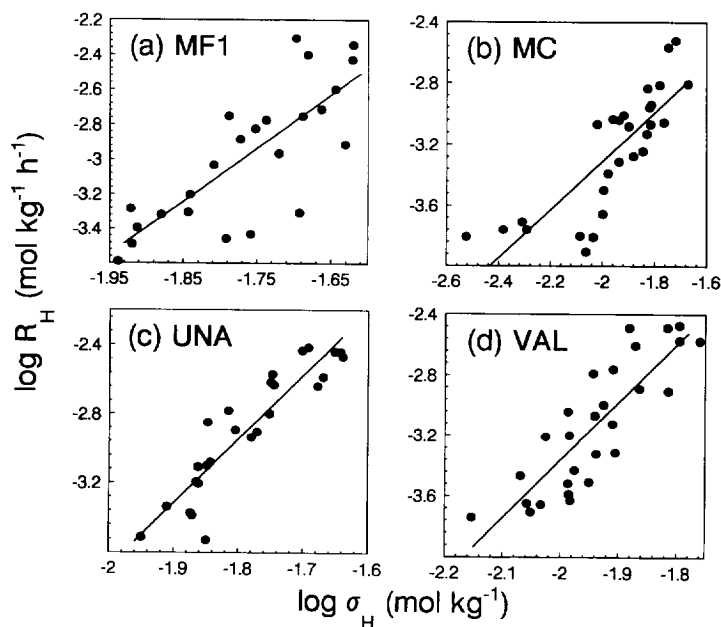


FIG. 10. Apparent Al dissolution rate (R_H) as a function of net proton surface charge density (σ_H) for four soils. Data at all ionic strengths are combined. Regression lines from Table 4 also are shown.

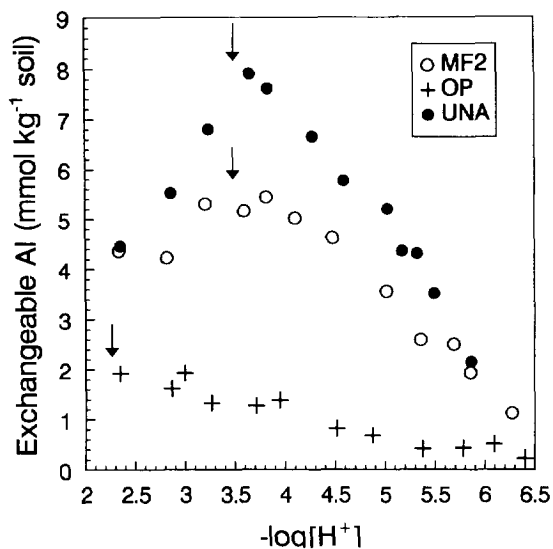


FIG. 11. "Exchangeable" Al following 3 h batch equilibration. Maximum values of exchangeable Al occur near the p.z.n.c. (denoted by arrow).

Mean Si release rates for the soils (in $\text{mmol kg}^{-1} \text{h}^{-1}$) below the p.m.d., calculated from the data in Fig. 5, ranged from 0.02–0.3 at "pH" 3.5 to 0.03–0.3 at "pH" 2. Steady-state Si release rates for kaolinite in the same units and similar pH range are much lower: 0.004–0.02 at pH 4 to 0.013–0.05 at pH 2 (Carroll-Webb and Walther, 1988; Wieland and Stumm, 1992). Chin and Mills (1991) found that addition of 5 mol m^{-3} oxalate at pH 4.25 increased the Si release rate of kaolinite by nearly three times. Wieland and Stumm (1992) reported a twofold increase with the same oxalate addition at pH 4, and significant increases in dissolution rate were observed throughout the pH range 2–6 in the presence of 1 mol m^{-3} oxalate. These rates of Si release from kaolinite provoked by complexing ligands are in the range of those observed in the present study. Thus, dissolved organic matter (Fig. 4) could have enhanced Si release from the soils. The rate of quartz dissolution also is enhanced in the presence of organic ligands, but the magnitude of enhancement depends on the structure of the organic ligand (Bennett et al., 1988). Even low ambient concentrations of Al can suppress the quartz dissolution rate, possibly by precipitating as a layer of aluminosilicate on the quartz surface (Beckwith and Reeve, 1963). Oxide coatings on silicate minerals also can reduce Si release by obstructing diffusion or adsorbing released Si (Beckwith and Reeve, 1964).

