GEOCHEMISTRY OF THE AMAZON
2. THE INFLUENCE OF GEOLOGY AND WEATHERING ENVIRONMENT ON THE DISSOLVED LOAD

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Abstract. In the Amazon Basin, substrate lithology and erosional regime (seen in terms of transport-limited and weathering-limited denudation) exert the most fundamental control on the chemistry of surface waters within a catchment. Secondary effects, such as the precipitation of salts within soils and in stream beds, biological uptake and release, and cyclic salt inputs, are more difficult to discern. Samples can be separated into four principal groupings based on relationships between total cation charge (TZ+) and geology. (1) Rivers with 0<TZ+<200 μeq/l drain the most intensely weathered materials (Upper Tertiary sediments, soils of the Negro Basin, and similarly weathered regions). These rivers show high levels of Fe, Al, H^+, and coloration and are enriched in Si relative to other major species; they exhibit cation ratios similar to those of substrate rocks. (2) Rivers with 200<TZ+<450 μeq/l drain siliceous terrains. These rivers are also rich in silica relative to other species. Rivers draining weathering-limited siliceous terrains exhibit the highest TZ+, and their cation load is typically preferentially enriched in Na over K and Ca over Mg when compared to the rocks in their catchments. (3) Rivers with 450<TZ+<3000 μeq/l drain marine sediments or red beds with high cation concentrations (resulting from the presence of carbonates and minor evaporites in the Peruvian Andes and reduced shales and minor carbonates in the Bolivian Andes). These rivers exhibit relatively high levels of Ca, Mg, alkalinity, and SO_4 (in rivers draining reduced shales and minor evaporites). (4) Rivers with TZ+>3000 μeq/l drain massive evaporites. These rivers are rich in Na and Cl. In the third and fourth categories, rivers tend to have 1:1 (equivalent) ratios of Na:Cl and (Ca+Mg):(alkalinity+SO_4), caused primarily by the weathering of carbonates and evaporites.

Introduction

A large river basin represents an obvious natural unit within which one can examine weathering geochemistry and erosion on a continental scale. A single large basin encompasses enough geological and morphological variablity to permit examination of processes occurring on different terrains while at the same time allowing comparison of their relative importance via their respective contributions to matter transported down the river. Much of what is known about denudation on a global scale is based on compilations of data from extremely diverse sources; however, for this approach, quality control is difficult. Data from systematic surveys of a large river system need not suffer from the inconsistencies of garnered data, yet only two large river systems have been the subject of comprehensive geochemical investigations: the Amazon [Sioli, 1954a, b, 1955, 1957a, b, 1963, 1964, 1968; Gibbs, 1965, 1967, 1972, 1977; Irion, 1975, 1976, 1978; Franzinelli, 1983]; and the Mackenzie [Hitchon et al., 1969; Hitchon and Krouse, 1972; Reeder et al., 1972; Peake et al., 1972].

The Mackenzie study is the only detailed examination, using modern instrumentation, of the dissolved load of a large river system. This work utilizes both an exceptionally high quality geological data base and well analyzed samples taken from throughout the basin. Reeder et al. [1972] use factor analysis to deduce that for the major dissolved species, clear relationships exist between the geology of the sample catchment and the chemistry of the samples. Relatively high concentrations of certain species have been related to catchment geologies in the following associations: Mg, Ca, Sr, HCO_3, and SO_4 with carbonate rocks and gypsum; K, B, and Na with illitic bedrock; Si with bentonites and hot spring areas; Na and Cl with evaporites; and Fe and B with glauconitic substrates. Both U and PO_4 show river-specific chemical behavior which, however, could not be related unambiguously to geology, while F, NO_3, Ni, Cu, and Zn show no clear geological relationships or exceptional behavior.

The present work focuses on the relationship between the chemistry of major dissolved species in rivers of the Amazon system, and the geology, topography, and soils of their catchments. Data were collected in conjunction the 1976-1977 R/V Alpha Helix Amazon expedition. Like the Mackenzie project, the bulk of the Amazon samples was collected during one part of the year. Precipitation chemistry, lacking in the Mackenzie work, was also studied [Stallard and Edmond, 1981], so that atmospheric chemical contributions to surface waters can be estimated prior to examination of terrestrial controls of surface water chemistry. The general relationship between geology and chemistry is discussed in this paper. Detailed discussions of individual catchments, as well as analytical procedures and analytical results, are given in microfiche appendices.[1]

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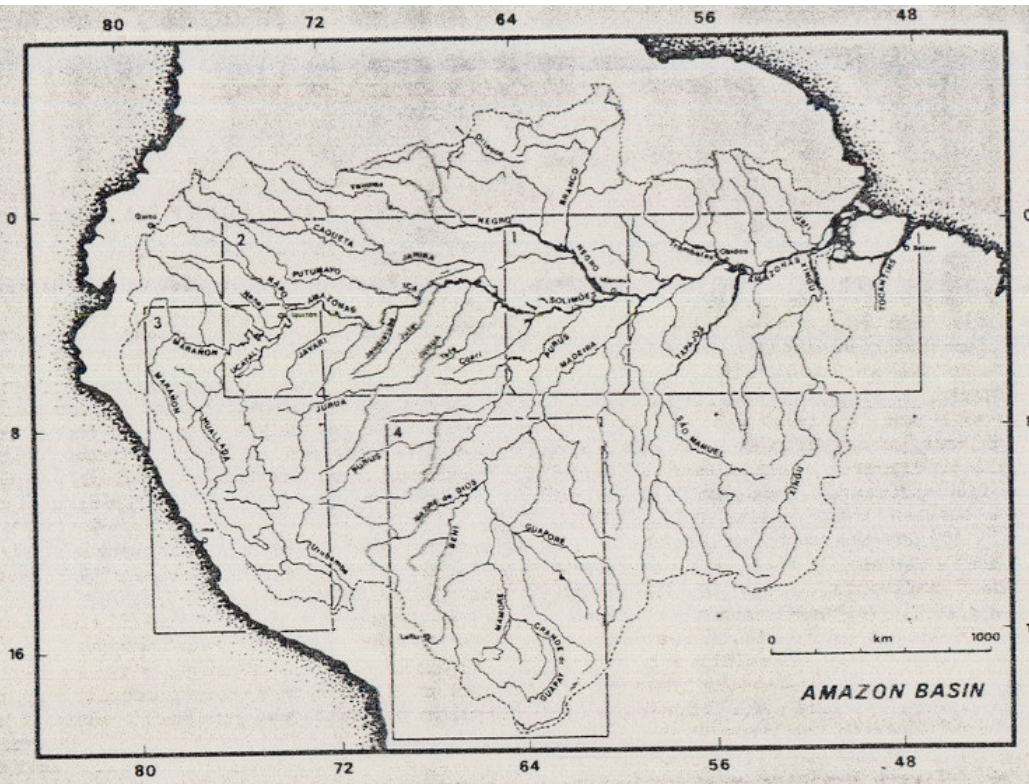

Fig. 1. Location map for the Amazon Basin. The rectangles are sample regions (referred to in Figure 5): 1, lower Amazon; 2, upper Amazon; 3, Peruvian Amazon (Marañon and Ucayali); and 4, Madeira headwaters.

