GEOCHEMISTRY OF THE AMAZON
3. WEATHERING CHEMISTRY AND LIMITS TO DISSOLVED INPUTS

R. F. Stallard

Department of Geological and Geophysical Sciences
Princeton University, Princeton, New Jersey

J. M. Edmond

Department of Earth, Atmospheric, and Planetary Sciences
Massachusetts Institute of Technology, Cambridge

Abstract. Chemical mass balance models of river solution chemistry, constrained by geologic data and thermodynamic models, provide a consistent description of the weathering processes that occur in the Amazon Basin. In areas with high weathering rates, such as the Andes, calcium, magnesium, sulfate, and alkalinity come from the weathering of evaporite minerals, sulfides, and carbonates. The inputs of calcium, magnesium, and alkalinity from exclusively carbonate terrains are limited by calcite, and perhaps by dolomite, saturation. When evaporites are present, only the alkalinity inputs are so limited because of additional weathering sources of calcium and magnesium. Dissolved silica, potassium, and sodium can be used to define mass balance relationships that in turn establish the nature of the clay mineral suites which are consistent with solute compositions. Use of thermodynamic constraints, specifically kaolinite and quartz stability, assists in data interpretation. At lowest weathering rates, all common primary minerals exposed to weathering are broken down to release silica and cations; quartz, kaolinite and (Fe,Al)-sesquioxides all appear to be unstable. At higher weathering rates, enough silica is available to stabilize kaolinite, then quartz. The stabilization of Si-bearing phases is reflected by a drop in the ratio of silica to other dissolved components. Finally, at the highest weathering rates, such as in the Andean catchments, high cation levels result in the formation of the 2:1 clays, which sequester even more silica, and any clear relationship between silica and other solutes degenerates.

Introduction

This is the third in a series of papers describing the aqueous geochemistry of the Amazon River system. The first [Stallard and Edmond, 1981] examines atmospheric contributions to the dissolved load of salts derived from outside the drainage basin proper. The second [Stallard and Edmond, 1983] relates the water chemistry of tributaries to the geology and environment particular to their individual catchments (all geologic background and chemical analyses are presented therein).

A primary objective of the present paper is to identify major chemical aspects of the weathering

process that control the breakdown of silicate and carbonate rocks. The basic approach is to construct simple reaction mass balance models which predict characteristic relationships between various dissolved species. To delimit the types of reactions which might play a major role during weathering, compositional information about bedrock, soils, and river solid load will be considered. A further constraint of possible reactions will come from thermodynamic models specifying mineral stability. Carbonate weathering will be examined first because of the simplicity of reactions.

Background

Erosion products are generated by a complex series of weathering reactions acting in tandem with a variety of physical processes. Erosional regimes in the Andean and lowland parts of the Amazon basin are characterized as weathering-limited and transport-limited, respectively [Stallard and Edmond, 1983; Stallard, 1985]. In the Andes, physical transport processes efficiently remove solids generated by weathering. Erosional contributions to rivers by different lithologies are proportional to both the fraction of their catchments underlain by the respective lithologies and the susceptibility of each lithology to weathering. As a result of limited reaction time, erosion products include fresh rock fragments, primary mineral grains, and partially degraded micas. In weathering-limited regimes, the solutes in river water result from reactions that presumably control susceptibility to weathering and thus rates of erosion. In the lowlands, transport processes are not particularly vigorous, because of the slight slopes, and are unable to effectively remove solid weathering products. This results in the accumulation of thick soils. Solid erosion products are cation-poor. Water does not circulate efficiently into deep or indurated soil profiles where it can contact fresh rock. Chemical weathering rates are thereby limited. The extreme case of transport-limited erosion would involve a completely flat landscape, being lowered at a uniform rate. Erosional contributions from different lithologies to a river draining this landscape would be proportional to the fraction of the area underlain by the respective lithologies. Parts of the Amazon lowlands approximate this condition rather well. In transport-limited regimes, solution products reflect varying degrees of reaction with primary and secondary minerals under conditions where weathering rates are presumably controlled

by hydrologic factors. For both types of weathering regimes, kinetic factors rather than thermodynamic equilibria appear to control weathering rate.

Reaction Mass Balance Models and Large River Systems

The net effect of weathering reactions can be examined, often graphically, through identification of reaction mass balance relationships for dissolved components. This approach is based on the observation that different weathering reactions produce dissolved species in characteristic, though not unique, proportions. The set of possible reactions can be constrained by examination of the composition of bedrock, soil, and solid load, and by thermodynamic models of mineral stability. The reaction mass balance approach as the strong advantage of being applicable to kinetically controlled reactions far from thermodynamic equilibrium.

The use of reaction product ratios for Amazonian waters is introduced by Stallard and Edmond [1983]. Here, the composition of dissolved erosion products is calculated from analyses of river waters by subtraction of cyclic salt contributions and consideration of other possible perturbations (biological, human). Characteristic 1 to 1 equivalent relationships between (Na+K) and Cl, (Ca+Mg) and (SO_4+alkalinity), and in most cases (Ca+Mg) and alkalinity are observed in waters high in total cations (TZ+ > 400-500 eq/L) typical of Andean rivers. In view of geologic constraints, the major ion chemistry of these waters is largely explained by the congruent dissolution of carbonate and evaporite minerals.

A similar treatment involving silicate rock weathering is much more difficult because of the variety of solid phases (typically clays and sesquioxides) generated by incongruent reactions. The extent to which primary silicate minerals degrade and the nature of secondary products which form are highly variable and depend on local geomorphic conditions; consequently, a potentially wide range in solution compositions can result from the breakdown of a single lithology.

Thermodynamic Models and Large River Systems

Thermodynamic models have proven valuable in geochemical studies of systems where local equilibration can be assumed. Such models provide a test of whether particular minerals might form or degrade as a result of weathering within a river basin.

Rivers do not fulfill many of the requirements that go into rigorous thermodynamic modeling of simple closed systems. They are very heterogeneous spatially and temporally, very open, and affected by complicated physical, biological, and chemical processes. Mineral assemblages found in soils and suspended loads of rivers are not equilibrium assemblages.

The utility of applying thermodynamic calculations to Amazon surface waters must therefore be evaluated. In doing such calculations, it is implicitly assumed that rivers draining silicates and carbonate rocks can be treated as having geologically homogeneous catchments. Two observations suggest that this should not lead to unrea-

sonable results. First, the nearly ubiquitous distribution of silicate rocks of acid to intermediate composition (containing roughly the same minerals, but in different proportions) limits the number of silicate weathering reactions that may occur, especially in smaller catchments. Second, weathering of reactive carbonate minerals dominates the chemistry of catchments where carbonates are abundant [Stallard and Edmond, 1983]. Thermodynamic models are formulated logarithmically; consequently, considerable dilution must occur before the equilibria that characterize the carbonate system are obscured in plots of grouped data. The chemistry of the rare evaporite-dominated stream is very distinctive and can be treated separately.