The close proximity of p.z.n.c. and p.m.d. values for each of the kaolinitic soils indicates that, like specimen mineral constituents, soil dissolution behavior is highly dependent upon particle surface charge. However, although the release patterns for all soils are remarkably consistent, these patterns differ fundamentally from those of specimen kaolinite and pure Fe and Al oxides. Proton promoted dissolution is evident below the p.m.d. (Fig. 10). But the low p.m.d. values (Figs. 1, 3–5) and the increased Fe and Si relative to Al as "pH" is increased above the p.z.n.c. (Figs. 6, 7) indicate the impor-

tance of a physical release of microcolloidal material, which is itself dependent upon surface charge.

The transition into a physical release, i.e., a "dispersive dissolution" regime, above the p.z.n.c. is consistent with a detailed investigation of the colloid chemistry of the same soils (Chorover and Sposito, 1995b). In that study, a change from slow to rapid colloid flocculation with decreasing "pH" was found to coincide with the p.z.n.c. values of the whole soils and was attributed to the progressive protonation of adsorbed organic matter. Electrophoretic mobilities of the soil colloids were very uniform and much more negative than their major mineralogical components. The data were consistent with the behavior of heterogeneous inorganic colloids coated with organic matter bearing carboxylic functional groups (Chorover and Sposito, 1995b). The close agreement between acid dissociation constants of carboxylic functional groups (Perdue, 1985) and the p.m.d. and p.z.n.c. values of the soils studied here, suggests that the charge behavior of organic matter is a major factor controlling element release patterns. Both aqueous complexation and colloidal stabilization mechanisms may be involved.

Heyes and Moore (1992) measured higher concentrations of Fe in supernatant solutions separated from suspensions of Fe-rich sediments than were predicted with thermodynamic data for model Fe-organic complexes. They attributed this discrepancy to the presence of colloidal Fe-organic aggregates. The present work supports their suggestion that such particles may be the natural "weathering products" of soils containing Al and Fe oxides and soluble organic C. At the field scale, dispersive dissolution may explain the high concentrations of "dissolved" ($<0.45 \mu\text{m}$) Fe and Al measured in dilute rivers of the humid tropics (Stallard, 1985) where the colloid chemistry of soil weathering may play an important role.

5. CONCLUSIONS

The short-time dissolution behavior of kaolinitic tropical soils exhibits a strong pH dependence, with dissolution minima (p.m.d.) occurring at 0.4–0.9 pH units above the p.z.n.c. Below the p.m.d., the release rate follows the order: Al > Si > Fe. The pH dependence of Al and Fe release are similar, although Al release dominates at low pH. Silicon release exhibits less pH dependence and, below the p.m.d., is consistent with Si release data for specimen kaolinite. The molar ratios of Si/Al and Fe/Al released approach 1.0 with increasing pH between 2.0 and the p.m.d. Although the soils investigated differ significantly in crystalline Fe and Al oxides, the release rates of Al and Fe do not differ much among the soils. At a given pH value, Al and Fe release also are correlated positively with organic carbon content. Below the p.m.d., the excess of Al released relative to Si and Fe may be attributed to rapidly mobilized Al in organic solid phases in the soils. The relative contribution of this organically bound pool increases with decreasing pH. Above the p.z.n.c., colloidal dispersion contributes to the measured values of "dissolved" metal and, as a result, could enhance metal mobility into drainage waters.

Acknowledgments—Gratitude is expressed to Cheryl Palm, Peter Motavalli, and Paul Smithson for their gracious provision of the soil samples and basic physicochemical data on those samples in support

of the present study. An earlier version of the manuscript was greatly improved by the thoughtful comments of Dr. Susan Carroll and two anonymous reviewers. Thanks also to Terri DeLuca and Darlene Berry for excellent typing of the manuscript. The research reported in this paper was supported in part by NSF grant no. EAR 92-21258 and the Kearney Foundation of Soil Science.