The Global Setting of the Amazon Basin

The Amazon Basin (Figure 1) encompasses the broadest range of continental geology, including modern orogenic zones, areas of epierogenic uplift and of long-term stability, and active sedimentary basins. Human activities, which have so thoroughly altered the environments of many large river basins, have yet to overwhelm the Amazon. The Amazon is the largest river in the world, having a discharge of 1.75×10^5 m^3/s [Oltman, 1968]. Recent studies of Meade et al. [1979] rank the Amazon third in sediment output to the ocean at 9×10^8 tonnes/year, less than the the Ganges-Brahmaputra (17×10^8 tonnes/year) and the Huang He (11×10^8 tonnes/year) [data from Milliman and Meade, 1983]. The Amazon ranks perhaps first in output of dissolved material, transporting about 2.9×10^8 tonnes/year [Gibbs, 1972], a value comparable to the Chiang Jiang [Hu et al., 1982].

Major Features of the Amazon Basin

The Amazon Basin occupies much of the South American continent between 5° north latitude and 20° south latitude and conforms to the classical picture of a large river catchment, being an extensive plain bordered by highlands. To the west is the Andean Cordillera ranging from 3000 to 7000 m; to the north and south are the highlands of the Guiana (500 - 3000 m) and the Brazilian (1000 - 2000 m) shields. To the east of the Andes there exists a trough in which the Amazon drainage is separated by poorly defined divides from the Orinoco Basin to the north and the Paraguay Basin to the south.

Four major morphostructural zones can be distinguished within the Amazon Basin. These are the Precambrian shields; the Andean Cordillera; the Amazon Trough or Basin; and the Subandean Trough, Foredeep, or Depression (Figure 2). These four zones correspond to regions of distinctive geology, soils, landscape, and, to some degree, climate and vegetation. Since the Phanerozoic, the shields have been topographic highs; the cordillera has been a locus of intermittant orogenic activity; the Amazon Trough has been an area of subsidence; and the Subandean Trough has had a more complex history, most recently acting as a zone of subsidence. The Andean Cordillera can be further divided into four major subzones: the Western Cordillera, the Intercordilleran Region, the Eastern Cordillera, and the Subandean Uplifts. These four subzones control the river drainage network within the Andes and are geologically different.

Distribution of Rock Types Within the Amazon Basin

Metamorphic and Igneous Rocks

The bulk of the igneous rocks throughout the shields and the Andes (primarily from the Western Cordillera) are acid to intermediate in composition (Figure 3). Likewise, the higher grade metamorphic rocks fall into this composition range.

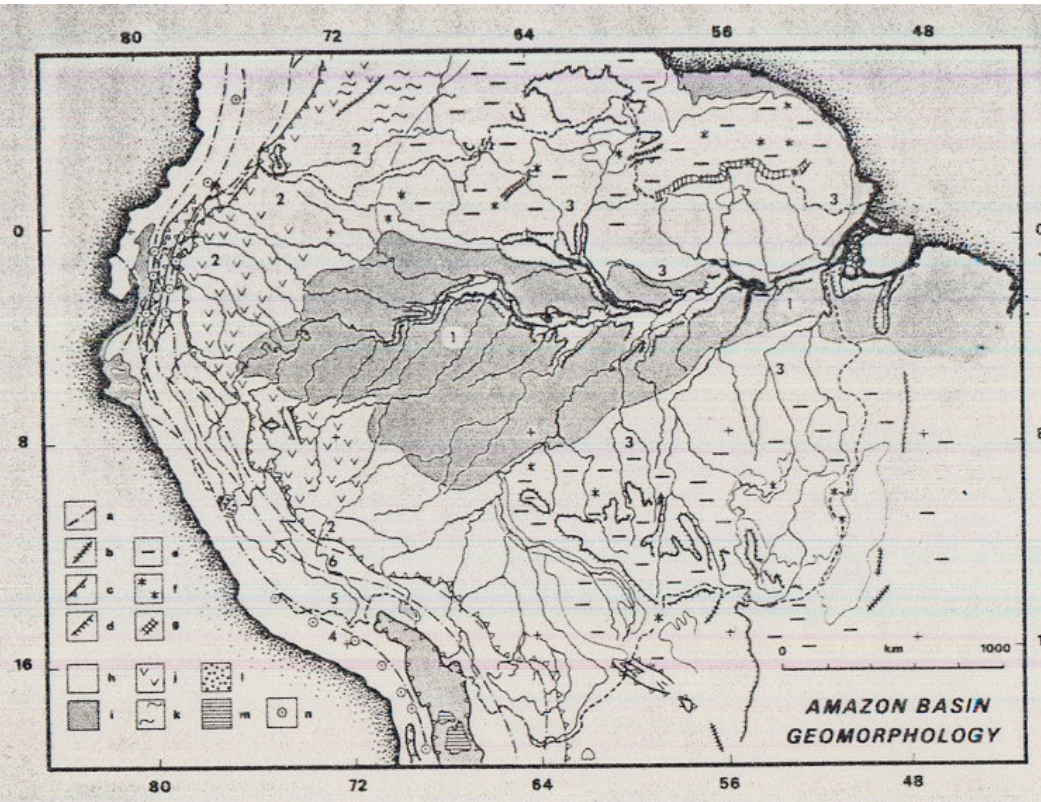

Fig. 2. Map of the morphostructural regions of the Amazon Basin. Regions: 1, Amazon Trough; 2, Subandean Trough; 3, Shields; 4, Western Cordillera; 5, Intercordilleran Zone (includes the altiplano regions); and 6, Eastern Cordillera. Symbol key for tectonic relief elements (see insert): a, trends of the folded young mountain ranges of the Andean system; b, crest of horst mountains and monoclines; and c, faults or flextures. Erosional relief elements: d, lithological step, escarpment; e, old erosion surfaces of Mesozoic-Tertiary age; f, occurrence of inselbergs; and g, crest of residual relief. Depositional relief elements: h, Quaternary fluvial, alluvial or eolian deposits (in the Andes, includes glacio-fluvial and tectonic mudflow deposits); i, occurrence of Late-Tertiary and Quaternary lacustrine or marine deposits; j, Pleistocene loess or fluvial deposits with ash admixtures; k, sand dunes; l, Pleistocene glacial deposits; m, salt flats; and n, occurrence of volcanoes.

Dominant Sedimentary Rocks

In the Andes the dominant sedimentary lithologies (oldest to youngest) are dark shales, carbonates (mostly limestones), and sandstones (mostly arenites), red beds, and fluvio-lacustrine sediments. The Eastern Cordillera is composed of Precambrian metamorphic rocks and Lower Paleozoic shales, which are in part metamorphosed. Exposures in the other Andean subzones are primarily younger sedimentary and igneous rocks, with continental units dominating to the east and marine and volcanic units to the west [Gansser, 1973; Audebaud et al., 1973]. Gray-green to black shales, mixed with sandstones, constitute the major lithology of the lower Paleozoic and upper Precambrian sediments for the entire Amazon Basin [Bigarella, 1973; Loczy, 1968]. Their greatest exposure is in the Bolivian Andes, where Ordovician dark shales and sandstones underlie an estimated 75% of the area [Ahlfeld, 1972]. Carbonate rocks in the Andes are predominantly limestones. In stratigraphic columns where dolomites are designated, they are a subordinate lithology (perhaps 5 to 10% of the total carbonates). There are no massive Paleozoic dolomite units such as one finds in the North American cordillera. Red beds are the predominant post-Permian continental sediments. They are typically red shales and sandstones with a widely varying amount of interlayers consisting of limestone, evaporites (mostly $CaSO_4$), reduced shales, volcanic ash, and conglomerates.