In rivers, a number of nonconservative changes in the fluid composition caused by processes not directly related to weathering can affect the results of thermodynamic modeling. The most important of these include gas exchange, mixing of different waters, precipitation of solids, ion exchange, and biological release and uptake of solutes. Observations from várzea (flood plain) lakes suggest that for samples from this study, biological effects on the major ions and silica are inconsequential [Stallard and Edmond, 1983]. Likewise, the cations sequestered on exchange sites on river-borne clays are a small fraction of those in the dissolved load [Sayles and Mangelsdorf, 1979]. For thermodynamic modeling in tropical rivers, perhaps the most significant problem involves fluctuations of carbon dioxide partial pressure (P_{CO_2}). These in turn affect the hydrogen ion activity in the river water.

Carbon Dioxide Loss and pH Changes

Soil and groundwaters tend to have high P_{CO_2} values. P_{CO_2} values in temperate soils range from 5 to >20 times that of the atmosphere [Holland, 1978]. There are few data for tropical rain forest soils. For rain forests of Costa Rica, Johnson et al. [1975] report soil P_{CO_2} values averaging 70 times atmospheric P_{CO_2}. Medina et al. [1986] report values at 30-cm depth forest soils to be 4-5 times ambient values and to increase linearly with depth. In poorly aerated caatinga soils nearby, CO_2 levels are more than tenfold higher than atmospheric levels. P_{CO_2} was not measured at greater depths, and values near fresh rock are probably higher. A range of 5-100 times atmospheric values for P_{CO_2} seems reasonable for tropical soils. Once groundwaters join surface waters, the loss of the carbon dioxide to the atmosphere or loss to the organic carbon reservoir via fixation will raise pH. This can lead to the supersaturation of some phases such as carbonates. Respiration adds CO_2 and has the opposite effect.

The Amazon River and most of its tributaries exhibit high levels of respiration relative to productivity [see Richey et al., 1980]. This situation is reversed in some ponded waters on the várzea and at the lakelike mouths of some tributaries (e.g., Xingu, Tapajós, Negro). Isotopically, the inorganic carbon in river waters throughout the basin is very light (-11 to -28 per mil). This is attributed to the high transfer rate of river-borne carbon from organic, to dissolved inorganic, thence to atmospheric reser-
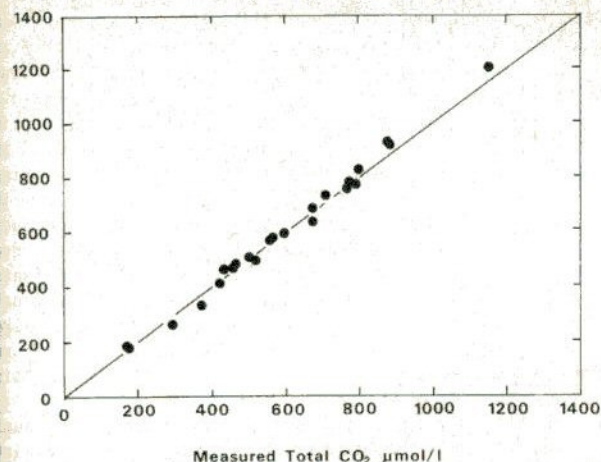
Fig. 1. Total carbon dioxide measured directly versus that predicted from alkalinity and pH. Errors are the greater of 10% or 10 mol/L for direct and 10% or 50 mol/L for predicted.

voirs [Longinelli and Edmond, 1983]. In such a respiration-dominated system, high P_{CO_2} values are expected.

For the samples from this study, total carbon dioxide (TCO_2) and P_{CO_2} were calculated from measured pH and alkalinity. To insure that sample pH was not affected by CO_2 loss, pH was either analyzed in situ or in a closed system using samples that were sealed while submerged. Data are tabulated by Stallard and Edmond [1983, Appendix III]:

$$TCO_2 = ((alk + [H] - K_w/[H])([H]/K_1 + 1 + K_2/[H])) / (1 + 2K_2/[H]) \quad (1)$$

$$PCO_2 = ([H](alk + [H] - K_w/[H])) / (K_0K_1(1 + 2K_2/[H])) \quad (2)$$

K_0, K_1, K_2, and K_w are the Henry's law and the apparent first and second association constants for carbonic acid, and the apparent association constant for water, respectively. These constants, corrected for temperature, are from Langmuir [1971]. The temperature of rivers not measured directly was assumed to be 27°C. Activity coefficients were calculated using the Davies equation [cf. Butler, 1964]. Ion-pairing coefficients are from Kester and Pytkowicz [1975]. To check the validity of assuming that titration alkalinities were being controlled by carbonate system species (rather than organic acids), TCO_2 was measured directly on some samples from ampules sealed in the field. Measured and calculated TCO_2 are in good agreement (Figure 1).

The levels of P_{CO_2} in Amazonian surface waters reflect both productivity and the dynamic state of the river from which the samples were taken (Figure 2). These observations indicate that major discrepancies between soil and surface water pH are minor, with both falling in the range of 5-100 times the atmospheric value. Waters from swift Andean rivers and highly productive lakes fall below this range, suggesting that the pH values for these waters are high relative to those of the soil environment. If soil P_{CO_2} from the Costa Rican rainforest is representative,

then partial pressures for these waters have been reduced by a factor ranging from roughly 10 to 100. The magnitude of the corresponding pH rise is easily calculated. In Andean rivers, alkalinity ranges from 10 to 3000 eq/L; pH 5.3-8.5. Thus alkalinity $\gg$ [H], [H] $\gg K_w$, and [H] $\gg K_2$. After dropping minor terms, equation (2) can be approximated by

$$log(alk) + pK_0 + pK_1 - pH = log(P_{CO_2}) \quad (3)$$

A tenfold to hundredfold drop in P_{CO_2} for waters moving from Andean soils into rivers would produce a pH rise of 1 to 2 pH units. As no good estimates are available for P_{CO_2} in either lowland or Andean soils, no attempt is made to correct pH values in subsequent calculations.