Editorial handling: J. D. Rimstidt

REFERENCES

- Anbeek C. (1993) The effect of natural weathering on dissolution rates. *Geochim. Cosmochim. Acta* **57**, 4963–4975.
- Beckwith R. S. and Reeve R. (1963) Studies on soluble silica in soils. I. The sorption of silicic acid by soils and minerals. *Aust J. Soil Res.* **1**, 157–168.
- Beckwith R. S. and Reeve R. (1964) Studies on soluble silica in soils. II. The release of monosilicic acid from soils. *Aust J. Soil Res.* **2**, 33–45.
- Bennett P. C. and Siegel D. I. (1987) Increased solubility of quartz in water due to complexing by organic compounds. *Nature* **326**, 684–687.
- Bennett P. C., Melcer M. E., Siegel D. I., and Hassett J. P. (1988) The dissolution of quartz in dilute aqueous solutions of organic acids at 25°C. *Geochim. Cosmochim. Acta* **52**, 1521–1530.
- Berner E. K. and Berner R. A. (1987) *The Global Water Cycle*. Prentice-Hall.
- Bertsch P. (1989) Aqueous polynuclear aluminum species. In *The Environmental Chemistry of Aluminum* (ed. G. Sposito), pp. 87–115. CRC Press.
- Bloom P. R. (1983) The kinetics of gibbsite dissolution in nitric acid. *Soil Sci. Soc. Amer. J.* **47**, 164–168.
- Bloom P. R. and Erich M. S. (1987) Effect of solution composition on the rate and mechanism of gibbsite dissolution in acid solutions. *Soil Sci. Soc. Amer. J.* **51**, 1131–1136.
- Cambier P. and Prost R. (1981) Etude des associations argile-oxyde: Organisation des constituants d'un matériau ferralitique. *Agronomie* **1**, 713–722.
- Carroll S. A. and Walther J. V. (1990) Kaolinite dissolution at 25°, 60°, and 80°C. *Amer. J. Sci.* **290**, 797–810.
- Carroll-Webb S. A. and Walther J. V. (1988) A surface complex reaction model for the pH-dependence of corundum and kaolinite dissolution rates. *Geochim. Cosmochim. Acta* **52**, 2609–2623.
- Chin P. K. F. and Mills G. L. (1991) Kinetics and mechanisms of kaolinite dissolution: effects of organic ligands. *Chem. Geol.* **90**, 307–317.
- Chorover J. (1993) Surface charge and colloidal properties of benchmark Brazilian Oxisols. Ph.D. thesis, Univ. California, Berkeley.
- Chorover J. and Sposito G. (1993) *Measurement of Soil Surface Charge Components*. Tech. rept. NSF grant EAR 9221258. Univ. California Berkeley.
- Chorover J. and Sposito G. (1995a) Surface charge characteristics of kaolinitic tropical soils. *Geochim. Cosmochim. Acta* **59**, 875–884.
- Chorover J. and Sposito G. (1995b) Colloid chemistry of kaolinitic tropical soils. *Soil Sci. Soc. Amer. J.* (in press).
- Dahlgren R. A. and Walker W. J. (1993) Aluminum release rates from selected Spodosol Bs Horizons: effect of pH and solid phase Al pools. *Geochim. Cosmochim. Acta* **57**, 57–66.
- Erich M. S. and Bloom P. R. (1987) The effect of solution composition on the rate and mechanism of gibbsite dissolution in acid solutions. *Soil Sci. Soc. Amer. J.* **51**, 1131–1136.
- Ertel J. R., Hedges J. I., Devol A. H., Richey J. E., and Ribeiro M. N. G. (1986) Dissolved humic substances of the Amazon River system. *Limnol. Oceanogr.* **31**, 739–754.
- Fontes M. P. F. (1992) Iron oxide-clay mineral association in Brazilian Oxisols: A magnetic separation study. *Clays Clay Mineral.* **40**, 175–179.
- Furch K. (1984) Water chemistry of the Amazon Basin: The distribution of chemical elements among freshwaters. In *The Amazon: Limnology and Landscape Ecology of a Mighty Tropical River and Its Basin* (ed. H. Sioli), pp. 167–200. Dr. Junk Publishers.
- Furrer G. and Stumm W. (1986) The coordination chemistry of weathering: I. Dissolution kinetics of δ - Al_2O_3 and BeO. *Geochim. Cosmochim. Acta* **50**, 1847–1860.
- Furrer G., Sollins P., and Westall J. C. (1990) The study of soil chemistry through quasi-steady-state models. II. Acidity of soil solution. *Geochim. Cosmochim. Acta* **54**, 2363–2374.