In the Amazon Trough the sediments include sandstones, evaporites, and shales, which are covered by Tertiary fluvio-lacustrine sediments, except for two narrow strips bordering the lower Amazon Valley. Sandstones (mostly orthoquartzites and arkoses) and some dark shales cover areas on the shields [Bigarella, 1973; Loczy, 1968]. The Tertiary fluvio-lacustrine sediments of the Amazon Trough and the soils of the shield are products of intense weathering and are extremely depleted in cations.

Evaporites

Formations in which evaporite minerals are observed are most abundant in the Andes (Figure

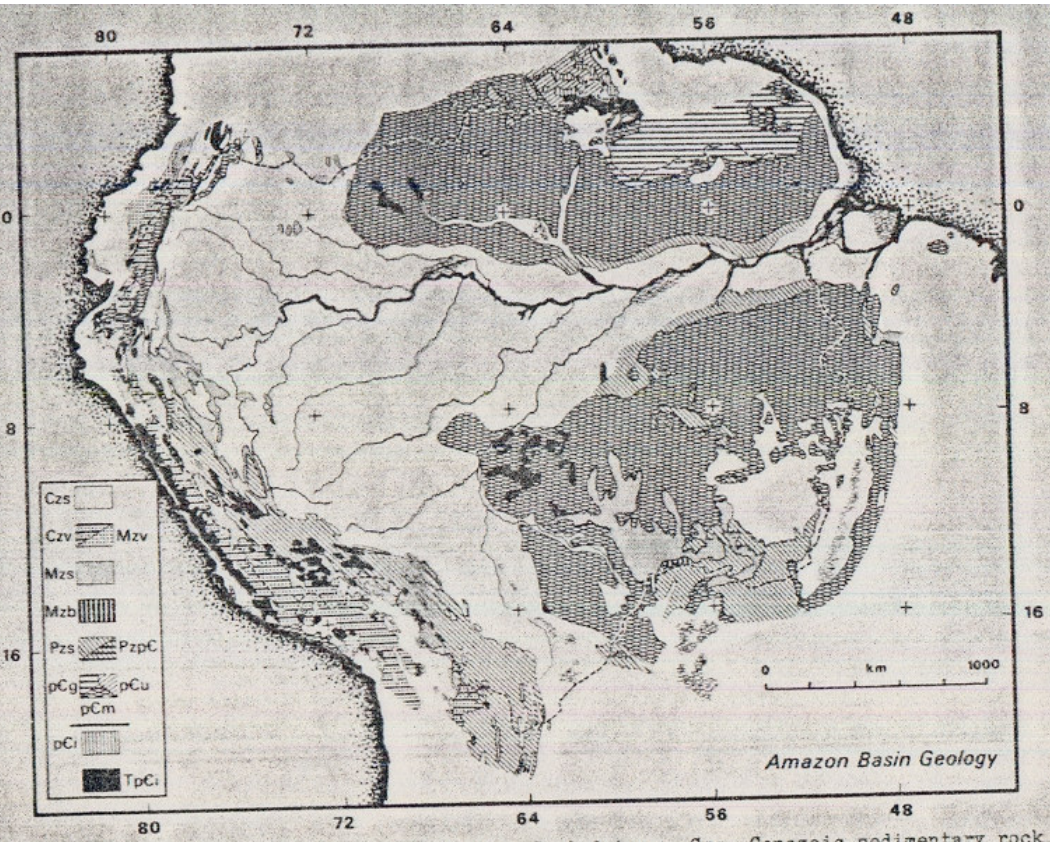

Fig. 3. Geologic map of the Amazon Basin. Symbol key: Czs, Cenozoic sedimentary rock (over much of the basin, Upper Tertiary fluvial-lacustrine sediment predominates). Czv, Cenozoic volcanic rock (abundant in western ranges of Andes, in north and south of basin). Mzv, Mesozoic volcanic rock (abundant in western ranges of Andes). Mzs, Mesozoic sediments (largely oxidized shales, sandstones and carbonates, sometimes with evaporites). Mzb, Mesozoic basalt (very uncommon lithology in Amazon Basin). Pzs, Paleozoic sediments (Upper Paleozoic sediments: mostly oxidized shales, sandstones, and carbonates with some evaporites, common in Peru and Ecuador. Lower Paleozoic sediments: mostly dark shales and sandstones, with some carbonates, common in southern Peru and Bolivia). PzpC, Paleozoic and/or Precambrian metamorphics. pCg, Precambrian granitic rock (mostly Guyana Shield). pCu, Precambrian unmetamorphosed rock (quartzites of the Guyana Shield). pCm, Precambrian metamorphic rock (the shields and the cores of the eastern ranges of the Andes). pCi, Intrusive rock.

4); those which contain halite tend to be restricted to central and northern Peru and southern Ecuador [Benevides, 1968]. Often the evaporite minerals (particularly gypsum and anhydrite) are dispersed in red beds and outcrop in the formations in which they were deposited. In north and central Peru (notably in the Huallaga River Basin), buried evaporites are brought to the surface as salt plugs or domes. The larger domes are composed mostly of gypsum and halite, have diameters on the order of 5 to 10 km, and have an aggregate area probably in the range of 100-200 km^2. Their extrusion rate is such that they are pronounced topographic highs, even though precipition is approximately 1.5 m/year. Salt springs have been reported from Peru and Ecuador [Benevides, 1968; Tschopp, 1953]. The springs are thought to be caused by the migration of formation waters up fault planes [Rigo de Righi and, Bloomer, 1975; Maribe et al., 1975]. The great input of salt to surface waters can be seen by the numerous "Cachiyacu" (salt waters) designated on maps of north-central Peru.

Soils and Denudation Throughout the Amazon Basin

In the Amazonian lowlands there are three major soil regions related to zones of differing vegetation and climate: the savanna (northeast and south), the Amazonian forest (straddling basin axis), and the campina-caatinga forest (northwest). These zones correspond to regions of progressively wetter climate, diminished dry seasons [cf., Hoffmann, 1975], and more siliceous, less ferrugenous, and less aluminous soils. In a general way, savanna soils tend to be kaolinitic with varying levels of iron and aluminum sesquioxides; forest soils consist largely of kaolinite with additional quartz; and the campina-caatinga soils are very quartz-rich with additional kaolinite and aluminum sesquioxides [Stallard, 1980].