Carbonate Weathering

Common carbonate minerals (calcite, aragonite, dolomite) weather completely to dissolved phases. Typically, groundwaters from carbonate terrains are just at or under saturation with respect to calcite, dolomite, or both, indicating strong thermodynamic control [Holland et al., 1964; Thrailkill, 1972; Langmuir, 1971]. P_{CO_2} values are usually high, approximately 10 to 100 times atmospheric. In carbonate-dominated waters, a 1:1 relationship should exist between (Ca+Mg) and alkalinity on an equivalent basis. Such a trend is clearly displayed in Figure 3 over much of the alkalinity concentration range. There is, however, an apparent upper limit for alkalinity at about 2000 eq/L above which (Ca+Mg) is independent and in excess of alkalinity. Presumably,
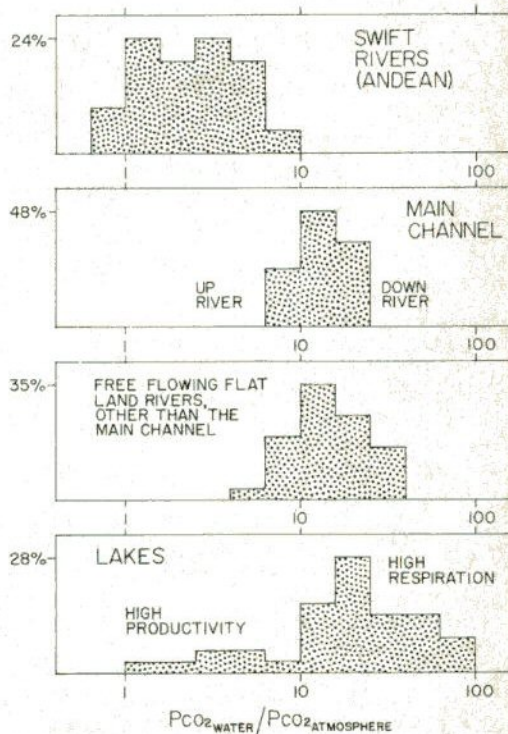

Fig. 2. Histograms of the ratio of river P_{CO_2} to atmospheric P_{CO_2} for hydrologically distinctive water types.
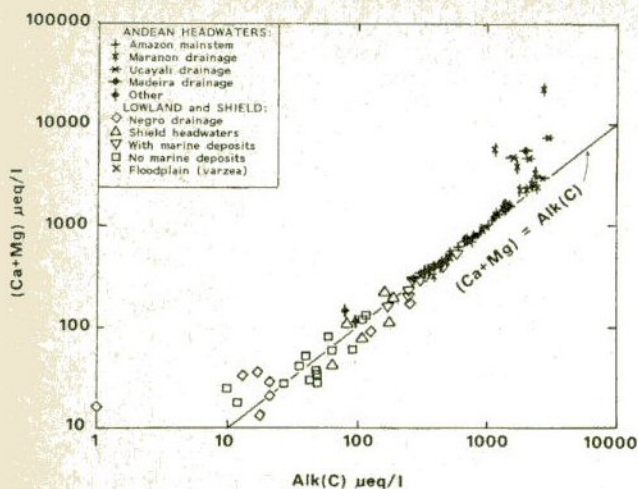
Fig. 3. Alkalinity plotted against (Ca+Mg) for rivers draining siliceous rocks, carbonates, and evaporites but not sulfidic black shales.
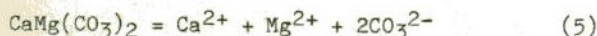
the excesses of Ca and Mg results from the dissolution of evaporite minerals in the numerous Andean evaporite deposits found in the catchments of these particular rivers [cf. Stallard and Edmond, 1983].

Thermodynamic models need consider only calcite and dolomite dissolution:

Calcite

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \qquad (4)$$

Dolomite

$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \qquad (5)$$

Saturation indices for calcite and dolomite are given by

Calcite

$$SI_C = log(a_{Ca} \cdot a_{CO_3} / K_{sp_{calcite}}) \qquad (6)$$

Dolomite

$$SI_D = log(a_{Ca} \cdot a_{Mg} \cdot a_{CO_3}^2 / K_{sp_{dol.}}) \qquad (7)$$

When SI_D is plotted against SI_C, a number of samples are seen to be slightly supersaturated with respect to calcite and/or dolomite (Figure 4). All of those samples which are supersaturated with respect to calcite have limestones as the dominant lithology in their catchments. Sample BPA05 (Guapay River) of the Madeira group is the only sample saturated with respect to dolomite alone. Redissolution of soil salts at the beginning of the rainy season is thought to control the chemistry of this sample [Stallard and Edmond, 1983, Appendix IV].

The degree of calcite supersaturation seen in these river samples is greater than that typically observed in groundwaters from carbonate terrains. Both loss of carbon dioxide during the transition from soil to surface water environment and the dissolution of $CaSO_4$ (A-05, A-10, A-16,

M-08, BPA08) may bring about supersaturation. Carbonate coatings are seen in a few springs and streams [cf. Stallard, 1980]. If the pH values of calcite-supersaturated samples are adjusted so that $SI_C = 0$, then calculated P_{CO_2} levels increase from the observed average of 2.7 times the atmospheric value up to an average 6.4 times atmospheric. The latter value is still at the low end of the probable range for tropical soil P_{CO_2}, but probably could be increased if corrections could be made for contributions of water from parts of the basins having no carbonate rocks. Thus it appears that the input of alkalinity is limited by either saturation with respect to calcite in soils, calcite precipitation in surface waters, or both.

The general agreement between thermodynamic and mass balance models for carbonates suggests that it is valid to apply a similar approach to the examination of silicate weathering. Models of silicate weathering, however, must deal with the problems of treating the various solid phases which result from incongruent reactions.

Silicate Weathering in Amazonia

A general description of the silicate weathering process has been developed over the past few decades [see Drever, 1985]. Cation-rich primary minerals are dissolved by proton-rich, cation-poor solutions that are initially far from equilibrium with the minerals. Alkalis and alkaline earths, silica, and some iron and aluminum are released into solution. It is accepted that the weathering rate of primary mineral grains is in part controlled by the availability of a source of protons in solution. This is typically carbonic and organic acids and less commonly mineral acids. The hydrogen ions displace exchangeable cations and hydrolyze the Si-O-, Al-O-, and Fe-O- bonds. The effect of hydrolysis may vary and can lead to a cation-depleted surface layer, a weathering rind, or congruent dissolution depending on the mineral and on conditions. Some of the cat-
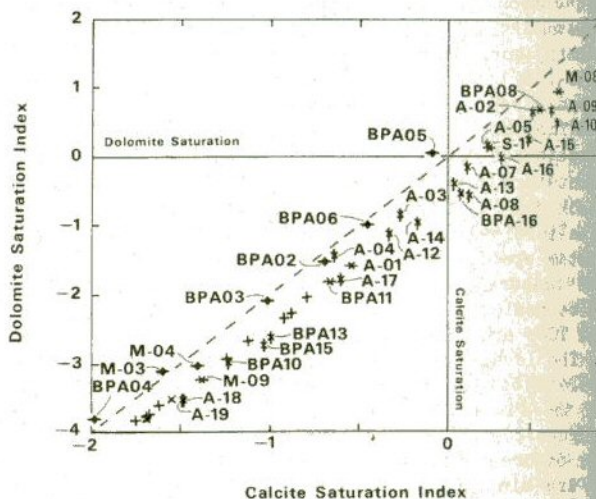

Fig. 4. Relationship between saturation indices for calcite and dolomite in the most concentrated samples. Symbols are defined in Figure 3. Consult Stallard and Edmond [1983, appendices I and IV] for station information.

ions, silica, iron and aluminum released from the degradation of primary grains reprecipitate as clay minerals and sesquioxides in the immediate vicinity, if not as a weathering rind.