- Gran G. (1952) Determination of the equivalence point in potentiometric titrations. Part II. *Analyst* **77**, 661–671.
- Hedges J. I. et al. (1986) Compositions and fluxes of particulate organic material in the Amazon River. *Limnol. Oceanogr.* **3**, 717–738.
- Heilman M. D., Carter D. L., and Gonzales G. L. (1965) The ethylene glycol monoethyl ether (EGME) technique for determining soil surface area. *Soil Sci.* **100**, 409–413.
- Heyes A. and Moore T. R. (1992) The influence of dissolved organic carbon and anaerobic conditions on mineral weathering. *Soil Sci.* **154**, 226–236.
- Hughes J. C. (1981) Mineralogy. In *Characterization of Soils in Relation to Their Classification and Management for Crop Production: Examples From Some Areas of the Humid Tropics* (ed. D. J. Greenland), pp. 30–50. Clarendon Press.
- Jackson M. L., Lim C. H., and Zelazny L. W. (1986) Oxides, hydroxides and aluminosilicates. In *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods* (ed. A. Klute), pp. 101–150. Soil Sci. Soc. America.
- Jardine P. M., Zelazny L. W., and Parker J. C. (1985) Mechanisms of aluminum adsorption by clay minerals and peat. *Soil Sci. Soc. Amer. J.* **49**, 862–869.
- Juo A. S. R. (1981) Chemical characteristics. In *Characterization of Soils in Relation to Their Classification and Management for Crop Production: Examples From Some Areas of the Humid Tropics* (ed. D. J. Greenland), pp. 51–79. Clarendon Press.
- Kronberg B. I., Fyfe W. S., Leonardos O. H., and Santos A. M. (1979) The chemistry of some Brazilian soils: Element mobility during intense weathering. *Chem. Geol.* **24**, 211–229.
- Leenheer J. A. (1980) Origin and nature of humic substances in the waters of the Amazon River Basin. *Acta Amazonica* **10**, 513–526.
- Lindsay W. L. (1979) *Chemical Equilibria in Soils*. Wiley.
- Motavalli P. P., Palm C. A., Elliott E. T., Parton W. J., and Frey S. D. (1994) Comparison of laboratory and modeling simulation methods for estimating soil carbon pools in tropical forest soils. *Soil Biol. Biochem.* **26**, 935–944.
- Motavalli P. P., Palm C. A., Elliott E. T., Frey S. D., and Smithson P. C. (1995) Nitrogen mineralization in humid tropical forest soils related to mineralogy, texture and measured N fractions. *Soil Sci. Soc. Amer. J.* (in press).
- Mulder J. and Stein A. (1994) The solubility of aluminum in acidic forest soils: long-term changes due to acid deposition. *Geochim. Cosmochim. Acta* **58**, 85–94.
- Oades J. M., Waters A. G., Vassallo A. M., Wilson M. A., and Jones G. P. (1988) Influence of management on the composition of organic matter in red-brown earth as shown by ^{13}C nuclear magnetic resonance. *Aust. J. Soil Res.* **26**, 289–299.
- Paçes T. (1983) Rate constants of dissolution derived from measurements of mass balance in hydrological catchments. *Geochim. Cosmochim. Acta* **47**, 1855–1863.
- Perdue E. M. (1985) Acidic functional groups of humic substances. In *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation and Characterization* (ed. G. R. Aiken et al.) pp. 493–526. Wiley.
- Reuss J. O., Walthall P. M., Rosali E. C., and Hopper R. W. E. (1990) Aluminum solubility, calcium-aluminum exchange, and pH in acid forest soils. *Soil Sci. Soc. Amer. J.* **54**, 374–380.
- Robarge W. P. and Johnson D. W. (1992) The effects of acidic deposition on forested soils. *Adv. Agron.* **47**, 1–83.
- Santos M. C. D., Mermut A. R., and Ribeiro M. R. (1989) Submicroscopy of clay microaggregates in an Oxisol from Pernambuco, Brazil. *Soil Sci. Soc. Amer. J.* **53**, 1895–1901.
- Schnoor J. (1990) Kinetics of chemical weathering: A comparison of laboratory and field weathering rates. In *Aquatic Chemical Kinetics* (ed. W. Stumm), pp. 475–504. Wiley-Interscience.
- Schwertmann U. (1991) Solubility and dissolution of iron oxides. *Plant and Soil* **130**, 1–25.