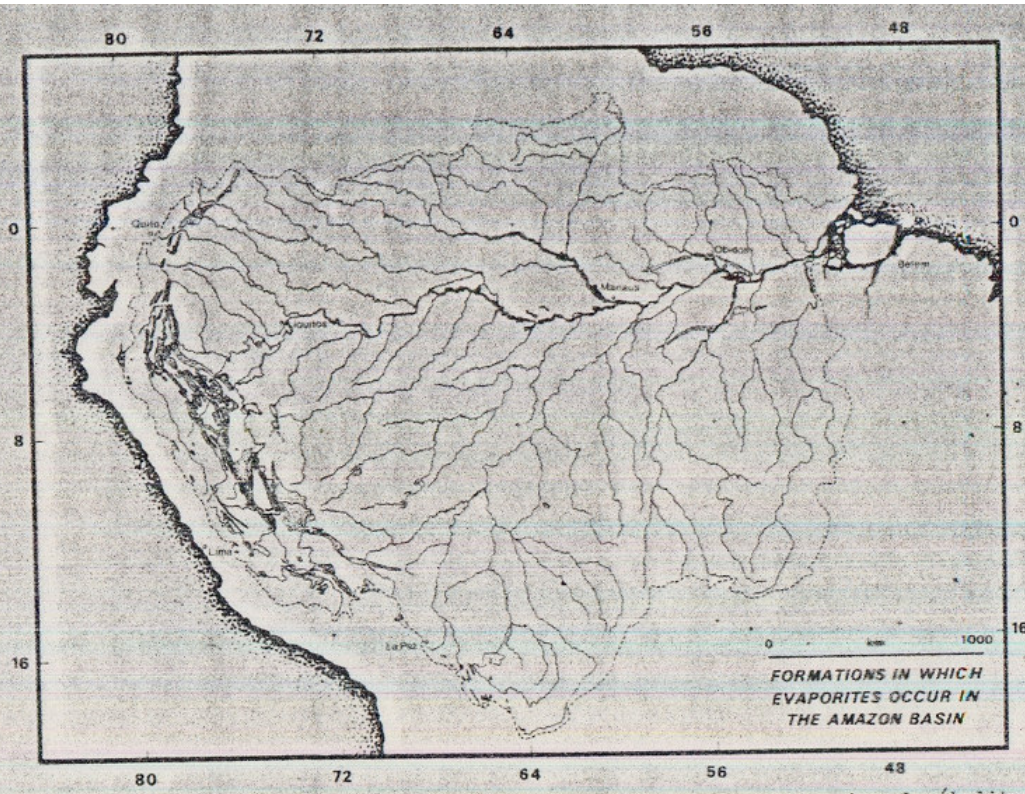

Fig. 4. Map of the distribution of formations from which evaporite minerals (halite, gypsum, or anhydrite) are reported. This is not a map of evaporite exposures, which are far more limited in area and extent than the regions indicated on the map.

Typically, savanna and forest soils on crystalline rocks tend to be quite thick, ranging from about 5-10 m to greater than 100 m on old erosion surfaces [King, 1962; Sombroek, 1966; FAO/UNESCO, 1971; Kronberg et al., 1979]. A hard saprolite (i.e., weathered bed rock) and an overlying soft saprolite can be distinguished in the lower part of the soil profile on crystalline rock. The latter is that part of the saprolite zone which is no longer structurally coherent, even though it is sometimes called a structured saprolite. The stability of primary minerals in Amazonian soils and its relationship to the saprolite zones have been described by Pasquali et al. [1972] and Lopez and Bisque [1975] (Table 1). Above the soft saprolite there is frequently several meters of less structured, highly leached, material, which is overlain by a surficial root mat. There is often a zone of mottling near the water table, and occasionally mottled or indurated zones appear elsewhere in the profile, perhaps indicative of previous water table levels.

Soil properties show a definite relationship to topography [Sombroek, 1966; Van Wambeke, 1978], with thick, cation-depleted soils being found on topographic highs and well-drained flat terrain, richer (but still cation-depleted) soils on slopes, and a wide variation of soils in low areas depending the nature of alluvium and colluvium deposited therein.

Quartz-rich soils, found primarily in the northwestern parts of the basin, underlie large areas of campina and caatinga vegetation [Sombroek, 1966; Sioli and Klinge, 1961; Klinge, 1965; Klinge, 1967]. These soils (giant podzols, tropical podzols, spodzols) are characterized by a surface humus layer, a thick (up to several meters) quartz A horizon, and an underlying layer, orstein, of aluminous clays (no iron) cemented by humic materials.

Contrary to popular belief, near-surface laterites are quite rare, covering about 2% of the basin [Van Wambeke, 1978; Sioli and Klinge,

TABLE 1. Mineral Stability in Tropical Soils

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MOST STABLE
Quartz* >>
    K-Feldspar*, Micas* >>
        Na-Feldspar >
            Ca-Feldspar, Amphiboles >
                Pyroxenes, Chlorite >
                    Dolomite >
                        Calcite >
                            Gypsum, Anhydrite+ >>
                                Halite+
                                LEAST STABLE
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* Quartz, Micas, and K-feldspars are stable in hard saprolites developed on acid to intermediate igneous and metamorphic rocks. Quartz frequently persists through entire soil profiles.

\+ Gypsum and anhydrite are observed in soils developed on salt domes in the Huallaga Basin; halite, however, is not.

1961], and where laterite does occur, it often appears to be "fossil" [Sombroek, 1966; Mousinho de Meis, 1971; Klammer, 1971; Grubb, 1979].

Soils formed on fine-grained sediments, carbonates, and basic rocks are often quite varied in composition, ranging from bauxites to cation-rich clays [Lopes and Bisque, 1975; Irion, 1978; Isphording, 1979]. The Tertiary sediments of the Amazon Trough (typically kaolinitic to sandy facies) are derived from the surrounding shields, and soils developed on them do not differ substantially from the upper horizons of mature soils in the source region. Soils of the Subandean Trough contain a more fine-grained and cation-rich suite of accessory minerals (e.g., montmorillonite from volcanic ash [Irion, 1975, 1976, 1978]) of Andean provenance.

Denudation Regimes

The concept of transport and weathering limited denudation regimes [cf., Carson and Kirby, 1972] can be used to analyze weathering in relatively flat and steep terrains, respectively. These regimes can be viewed as limiting cases in a spectrum of erosional processes. If the transport processes removing weathered material from an area are potentially more rapid than the processes generating the weathered material, the erosion is said to be weathering-limited. Only a thin soil develops, and a significant control in the topogaphic expression of different rock types is their susceptibility to weathering. If, in contrast, the maximum weathering rate exceeds the ability of transport processes to remove the material, the process is said to be transport-limited; with time, under these conditions, a thick soil develops, and dynamic equilibrium is not reached until weathering rates are reduced by the accumulation of soil. Topographic highs developed on the soil tend to be more vulnerable to erosion and are smoothed. Consequently, lithologic variation plays a lesser role in controlling topography, and such terrains tend to be relatively flat. Various factors, particularly vegetation, can act to make erosion more transport-limited.

A corollary to these geomorphological observations is that in a drainage basin exhibiting transport-limited denudation, contributions to the river load by different lithologies should be proportional only to their area of exposure. For a weathering-limited catchment, however, contributions by various lithologies should be proportional to both their area exposed and to their relative susceptibility to weathering.

A principal difference between transport-limited and weathering-limited conditions is that the physical products of weathering have a much longer time to react with soil and ground waters in the former, while partially weathered solid material is eroded in the latter. In reasonably coherent siliceous lithologies, the transition between a hard and soft saprolite may be critically important in controlling river load compositions. Solifluction and soil avalanching in moist vegetated areas do not involve the hard saprolite [Zonneveld, 1975; Scott and Street, 1976; Garwood et al., 1979]. Therefore, minerals which survive the transition from hard to soft saprolite should be enriched in the fluvial solid load, and elements leached from the soft saprolite should be enriched in the dissolved phases.

Vast tracts of the Amazon lowlands can be classified as having largely transport-limited denudation regimes, and the chemistry of the solid load of lowland rivers is consistent with such erosion. The suspended and bed loads of these rivers, like the soils, are rich in quartz, kaolinite, and iron sequioxides, all of which are cation-depleted phases.