The extent of leaching during weathering is thought to be reflected in the chemical and mineralogical composition of the clays and sesquioxides found in soils. Al and Fe (as Fe^{3+}) are extremely insoluble under oxidizing conditions at near-neutral pH, with low concentrations of organic complexing agents. With increasing degree of dissolution of soil material, the major cation (Ca > Na > Mg, K) and Si content of bulk soils decrease relative to Al and Fe. This corresponds to a progression of Al-bearing minerals starting with zeolites and 2:1 clays, then kaolins, and finally Al-sesquioxides (gibbsite). Iron-bearing minerals formed during weathering are mostly Fe-sesquioxides; however, some iron is sequestered in clay lattices.

In Amazonian soils, the end products of extreme leaching are not a mixture of pure Al-sesquioxides and Fe-sesquioxides. Several common soil mineral associations are found: (1) (Al,Fe)-sesquioxides, (2) (Al,Fe)-sesquioxides + quartz, (3) (Al,Fe)-sesquioxides + kaolinite + quartz, (4) Fe-sesquioxides + kaolinite + quartz, and (5) quartz [see Camargo and Falesi, 1975; Irion 1976, 1978, 1984a; Klinge, 1967; Lopez and Bisque, 1975; Menendez and Sarmentero, 1984; Pasquali et al., 1972; Sombroek 1966, 1984; Van Wambeke, 1978]. The third association is particularly common in ancient soils (>10 Ma) formed on granite rocks [see Aleva, 1984; Menendez and Sarmentero, 1984]. The nature of the protolith influences the composition of highly leached soils, for example, the presence or absence of quartz or especially high levels of iron [see Lopez and Bisque, 1975; Irion, 1984a]. Montmorillonite following volcanic ash is abundant in soils in the southwest lowlands [Irion, 1984a]. Micas are the only common primary minerals, other than quartz, that persist in soils, and illite and vermiculite represent important minor constituents of many less-developed Amazon soils.

Moisture levels also appear to be important in determining soil composition, and there is a rough correlation between moisture levels and silica content of Amazonian soils [Stallard, 1987]. The most aluminous soils are found in well-drained localities and in regions having seasonal wet-dry climates with a pronounced dry season. Kaolinite-quartz soils are especially well developed in regions where the dry season is not so marked. In poorly drained localities within the region of continuously wet climates which straddles the equator, quartzose podzols are found.

The very slow dissolution of quartz combined with the mobilization of Al and Fe by organic complexing agents probably are major factors in the development of the more siliceous soil suites [Stallard, 1987]. Quartz dissolution is clearly important during weathering in lowland areas, as is evidenced by the breakdown of soil quartz grains into fine particles [see Pasquali et al., 1972], extreme etching of soil quartz grains [see Brantley et al., 1986], and solution pitting of river sands [see Potter, 1978]. If one assumes that quartz dissolves to roughly the same extent per volume of water passing through the soil,

then the trend to less Al and Fe in soils with increasing wetness would correspond to higher Al and Fe mobility. This is reflected in the high Al and Fe content relative to Si ((Fe+Al)/Si > 0.2) of river waters in the wettest areas [Stallard, 1987].

The suspended loads of lowland rivers, like the most common lowland soils, are especially rich in kaolinite and quartz. Illite and gibbsite are less abundant [Gibbs, 1965, 1967; Irion, 1976, 1984b; Stallard, 1987]. Smectites are only abundant in the southwest lowlands where relatively recent volcanic ash falls may be important [Irion, 1976]. All river sands are very quartzose [Potter, 1978; Franzinelli and Potter, 1983]. Iron coatings are seen on particles in the less acid (pH > ~5) rivers.

In contrast to lowland rivers, 2:1 clay minerals are abundant in sediments in rivers draining the Andes and some foreland uplifts. Talc, micas, illites, vermiculites, and smectites have been identified [Gibbs, 1965, 1967; Irion, 1976; Stallard, 1987]. Talc and micas are probably intact primary minerals. Illites and vermiculites may reflect some degradation of micas. The smectites are widely distributed but are especially abundant where deposits of volcanic ash occur. Smectites are therefore the only 2:1 clays in Andean rivers that clearly result from the degradation of primary minerals other than mica. Kaolinite is found in the suspended load of most Andean rivers.

Erosion in the Andes is sufficiently rapid that unstable primary minerals in bedrock are not completely broken down chemically. Primary mineral and lithic fragments are common in the sand-sized bed material [Franzinelli and Potter, 1983], and the suspended load [Gibbs, 1965, 1967] in Andean rivers.

Mass Balance Model for Silicate Weathering

Kaolins and smectites are the principal secondary clays to be considered in Amazonian weathering. Two simple mass balance parameters, the alkalinity: Si ratio and the Na:Si ratio have been used as a test of whether smectites are forming during the weathering process [Feth et al., 1964; Polzer, 1967; Garrels, 1967]. Both ratios are higher in soil solutions when a smectite rather than a kaolin is the weathering product. The alkalinity:Si ratio is obviously not directly usable where carbonates are also weathering. Meybeck [1979] used the alkalinity:Si ratio after correcting for carbonates in preparing his global mass balance of dissolved inputs to the ocean. He assumed that the ratio is 1:2 for silicate weathering in the tropics, reflecting the predominance of kaolinite formation, while in cooler climates it is 1:1, reflecting montmorillonite formation.