- Singh R. and Gilkes R. J. (1992) Properties of soil kaolinites from south-western Australia. *J. Soil Sci.* **43**, 645–667.
- Stoli H. (1975) Tropical rivers as expressions of their terrestrial environments. In *Tropical Ecological Systems. Trends in Terrestrial and Aquatic Research* (ed. F. B. Golley and E. Medina), pp. 275–288. Springer Verlag.
- Sposito G. (1989) *The Chemistry of Soils*. Oxford Univ. Press.
- Stallard R. F. (1985) River chemistry, geology, geomorphology, and soils in the Amazon and Orinoco Basins. In *The Chemistry of Weathering* (ed. J. I. Drever), pp. 293–316. D. Reidel.
- Stallard R. F. (1988) Weathering and erosion in the humid tropics. In *Physical and Chemical Weathering in Geochemical Cycles* (ed. A. Lerman and M. Meybeck), pp. 225–246. Kluwer.
- Stallard R. F. and Edmond J. M. (1983) Geochemistry of the Amazon. 2. The influence of geology and weathering environment on the dissolved load. *J. Geophys. Res.* **88**, 9671–9688.
- Stumm W. (1992) *Chemistry of the Solid-Water Interface*. Wiley.
- Stumm W. and Wollast R. (1990) Coordination chemistry of weathering: Kinetics of the surface controlled dissolution of oxide minerals. *Rev. Geophys.* **28**, 53–69.
- Stumm W., Furrer G., and Kunz B. (1983) The role of surface coordination in precipitation and dissolution of mineral phases. *Croat. Chem. Acta* **56**, 593–611.
- Stumm W., Furrer G., Wieland E., and Zinder B. (1985) The effects of complex forming ligands on the dissolution of oxides and aluminosilicates. In *The Chemistry of Weathering* (ed. J. I. Drever), pp. 55–74. D. Reidel.
- Van Grinsven J. J. M. and Van Riemsdijk W. H. (1992) Evaluation of batch and column techniques to measure weathering rates in soils. *Geoderma* **52**, 41–57.
- Velbel M. A. (1985) Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge. *Amer. J. Sci.* **285**, 904–930.
- Vitorello V. A., Cerri C. C., Andreux F., Feller C., and Victoria R. L. (1989) Organic matter and natural carbon-13 distribution in forested and cultivated Oxisols. *Soil Sci. Soc. Amer. J.* **53**, 773–778.
- Wieland E. and Stumm W. (1992) Dissolution kinetics of kaolinite in aqueous solutions at 25°C. *Geochim. Cosmochim. Acta* **56**, 3339–3355.
- Wollast R. and Chou L. (1985) Kinetic study of the dissolution of albite with a continuous flow through fluidized bed reactor. In *The Chemistry of Weathering* (ed. J. I. Drever), pp. 75–96. D. Reidel.
- Xie Z. and Walther J. V. (1992) Incongruent dissolution and the surface area of kaolinite. *Geochim. Cosmochim. Acta* **56**, 3357–3363.
- Zelazny L. W. and Jardine P. M. (1989) Surface reactions of aqueous aluminum species. In *The Environmental Chemistry of Aluminum* (ed. G. Sposito), pp. 147–184. CRC Press.
- Zinder B., Furrer G., and Stumm W. (1986) The coordination chemistry of weathering. II. Dissolution of Fe(III) oxides. *Geochim. Cosmochim. Acta* **50**, 1861–1869.