The rivers which drain elevated shield terrains and hilly regions of fluvio-lacustrine sediments also tend to carry cation-poor solid phases. There appear to be three principal reasons for this. (1) The relief is stabilized by a layer of indurated cation-poor material, often quartzite or laterized soil. (2) The relief is developed on cation-depleted sediments. (3) The flat erosion surfaces of the shields contribute more to overall denudation than do the local escarpments which separate them.

The presence of unstable and cation-rich minerals in the suspended and bed loads of rivers which drain the Andes reflects extraordinarily rapid erosion, consistent with weathering-limited conditions. This is evidenced by the occurrence of carbonates in the bed load of the lower Amazon [cf., Potter, 1978], the only source of which could be the Andes, and by the presence of unstable primary igneous and metamorphic silicates in Andean rivers [cf., Gibbs, 1965, 1967; Irion, 1975]. Furthermore, preferential erosion of very poorly lithified deposits is seen throughout the Andes and in the Subandean uplifts. Rapid removal of Andean Pleistocene sediments has been described [Garner, 1968; Ballivián, 1978]. The effect of the erosion of red beds is easily seen, and Andean rivers which traverse them acquire in intense red color.

Clay minerals in Andean rivers are also cation-rich [Gibbs, 1965, 1967; Irion, 1975]. Irion [1975, 1976, 1978] shows that much of the montmorillonite is derived from the weathering of volcanic glass. Bentonite layers being eroded out of red beds may also be important and, hence, the contrast between high Andean rivers, which have not yet crossed the red beds and are rich in chlorite and mica, and the lower courses of the same rivers, which are rich in montmorillonite and kaolinite. Finally, the Paleozoic sediments, which make up the Bolivian Cordillera Oriental, are very rich in illite and biotite [Brockman et al., 1972] and are undoubtedly the principal source of mica in the Madeira Basin rivers.

Biological Processes and Weathering

Roots and root-fungi symbiotic associations (mycrorrhiza) play a significant role in the geochemistry of many biologically important elements which are depleted in lowland soils (e.g. Ca, Mg, K, and P), by transporting the elements to and maintaining them in the biomass through efficient recycling. Under forest, campina, and Amazonian caatinga vegetation, a dense root mat is typically found near the surface of the soil [Went and Stark, 1968]. Direct transfer of phosphorus from litter to roots occurs [Herrera et al., 1978b]. It is estimated that from 99 to 99.9% of calcium and phosphorus in solutions passing through the mat is assimilated into the biomass

[Stark and Jordan, 1978]. The ability to retain a wide range of elements in a non-labile form has been demonstrated by Stark [1972]. Notably, the mass of K, Ca, and Mg in the total biomass may be 3 to 5 times that in the A and B soil horizons [cf., Stark, 1971a, b; Herrera et al., 1978a].

Previous Observations on Regional Water Chemistry

The earliest studies of surface waters in the Amazon region recognized the geographic contrasts in chemical properties. Raimondi [1884] observed that the Marañon and Ucayali Rivers were low in dissolved inorganic species and enriched in organics compared to many waters from the Andes. He attributed these observations to biological activity. Katzer [1897, 1903] noted that the lowland tributaries are more dilute than the main channel, which in turn is dilute compared to other large rivers.

Waters from the Brazilian Amazon region have long been classified on the basis of their appearance. Three types are recognized: white waters, which are rich in dissolved and suspended materials; clear waters, which are depleted; and black waters, which are typically more dilute than clear waters and intensely colored by humic matter [cf., Sioli, 1967]. The white water type is characteristic of all rivers that have substantial drainage in the Andes, especially the main channel of the Amazon and the Madeira River [Sioli, 1957, 1968, 1975; Gibbs, 1965, 1967; Schmidt, 1972a; Furch, 1976] and is much closer compositionally to typical river waters than any originating in the lowlands. Clear waters are the most widely distributed type in the basin and originate in areas of clay-rich soils on the shield and raised Tertiary terrains. The black waters are found in extremely flat areas and have been linked to campina - Amazonian caatinga vegetation and the nutrient-poor giant podzol soils [Sioli, 1968; Sioli and Klinge, 1961; Klinge and Ohle, 1964; Klinge, 1965, 1967; Schmidt, 1972b, Ungemach, 1967, Anonymous, 1972]. Clear waters with exceptionally high dissolved concentrations and near-neutral pH drain the isolated bands of carbonates and sulfates of the lower Amazon Basin [Sioli, 1963]. In contrast to these regional models, Gibbs [1970] has suggested that the chemistry of Amazon lowland rivers is controlled by atmospheric inputs. As will be shown, this is not supported by the present study.

Studies of Andean and Subandean surface waters have been confined to Peru. Patrick [1966], Swabey [1966], and Hegewald et al. [1976, 1977] note the wide range of concentrations and chemistry in these regions. Swabey [1966] suggests that the spread of Mg:Ca ratios might be explained by variations in limestone chemistry. Furthermore, salt deposits (e.g. "salt hills" of Herndon [1854] and the "saline waters of the Huallaga" of Spruce [1908]) are suggested to be the principal source of chloride. They note that the Amazon at Iquitos is about 3 times as concentrated in dissolved solids as the lower reaches, below Manaus. Hegewald et al. [1976, 1981] observe that lakes in the northern Peruvian Andes are more dilute than those of the south and that their Mg:Ca ratio increases to the south; sodium-rich lakes are comparatively uncommon.

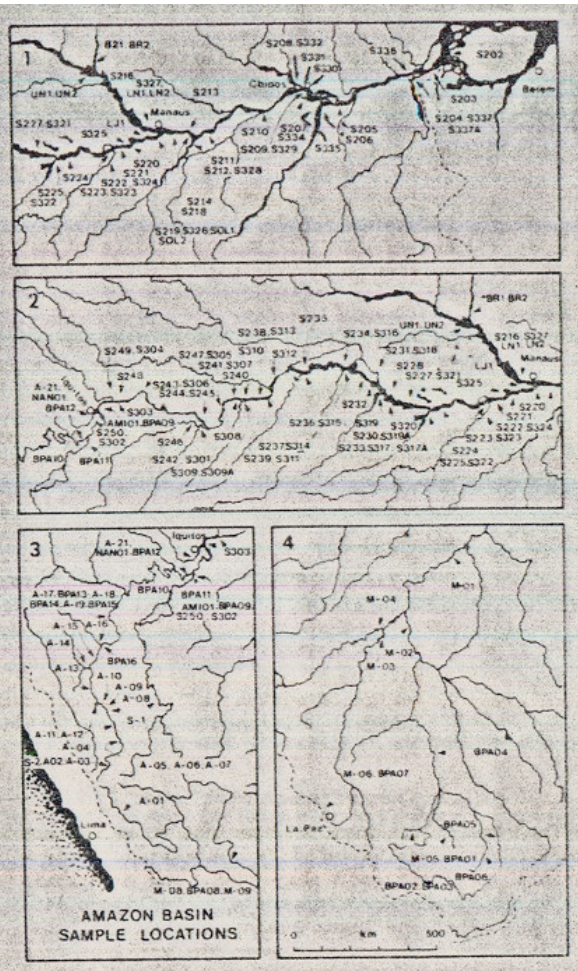

Fig. 5. Sample location map. Regions are indicated in Figure 1. For collection dates and location descriptions, refer to Appendix I.