The ratios of silica to cations in solutions derived from leaching lowland soils are expected to differ markedly from those derived from Andean soils. This is because the secondary 2:1 clays, like those in Andean soils, retain the major ions in exchange sites, retain Mg and Fe in lattice sites, and generally have a higher Si:Al ratio than kaolinite. Tardy and Fritz [1981] argue that the compositions of typical 2:1 clays (containing Si, Al, Fe^{2+}, Fe^{3+}, Mg, Ca, K, Na, O,

H) can be formulated in terms of solid solutions having 16 end-members. Muscovites ($M^+\text{-}Si_3Al_3O_{10}(OH)_2$) have the lowest Si:Al ratio (1:1) of these end-members, the same value as kaolinite ($Al_2Si_2O_5(OH)_4$). Beidellites ($M_{.33}^+\text{-}Al_{2.33}Si_{3.67}O_{10}(OH)_2$) have the lowest Si:Al ratio (11:7) of all the smectites. Ideal nontronite ($M_{.33}^+\text{-}Fe_2^{3+}Al_{.33}Si_{3.67}O_{10}(OH)_2$) and montmorillonite ($M_{.33}^+\text{-}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2$), like all smectites with Fe and Mg substitutions in their lattice, have still higher Si:Al ratios (11.1 and 12:5, respectively).

Unlike Ca and Mg which have major carbonate sources, Na and K receive major inputs only from cyclic salts, silicate weathering, and halite dissolution. The effects of cyclic salt inputs can be corrected for ("*" superscript; see Stallard and Edmond [1981, 1983] for procedure), and the Na* derived from halite can be removed by subtracting Cl* ($Na_{silicate} = Na^*\text{-}Cl^*$). Rivers draining massive halite deposits cannot be examined using this procedure, however, because when Na is greater than 1000 mol/L the analytical error propagated through this halite correction is unacceptably large (> 10% of Si).

A mass balance scheme to use dissolved Si, K, and Na to study incongruent silicate weathering reactions is easily formulated. In the case of a primary mineral (subscript "p") going to a secondary mineral (subscript "s"), the dissolved (subscript "d") sodium plus potassium ratio to silica ratio $[(Na+K):Si]_d$ can be calculated using the following formula, assuming that aluminum is immobile:

$$[(Na+K):Si]_d = \frac{[(Na+K):Al]_p - [(Na+K):Al]_s}{[Si:Al]_p - [Si:Al]_s} \quad (7)$$

When this formulation is extended to bedrock (subscript "b") going to a secondary mineral suite (subscript "w"), quartz (subscript "q") dissolution must be taken into account:

$$[(Na+K):Si]_d = \frac{[(Na+K):Al]_b - [(Na+K):Al]_w}{[Si:Al]_b - X[Si_q:Al]_b - [Si:Al]_w} \quad (8)$$

X varies between 0 (complete dissolution of quartz) and 1 (no dissolution of quartz). These formulas can be used to prepare a number of reference reactions of minerals and bedrock for graphical presentation of water chemistry data.

Inspection of these equations shows that the incongruent weathering of minerals or rocks with particularly high $[(Na+K):Al]$ ratios and particularly low Si:Al ratios will produce solutions with high $[(Na+K):Si]_d$ ratios. The breakdown of all other common minerals to the same mineral suite will produce solutions with lower $[(Na+K):Si]_d$ ratios. This provides a means of delimiting permissible solution compositions associated with specific soil mineral suites. The common minerals which produce the highest $[(Na+K):Si]_d$ ratios are alkali feldspars $[(Na,K)AlSi_3O_8]$ and muscovite $[KSi_3Al_3O_{16}(OH)_2]$. Uncommon minerals including paragonite $[NaSi_3Al_3O_{10}(OH)_2]$, Leucite $[KAlSi_2O_6]$, (Na,K)-nephelines $[(Na,K)AlSiO_4]$, and (Na,K)-zeolites $[(Na,K)AlSi_2O_6 \cdot 2H_2O]$ would produce even higher $[(Na+K):Si]_d$ ratios, but they will not be considered. The breakdown of feldspars to kaolinite is an especially useful reference reaction because the ratio $[(Na+K):Si]_d$ is

always 1:2, since the ideal reaction for anorthite to kaolinite releases no Si, Na or K into solution:

$$H_2O + 2H^+ + CaAl_2Si_2O_8 => Ca^{2+} + Al_2Si_2O_5(OH)_4 \quad (9)$$
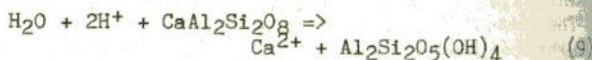
Discussion of Silicate Weathering

Figure 5 is a ternary diagram which relates Si, K* and (Na*-Cl*) for waters from the Amazon system along with fields that correspond to certain siliceous rock and mineral weathering scenarios. The lines are calculated from (7) for the weathering of feldspars or Na-feldspar plus muscovite mixtures to gibbsite, kaolinite, beidellite, or montmorillonite. When a sample falls on the high-silica side of a line, its composition is consistent with the formation of the secondary clay described by that line. The only way for a sample plotting below the line to be consistent with the formation of a specific clay would be to invoke the weathering of minerals with higher $[(Na+K):Al]_p$ ratios and lower $[Si:Al]_p$ ratios than a Na-feldspar plus muscovite mixture. This is very unlikely in view of the geology. Smaller ovoid fields are calculated using (8) for the weathering of common igneous rocks to typical soil suites.

The interpretation can be refined somewhat by analyzing the data in light of the thermodynamic stability of gibbsite and quartz. Recall that these models are only a guide as to what is kinetically permissible. Many very old (>10 Ma) Amazonian soils, for example, contain the thermodynamically impermissible suite quartz-kaolinite-gibbsite; thus some reactions are clearly very slow. In Figure 6, Si is plotted against (Na*-Cl*). The stability fields for gibbsite, kaolinite, and quartz depend only on $Si(OH)_4$ activity. These fields have been drawn, as has the Na-feldspar plus muscovite to kaolinite line, characterized by $Si = 2(Na^*\text{-}Cl^*)$. In addition, regions, calculated from (8), corresponding to the formation of soil suites derived from common igneous rocks are indicated. There is very little overlap between these fields. Samples with a short bar underneath fall between the feldspar to kaolinite and the Na-feldspar plus muscovite to kaolinite lines in Figure 5. Note that gibbsite may be thermodynamically stable in at best one sample. This does not preclude its formation, which could happen in the uppermost parts of soil profiles, but it is certainly consistent with its low level of abundance in the river solid load. Quartz, however, is undersaturated in a number of samples. The commonness of the quartz-kaolinite-gibbsite association in very ancient soils suggests that these reactions are exceedingly slow. Andean data show no relationship of Si to (Na*-Cl*), and many data plot below the Na-feldspar plus muscovite to kaolinite trend.