Sampling and Analysis

Sampling of lowland rivers centered around two mainstem transects of the Amazon Basin, by the R/V Alpha Helix, going upriver in June-July 1976 and going downriver in May-June 1977 (Figure 5). Boston Whalers were used to sample tributaries above the Tefé on the first transect and all but the Içá, Negro, and Madeira rivers during the second. Samples from several lowland sites were obtained for other parts of the year.

The Andean rivers, lowland Madeira and Peruvian rivers were sampled after transect 1, before and after transect 2, and during November-December 1978 (Figure 5).

Sampling dates and locations and site descriptions are given in Appendix I. Analytical methods are summarized in Appendix II, and the data are presented in Appendix III, with supplimentary figures. Geology of the catchment corresponding to each sampling location and its relationship to sample chemistry is described in Appendix IV. Many details and specific examples are given to supplement the discussion below.

TABLE 2. Comparison of the Composition of Dissolved, Suspended, and Bed Materials From the Amazon Mainstem With Estimated World Average Values

Element	Dissolved, μmol/l			Suspended, mole %		Bed Load mole %	
	World Average[a]	Upper Amazon[b]	Lower Amazon[c]	World Average[d]	Lower Amazon[d]	World Average[e]	Lower Amazon[e]
Sodium	223.	278.	63.4	1.9	2.1	0.44	2.3
Potassium	33.	28.9	20.8	3.1	2.8	1.4	2.5
Magnesium	130.	96.7	39.8	2.9	2.8	1.5	1.3
Calcium	335.	477.	129.	3.2	2.4	1.2	3.5
Carbon[f]	850.	1122.	323.	--	--	0.72	2.82
Chloride	162.	183.	30.5	--	--	--	--
Sulfur	86.	73.	17.8	--	--	0.02	0.04
Silicon	173.	185.	120.	61.5	51.2	83.4	78.9
Iron	0.7	1.0	1.9	5.2	5.9	2.0	1.9
Aluminum	1.9	0.8	0.7	21.1	25.6	8.6	7.5
Manganese	0.2	0.1	0.3	0.12	0.11	0.03	0.03
Titanium	0.2	--	--	0.71	0.88	0.58	0.31
Phosphorous	1.3	0.6	0.3	0.23	0.32	0.02	0.05
Nitrogen[g]	16.	9.4	4.8	--	--	--	--

[a]Meybeck [1979b, calculated from Table 4] and Martin and Meybeck [1978].
[b]This study, S250, Upper Amazon at Iquitos.
[c]This study, S209, Lower Amazon at Obidos.
[d]Martin and Meybeck [1978].
[e]Potter [1978].
[f]Inorganic carbon as bicarbonate or carbonate.
[g]Inorganic nitrogen as nitrate, nitrite, or ammonia.

River Chemistry and Rock Types

The Amazon is not a chemically remarkable river. Recent estimates of "world average" compositions of dissolved, suspended, and bed loads for world rivers are compared with analogous data from the upper and lower Amazon mainstem in Table 2. Note the similarity between the world average river chemistry and water from Iquitos. This similarity belies the great variety of water types found in the Amazon Basin. The range of total dissolved solids (TDS) represented by the samples from this study is roughly 6 ppm to 4000 ppm (Table 3), comparable to the range of 37 ppm to 8000 ppm for rivers within the United States [Holland, 1978].

Several preliminary geological observations must be made. First, with regard to total cation concentration (TZ+), rivers showing a TZ+<450 μeq/l (slightly higher in Andean rivers) drain siliceous terrains lacking marine deposits; rivers with 450<TZ+<3000 μeq/l drain marine sediments, and rivers with TZ+>3000 μeq/l drain major exposures of evaporites (cf., Appendix IV). These lithological contrasts are often quite pronounced. Second, the larger river subbasins within the Amazon system tend to display regional geologies that are quite distinctive. Hence, different symbols are used to distinguish the major subbasins or terrain types in most subsequent figures (Table 4). Third, when individual concentrations are plotted against total cations (Appendix III), five groupings of data can be identified, and trends correlated with geology (Table 5).

Geologic Controls of High TZ+ Rivers

Only a few readily weathered minerals are abundant in marine sedimentary rocks, red beds, and marine and continental evaporites in the Amazon Basin. These minerals are calcite ($CaCO_3$, with some Mg), dolomite ($CaMg(CO_3)_2$), gypsum or anhydrite ($CaSO_4 \cdot 2H_2O$, $CaSO_4$), and Halite ($NaCl$). Some evaporites may contain potassium and magnesium salts at low concentrations (Table 5). All of these minerals weather congruently:

TABLE 3. Observed Ranges for Various Parameters

Element/ Species	Precip- itation, Minimum	Lowland River Minimum	Lowland River Maximum	Andean river, Maximum	Units
pH	4.71	4.64	7.50	8.5	
Sodium	0.3	8.1	278.	71400	μmol/l
Potassium	0.2	3.8	36.6	178.	μmol/l
Magnesuim	0.17	2.6	98.6	2660	μmol/l
Calcium	0.0	3.6	552.	8290	μmol/l
Alkalinity	--	-16.	1285.	2976.	μeq/l
Chloride	1.1	2.6	183.	71600	μmol/l
Sulfate	1.6	0.0	76.2	9320	μmol/l
Silica	0.0	40.5	196.	244.	μmol/l
Iron	0.0	0.0	7.3	3.[a]	μmol/l
Aluminum	0.0	0.1	4.4	20.[a]	μmol/l
Nitrate	0.0	0.0	16.0	61.	μmol/l
Color[b]	0.0	65.	627.	19.[c]	--
TZ+	11.	51.	1570	77200	μeq/l
TDS	0.5	4.8	133.	4560	ppm

[a]These high Andean values appear to include material from dissolution of fine particles forced through filter.
[b]Units, absorbance in 1 cm cell at 270 nm x 100.
[c]Andean minimum.

TABLE 4. Sample Categories and Associated Characteristics

Type	Symbol	Category	General Characteristics
1	+	main channel	Mainstem below Marañon-Ucayali confluence; Amazonas (Peru) - Solimões (Brazil, above Negro) - Amazonas (below Negro); "white water" river: 1560>TZ+>400 µeq/l.
2	*	Marañon drainage	Andean "white water" rivers draining metamorphic rocks, carbonates, red beds, dark shales, fluvio-lacustrine sediments, some evaporites: 77000>TZ+>460 µeq/l.
3	✳	Ucayali drainage	Andean "white water" rivers draining metamorphosed dark shales, carbonates, red beds, andesitic volcanics, fluvio-lacustrine sediments, some evaporites: 13000>TZ+>1000 µeq/l.
4	⊕	Madeira drainage	Andean "white water" rivers draining extensive lower Paleozoic black shales, shield, fluvio-lacustrine sediments, red beds, quartzites: 7000>TZ+>400 µeq/l.
5	⊕	other Andean headwater rivers	Andean "white water" rivers including Napo, Iça, Japurá, draining fluvio-lacustrine sediment, red beds, volcanics; large lowland drainage: 600>TZ+>150 µeq/l.
6	◇	Negro drainage	Lowland "black water" rivers, draining Precambrian shield, extensive caatinga-campina vegetation: 280>TZ+>50 µeq/l.
7	△	rivers draining shield areas (non-Negro)	Lowland "clear water" rivers including Xingu, Tapajós, Trombetas, draining Precambrian shield, minor shales and sandstones, extensive areas of savanna in head waters: 280>TZ+>100 µeq/l.
8	▽	lowland rivers with extensive areas of marine sediments	Lowland "white water" rivers including Javari, Juruá, Purus, draining fluvio-lacustrine sediment, red beds, carbonates, minor gypsum deposits: 650>TZ+>200 µeq/l.
9	□	rivers draining only Upper Tertiary and Quaternary sediments	Lowland "black or clear water" rivers including Nanay, Jandiatuba, Tefé, Coari, Matari, draining mostly fluvio-lacustrine sediments: 180>TZ+>40 µeq/l.
10	×	várzea (floodplain) waters	Waters standing on or flowing through the várzea (flood plain) - can be a mixture of mainstem water with types [4]-[9]: 1200>TZ+>120 µeq/l.

$$NaCl = Na^+ + Cl^- \quad (1)$$

$$CaSO_4 = Ca^{2+} + SO_4^{2-} \quad (2)$$

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- \quad (3)$$

$$CaMg(CO_3)_2 + 2H_2CO_3 = Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad (4)$$

$$CaCO_3 + H_2SO_4 = Ca^{2+} + SO_4^{2-} + H_2CO_3 \quad (5)$$

$$CaMg(CO_3)_2 + H_2SO_4 = Ca^{2+} + Mg^{2+} + 2SO_4^{2-} + 2H_2CO_3 \quad (6)$$

A source of protons is necessary for the rapid weathering of carbonates. This is typically carbonic acid (equations (3) and (4)); however, sulfuric acid (derived from precipitation and from the weathering of reduced sulfur, e.g., from black shales, equations (5) and (6)), nitric acid (precipitation, oxidation of reduced nitrogen), and organic acids are also potential proton sources.

The analyzed inorganic species are charge balanced at high TZ+. If the above reactions are the sources of the inorganic ions in these samples, then stoichiometric balances would be expected between (Na+K) and Cl (assuming that the trace evaporitic K is a Cl salt) and between 2(Ca+Mg) and (alkalinity + $2SO_4$). A stoichiometric balance might be expected between 2(Ca + Mg) and alkalinity in terrains where sulfur-containing minerals are not common, as is the case in many of the carbonate areas of the Andes. Without additional geological information, it would not be possible to differentiate situations where combinations of reactions (2) to (6) are occurring, as there are only four conservative dissolved phases (Ca, Mg, SO_4, and alkalinity = HCO_3).

A plot of (Na + K) versus Cl (Figure 6) demonstrates that at high concentrations the data distribution approaches a 1:1 trend characterizing a pure evaporite source. All of these rivers drain evaporites. The dispersion of samples above this trend, at lower chloride concentrations, undoubtedly reflects inputs from the weathering of

TABLE 5. Parameters Grouped According to Similar Relationships With Total Cations (TZ+)

Parameter Grouping	Description of Relationship
Na and Cl	The ratio of these elements to TZ+ increases at high concentrations (waters associated with evaporites).
Ca, Mg, SO_4	The ratio of these species to total cations decreases at high concentrations (showing a predominance of NaCl in evaporites). Rivers that fall above the main SO_4 - TZ+ trend drain reduced sediments.
alk(C)[a], NO_3, PO_4	These species show little correlation with TZ+ at low TZ+ (<200 μeq/l). (This may reflect biological influence via production of organic acids and production/consumption of nutrients.) They are then correlated with TZ+ at intermediate TZ+ (200<TZ+<3000 μeq/l), and finally noncorrelated with TZ+ at high TZ+ (TZ+>3000 μeq/l) (likely due to a lack of evaporite inputs of these species). Rivers that fall below the alk(C) - TZ+ trend drain reduced sediments.
Si, K	These two species are grouped together because for most samples they show similar behavior, a TZ+ correlated rise at lower concentrations (TZ+<200 μeq/l) and little correlation at high TZ+ (>200 μeq/l). The latter samples are from rivers draining marine sediments and red beds. K is enriched in some rivers draining evaporites and black shales.
H, Fe, Al, Color, NICB[b]	These parameters show a decrease in value with increasing TZ+ (TZ+<200 μeq/l). The plots of iron and aluminum are complicated by high levels in some Andean rivers, thought to be caused by the passage of fine clays through the 0.45 um filters, and subsequent dissolution, as a result of acidification.

[a]Carbonate alkalinity = HCO_3 + CO_3.
[b]NICB = (total inorganic charge) / (total inorganic cation charge (TZ+)).

sodium and potassium aluminosilicates which, like carbonates, need a source of protons for weathering reactions to proceed efficiently.

The plot of 2(Ca + Mg) versus (alkalinity + $2SO_4$) (Figure 7) shows a high correlation throughout the entire data range and closely approaches the theoretical 1:1 trend at higher concentrations. The tendency for data to fall below the 1:1 trend reflects the requirement that a portion of the anions balances Na and K produced by the weathering of silicate rocks. This is a minor contribution in high TZ+ rivers, hence the convergence to the 1:1 trends in Figures 6 and 7. Greater scatter in the data at low

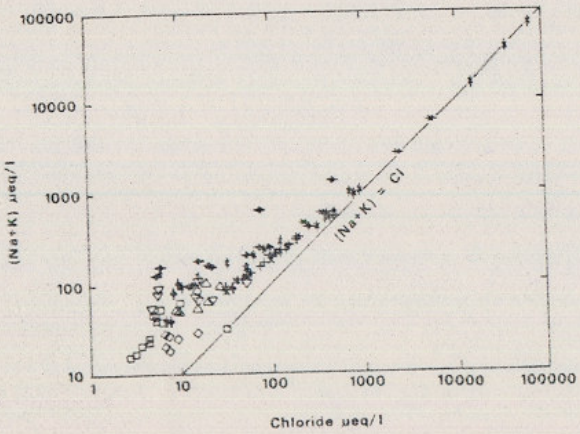

Fig. 6. Graphs of sodium plus potassium versus chloride, showing the effects of chloride mineral weathering at high TZ+ and cyclic salt inputs at low TZ+. Note that all of the samples fall on or above the one to one trend, interpreted as reflecting contributions of Na and K from silicate weathering.

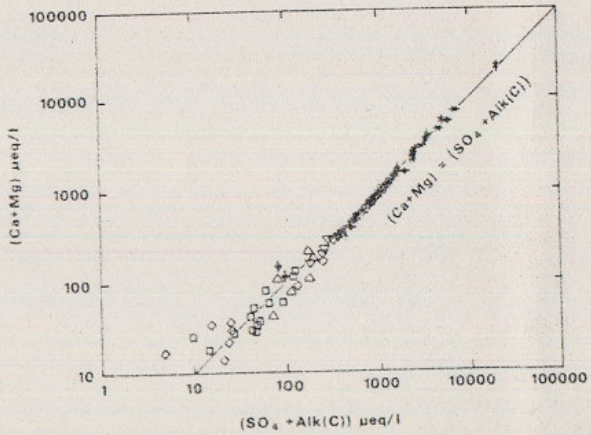

Fig. 7. Graph of calcium plus magnesium versus carbonate alkalinity plus sulfate. This graph illustrates the charge balance between these parameters, especially at higher concentrations. The chemistry of the more concentrated rivers that cluster tightly along the trend is dominated by the dissolution of carbonates and sulfates. Data are not corrected for atmospheric inputs.

concentrations in Figure 7 reflects the opposing effects of an increased contribution of Na and K relative to Ca and Mg (causing a downward shift in the data), and an increased contribution of NO_3 and organic anions relative to alkalinity and SO_4 (causing an upward shift).