The marked separation of lowland from Andean data in Figures 5 and 6 is consistent with soil mineral suites described for the respective areas. Most Andean samples plot below the Na-feldspar plus muscovite to kaolinite line in Figures 5 and 6. This can only happen if the production of 2:1 clays is important and agrees with the presence in these rivers of smectites, illites, and vermiculites (some part of which can
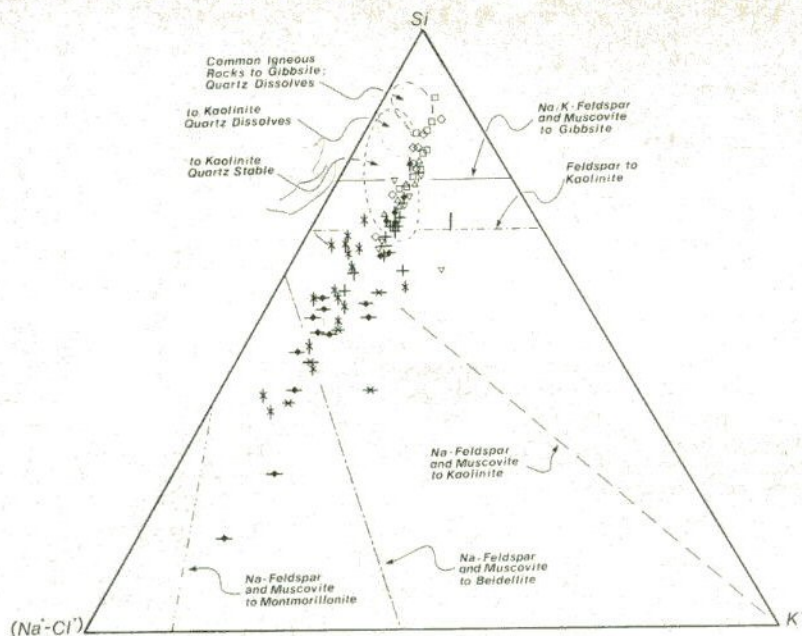
Fig. 5. Ternary diagram relating dissolved Si, K*, and (Na*-Cl*) in the Amazon and Orinoco basins. The "*" refers to cyclic salt corrected values [see Stallard and Edmond, 1983]; Cl* has been subtracted to correct for halite inputs. Si, K* and (Na*-Cl*) presumably relate to inputs from silicate mineral weathering. The lines correspond to various weathering reactions calculated using (7). These were chosen to have the highest Si:(K*+Na*-Cl*) ratio for reactions involving common minerals and resulting in the particular product. Data falling on the low-silica side of a reaction line are not consistent with that reaction. In addition, water composition fields calculated from (8) for various reaction scenarios involving common igneous rocks going to typical soil suits are indicated. Rock compositions were taken from Le Maitre [1976, appendices 8-16, 23-28], who includes C.P.I.W. norms for quartz content. Symbols are defined in Figure 3.
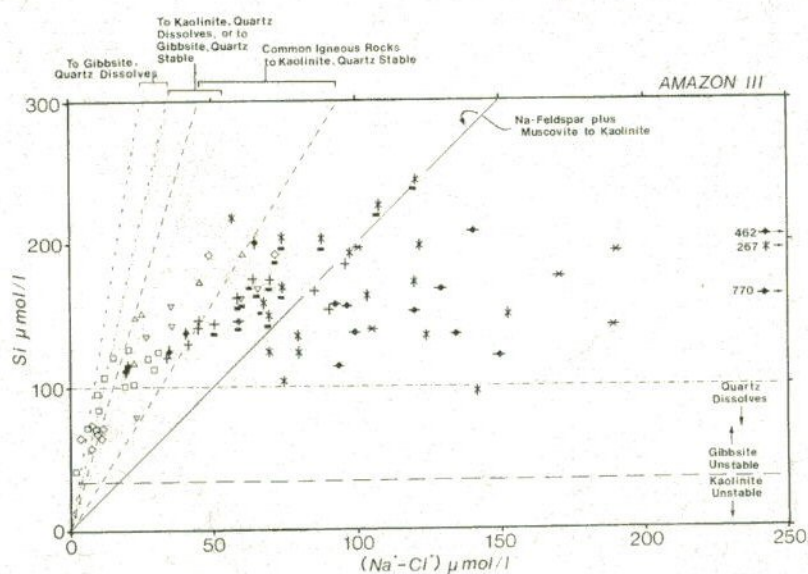

Fig. 6. Si versus (Na*-Cl*) for Amazonian surface waters. The value for quartz saturation was taken from Brantley et al. [1986]. Estimates for the silica concentration for gibbsite-kaolinite equilibrium vary widely, from 7-70 mol/L Si(OH)$_4$, and an intermediate value of 35 mol/L was chosen [see Garrels, 1984]. Samples with the short bar underneath fall between feldspar to kaolinite and the Na-feldspar plus muscovite to kaolinite lines in Figure 5. Symbols are defined in Figure 3.

be products of physical erosion). Note that some Andean samples fall between the Na-feldspar plus muscovite to kaolinite line and the feldspar to kaolinite line. In these, 2:1 clays do not have to be forming, but the reaction muscovite to kaolinite would have to be important. Silica levels in the Andean rivers are no higher than those in the most concentrated lowland rivers. This suggests that high levels of cations rather than of silica are driving the formation of 2:1 clays in the Andes. The formation of these clays would in turn limit the silica concentrations.

Two factors may lead to high levels of solute cations in Andean soils. First, most of the samples where the formation of 2:1 clays is indicated are from catchments having marine sediments, red beds, or volcanic ash deposits, all of which contain easily weathered minerals capable of releasing abundant cations. These lithologies, however, are not common in other parts of the Amazon basin. Second, the presumed higher solute concentrations in waters in Andean soils may result from the evaporative concentration of water migrating down the long vegetated slopes [Stallard, 1985]. Evaporative concentrations of water can occur when the efficiency of evapotranspiration increases downslope due to more vegetation (more reliable water supply) and higher temperatures [cf. Carson and Kirkby, 1972].

Outside of the Andes, data are consistent with the genesis of soil mineral suites ranging from kaolinite plus quartz to the complete dissolution of bedrock and/or gibbsite formation. The observation that data plot close to the igneous rock to kaolinite fields is certainly in agreement with the prevalence of kaolinite in soils and river sediment.

Chemical trends for these data can be interpreted in terms of weathering rate. Presumably, since runoff does not vary widely over the basin, sample concentration is simply related to weathering rate or mobilization rate for a given element. Note that in Figure 6, Si increases with increasing $(Na*-Cl*)$, while the $Si:(Na*-Cl*)$ ratio gradually drops. At the same time, referring to Figure 5, the $K*:(Na*-Cl*)$ ratio and the $Si:(K*+Na*-Cl*)$ ratios also drop. Where weathering is sufficiently rapid, cation and silica concentrations are high, kaolinite forms, and quartz is stable. Where weathering rates are lower, perhaps because of thicker soils or soils with indurated zones (e.g. the podzols) silica concentrations decrease, and quartz dissolution can start contributing additional silica. At this point there is no limit to the $Si:(Na*-Cl*)$ ratio, especially where weathering occurs on quartzose substrates. Eventually, with sufficiently low concentrations of silica, kaolinite is no longer stable, and any rock that is exposed to weathering can presumably have all its silica dissolved, leaving either gibbsite or nothing. The proportions of Fe and Al to other major dissolved elements in some of these rivers are close to those in average shield rocks, suggesting that bedrock is actually dissolving completely [Stallard and Edmond, 1983].

Stallard and Edmond [1983] observe that the ratio of dissolved $(Na*-Cl*)$ to $K*$ in Andean rivers is considerably higher than would be expected if bedrock weathered completely. This presumably reflects a greater resistance of K-feldspar and

micas to chemical breakdown and their enrichment in the river solid loads during rapid erosion. Recall that illite is a minor component of the solid load of many lowland rivers, implying that some fraction of K is being eroded in a solid form outside of the Andes. The increasing $K*/(Na*-Cl*)$ ratio in Figure 5 with decreasing erosion rate (higher $Si:(Na*-Cl*)$ ratio) may reflect more efficient breakdown of micas and thus more complete leaching of K into solution.

Conclusion

Chemical mass balance models, constrained by geologic data and thermodynamic models, provide a consistent description of the weathering processes that occur in the Amazon Basin. These results indicate that thermodynamic models can be used to constrain the interpretation of river chemical data even though, in a strict sense, their application is not proper. In particular, carbon dioxide loss to the atmosphere and a corresponding pH rise does not appear to be a problem for modeling. Most surface water samples have P_{CO_2} and pH values in the range of those in soils, because of high levels of respiration; high-productivity lakes and turbulent rivers are exceptions.

Calcium, magnesium, sulfate, and alkalinity inputs in concentrated waters ($TZ+ > 400-500$ eq/L) come from the weathering of evaporite minerals, sulfides, and carbonates [Stallard and Edmond, 1983]. The inputs of calcium, magnesium, and alkalinity from exclusively carbonate terrains are limited by calcite, and perhaps by dolomite, saturation. When evaporites are present, however, only the alkalinity inputs are so limited because of additional weathering sources of calcium and magnesium inputs.

Dissolved silica, potassium, and sodium can be used to define mass balance relationships that in turn establish the nature of the clay mineral suites which are consistent with solute compositions. Use of thermodynamic constraints, specifically kaolinite and quartz stability, assists in data interpretation. The attainment of thermodynamic equilibria does not appear to control water composition. Instead, differences in geology and kinetic factors, described in terms of transport-limited and weathering-limited erosion, influence possible reactions and exert dominant control.

In the Andes, cation-rich 2:1 layer clays must be forming, while elsewhere in the basin, formation of 2:1 clays appears to be important, and cation-depleted phases such as kaolinite are dominant. Si concentration, and presumably regional weathering rate, increases with $(Na*+K*-Cl*)$. At the same time, $Si:(Na*+K*-Cl*)$ decreases. At low weathering rates, all common primary minerals exposed to weathering are broken down to release silica and cations; both kaolinite and quartz do not appear to be stable. The lack of abundant pure sesquioxide soils indicates that (Fe,Al)-sesquioxides are unstable as well. At higher weathering rates enough silica is available to stabilize kaolinite, then quartz. The stabilization of Si-bearing phases is reflected by a drop in the $Si:(Na*+K*-Cl*)$ ratio. Finally, in the Andes samples, high cation levels result in the formation of the silica-rich 2:1 clays, and the

clear relationship between Si and $(Na^*+K^*-Cl^*)$ degenerates. The presence of unstable litholo-gies, notably evaporites, carbonates, and volca-nic ash, under weathering-limited erosional con-ditions is the main factor that distinguishes the weathering environment of the Andes from the rest of the Amazon basin, where unstable cation-rich lithologies are rare.

The weathering reactions that control erosion rates in the Andes are probably carbonate disso-lution and the breakdown of calcium and sodium-bearing silicates. In the case of carbonates, dissolution reactions approach equilibrium with calcite, and erosion can proceed as rapidly as dissolved erosion products are removed. This would apply to both pure carbonate terrains and to carbonate-cemented clastic rocks. The low silica level in Andean rivers indicates that in exclusively siliceous terrains, equilibria with bedrock minerals and concomitant removal of dis-solved products, in a manner analogous to carbo-nates, is not rate limiting. Instead, it seems more likely that reaction rates are controlled by rates of water penetration of soils and bedrock. The low weathering rates seen outside the Andes are probably hydrologically controlled and rela-ted to the development of thick or indurated soils under transport-limited conditions.

References

Aleva, G. J. J., Laterization, bauxitization and cyclic landscape development in the Guiana Shield, in Bauxite, Proceedings of the 1984 Bauxite Symposium, edited by L. Jacob, Jr., pp. 297-318, American Institute of Mining Met-allurgical and Petroleum Engineers, New York, 1984.

Brantley, S. L., S. R. Crane, D. A. Crerar, R. Hellmann, and R. F. Stallard, Dissolution at dislocation etch pits in quartz, Geochim. Cosmochim. Acta, 50, 2349-2361, 1986.

Butler, J. N., Ionic Equilibrium, Addison-Wesley, Reading, Mass., 1964.

Camargo, M. N., and I. C. Falesi, Soils of the Central Plateau and Transamazonic Highway, in Soil Management in Tropical America, edited by E. Bornemisza and A. Alvarado, pp. 25-45, Uni-versity Consortium on Soils of the Tropics, Raleigh, N. Ca., 1975.

Carson, M. A., and M. J. Kirkby, Hillslope, Form and Process, Cambridge University Press, New York, 1972.

Drever, J. I. (Ed.), The Chemistry of Weathering, D. Reidel Publishing Company, Hingham, Mass. 1985.

Feth, J. H., C. E. Roberson, and W. L. Polzer,

Sources of mineral constituents in water from granitic rocks of Sierra Nevada, California, Nevada, U.S. Geol. Surv. Water Supply Pap. 1535-I, 70 pp., 1964.

Franzinelli, E., and P. E. Potter, Petrology, chemistry, and texture of modern river sands, Amazon River system, J. Geol., 91, 23-39, 1983.

Garrels, R. M., Genesis of some ground waters from igneous rocks, in Researches in Geochemi-stry, edited by P. H. Abelson, pp. 405-420, John Wiley, New York, 1967.

Garrels, R. M., Montmorillonite/illite stability diagrams, Clays Clay Miner., 32, 161-166, 1984.

Gibbs, R. J., The geochemistry of the Amazon Ri-ver Basin, Ph.D. thesis, Department of Geol., Univ. of Calif., San Diego, 1965.

Gibbs, R. J., The geochemistry of the Amazon Ri-ver system, I, The factors that control the salinity and composition and concentration of suspended solids, Geol. Soc. Am. Bull., 78, 1203-1232, 1967.

Holland, H. D., The Chemistry of the Atmosphere and Oceans, John Wiley, New York, 1978.

Holland, H. D., T. V. Kirsipu, J. S. Huebner, and U. N. Oxburgh, On some aspects of the chemical evolution of cave waters, J. Geol., 72, 36-67, 1964.

Irion, G., Mineralogische-geochemische Unter-schungen an der pelitischen Fraktion amazoni-scher Oberboden und Sedimente, Biogeographica, 7, 7-25, 1976.

Irion, G., Soil infertility in the Amazonian rain forest, Naturwissenschaften, 65, 515-519, 1978.

Irion, G., Clay minerals of Amazonian soils, in The Amazon, Limnology and Landscape Ecology of a Mighty Tropical River and its Basin, edited by H. Sioli, pp. 537-579, W. Junk, The Hague, Netherlands, 1984a.

Irion, G., Sedimentation and sediments of Amazo-nian rivers and the evolution of the Amazonian landscape since Pliocene times, in The Amazon, Limnology and Landscape Ecology of a Mighty Tropical River and its Basin, edited by H. Sioli, pp. 201-214, W. Junk, The Hague, Neth-erlands, 1984b.

Johnson, D., D. W. Cole, and S. P. Gesses, Pro-cesses of nutrient transfer in a tropical rain forest, Biotropica, 7, 208-215, 1975.

Kester, D. R., and R. M. Pytkowicz, Theoretical model for the formation of ionpairs in sea-water, Marine Chem., 3, 365-374, 1975.

Klinge, H., Podzol soils: A source of black water rivers in Amazonia, Atas do Simposio sobre a Biota Amazonica, 3, 117-125, 1967.

Langmuir, D., The geochemistry of some carbonate ground waters in central Pennsylvania, Geo-chim. Cosmochim. Acta, 35, 1023-1045, 1971.

Le Maitre, R. W., The chemical variability of some common igneous rocks, J. Petrol., 17, 589-637, 1976.

Longinelli, A., and J. M. Edmond, Isotope geo-chemistry of the Amazon Basin: A reconnais-sance, J. Geophys. Res., 88, 3703-3717, 1983.

Lopez Eyzaguirre, C., and R. E. Bisque, Study of the weathering of basic, intermediate and aci-dic rocks under tropical humid conditions, Q. Colo. Sch. Mines, 70, 1-59, 1975.

Medina, E., G. Montes, E. Cuevas, and Z. Rokzan-

dic, Profiles of CO_2 concentrations and ^{13}C values in tropical rain forests of the upper Rio Negro Basin, Venezuela, J. Trop. Ecol., 2, 207-217, 1986.

Menendez, A., and A. Sarmentero, Geology of the Los Pijiguaos bauxite deposits, Venezuela, in Bauxite, Proceedings of the 1984 Bauxite Symposium, edited by L. Jacob, Jr., pp. 387-406, American Institute of Mining Metallurgical and Petroleum Engineers, New York, 1984.

Maybeck, M., Concentrations des eaux fluviales éléments majeurs et apports en solution aux océans, Rev. Géogr. dynam. Géol. phys., 21, 215-246, 1979.

Pasquali, Z. J. C., E. Lopez, and H. Meinhard, Meteorización de rocas del escudo de Guayana en ambiente tropical, Bol. Geol. Publ. Esp. Venez. Dir. Geol., 5, 2245-2302, 1972.

Polzer, W. L., Geochemical control of solubility of aqueous silica, in Principals and Applications of Water Chemistry, edited by S. D. Faust, and J. V. Hunter, pp. 505-519, John Wiley, New York, 1967.

Potter, P. E., Petrology and chemistry of modern big river sands, J. Geol., 86, 423-449, 1978.

Richey, J. E., J. T. Brock, R. T. Naiman, R. C. Wissmar, and R. F. Stallard, Organic carbon: Oxidation and transport in the Amazon River, Science, 207, 1348-1351, 1980.

Sayles, F. L., and P. C. Mangelsdorf, Jr., Cation-exchange characteristics of Amazon River suspended sediment and its reaction with seawater, Geochim. Cosmochim. Acta, 43, 767-779, 1979.

Sombroek, W. G., Amazon Soils, Centre for Agricultural Publications and Documentation, Wageningen, Netherlands, 1966.

Sombroek, W. G., Soils of the Amazon region, in The Amazon, Limnology and Landscape Ecology of a Mighty Tropical River and its Basin, edited by H. Sioli, pp. 521-535, W. Junk, The Hague, Netherlands, 1984.

Stallard, R. F., Major element geochemistry of the Amazon River system, Ph.D. thesis, Publ. WHOI-80-29, Joint Program in Oceanogr., Mass. Inst. of Technol.-Woods Hole Oceanogr. Inst., Woods Hole, Mass., 1980.

Stallard, R. F., River chemistry, geology, geomorphology, and soils in the Amazon and Orinoco basins, in The Chemistry of Weathering, edited by J. I. Drever, pp. 239-316, D. Reidel Pub. Co., Hingham, Mass., 1985.

Stallard, R. F., Weathering and erosion in the humid tropics, in Physical and Chemical Weathering in Geochemical Cycles, edited by A. Lerman, M. Meybeck, and J. I. Drever, D. Reidel, Hingham, Mass., in press, 1987.

Stallard, R. F., and J. M. Edmond, Geochemistry of the Amazon, 1, Precipitation chemistry and the marine contribution to the dissolved load at the time of peak discharge, J. Geophys. Res., 86, 9844-9858, 1981.

Stallard, R. F., and J. M. Edmond, Geochemistry of the Amazon 2. The influence of the geology and weathering environment on the dissolved load, J. Geophys. Res., 88, 9671-9688, 1983.

Tardy, Y., and B. Fritz, An ideal solid solution model for calculating solubility of clay minerals, Clay Miner., 16, 361-373, 1981.

Thrailkill, J., Carbonate chemistry of aquifer and stream water in Kentucky, J. Hydrol., 16, 93-104, 1972.

Van Wambeke, A., Properties and potentials of soils in the Amazon Basin, Interciencia, 3, 233-242, 1978.

J. M. Edmond, Department of Earth Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139

R. F. Stallard, Department of Geological and Geophysical Sciences, Princeton University, Princeton, NJ 08544