It is not possible to distinguish between inputs of calcium and magnesium from silicate rocks and products of reactions (3)-(6) on the basis of chemistry alone [cf., Garrels, 1967; Garrels and Mackenzie, 1971; Holland, 1978]. However, inputs from the weathering of calcium and magnesium silicates should be similar in spatial distribution and magnitude to inputs from the weathering of sodium and potassium silicates, as there are no terrains in the basin dominated by silicates that are extremely rich in either alkalis or alkaline earths.

There is apparently an upper limit to alkalinity input from the weathering of carbonates, as clearly seen in a plot of (Ca + Mg) versus alkalinity (Figure 8). The concentration of (Ca + Mg) varies independently of alkalinity at high concentrations, and sulfate replaces alkalinity as the principal species in the charge balance. This is illustrated in a ternary plot of (Ca + Mg), alkalinity, and SO_4 (Figure 9). Note that the samples tend to be confined to a field defined by stoichiometric trends expected for reactions (3)-(6). The weathering of calcium and aluminum silicates also would be expected to fall in this field. However, only Andean rivers draining marine sediments are plotted, and silicate contributions are expected to be minimal. The samples which deviate from the trend at lower TZ+ in Figure 8 are from the Madiera Basin where the sulfate appears to be derived from the weathering of reduced sulfur in black shales.

Geologic Controls of Low TZ+ Rivers

There are two reasonable sources for dissolved materials in Amazon lowland rivers: weathering of

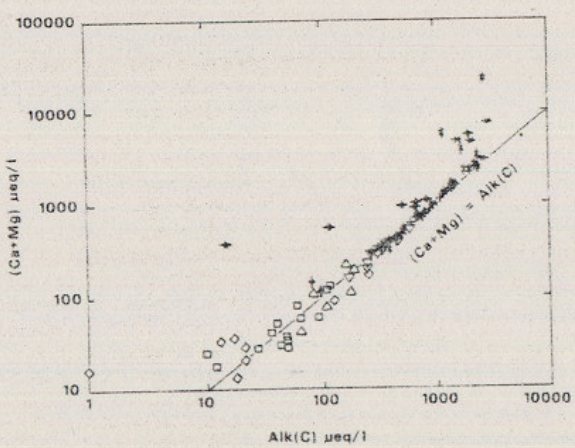

Fig. 8. Graph of calcium plus magnesium versus carbonate alkalinity. These data reflect a charge balance of these parameters over most of the concentration range. At high concentrations, the alkalinity input levels off, perhaps reflecting control by saturation. Data are not corrected for atmospheric inputs.

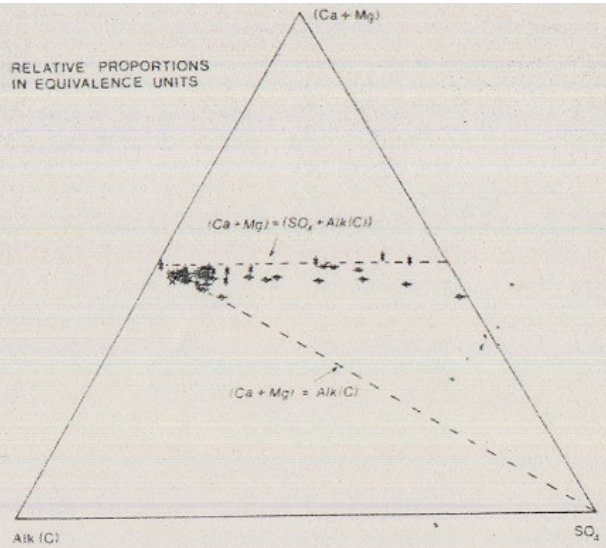

Fig. 9. Ternary diagram relating relative amounts, in equivalents, of magnesium plus calcium, carbonate alkalinity, and sulfate. Data for Andean rivers which drain marine sediments and red beds are plotted. The data fall into a triangular field that would be expected if the weathering of carbonates and sulfates were contributing these phases (equations (1)-(6)). Data are not corrected for atmospheric inputs.

siliceous rocks and precipitation. Gibbs [1970] argues that the latter is of overwhelming importance. He observes that if TDS is plotted against Na/(Na+Ca) for continental waters, a distinctive "boomerang" pattern results. Samples from this study conform in a general way to the field defined by Gibbs (Figure 10); however, at lower concentrations they are not nearly so sodium-rich. Chloride in most of the lowland rivers appears to be atmospheric, and the cyclic salt correction [Stallard and Edmond, 1981] provides a test (Figure 10) of whether precipitation, in fact, controls the chemistry of those rivers that fall into the "precipitation dominance" field. It is clear that a cyclic salt correction makes only a minor change in the appearance of the right-hand graph. A marked shift downward and to the left would be expected for these samples if cyclic salt contributions were important. The greatest TDS drop was 42% in the near-coastal, Matari River (S337A), followed by 16%, 10%, and 8% drops for different Negro samples. The weathering of silicates clearly controls the the major cation chemistry of lowland rivers.

Contributions by Silicate Weathering

The relationships between chemistry and geology are well illustrated by a ternary diagram relating silica, alkalinity, and sulfate plus chloride (Figure 11). Dissolved silica is derived uniquely from the weathering of silicates. By subtracting out cyclic salt contributions, silicate inputs can be compared to evaporite inputs, since the remaining chloride must be derived largely from halite and the sulfate from

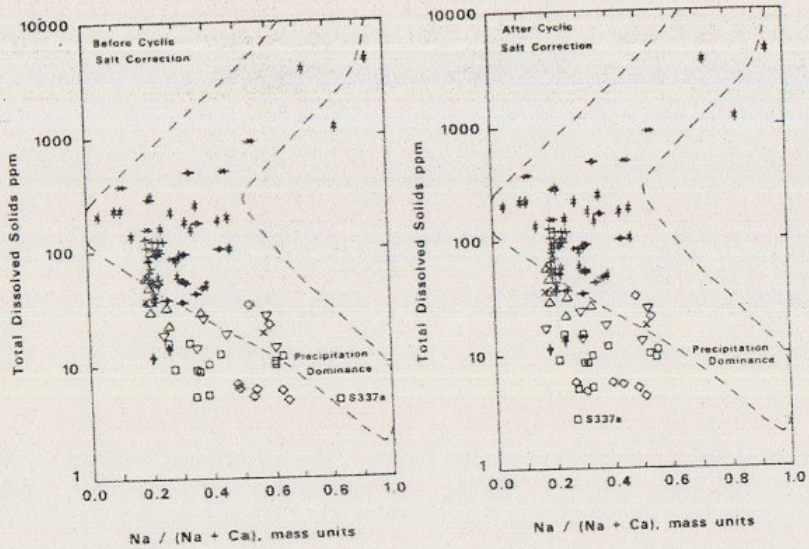

Fig. 10. Graphs of Amazon River data drawn according to Gibbs [1970, Figure 3]. The graph on the left is the Amazon Basin data, uncorrected for atmospheric inputs. Note that the data conform adequately to the field defined by Gibbs. The graph on the right is of the same data, corrected for cyclic salt inputs. If the cyclic salt contribution to the cations in the sample were large, the points in the precipitation dominance field should shift down and to the left. This occurs for only one sample, S337a, from a river near the coast.

evaporite minerals or sulfides. There is no unique tracer of carbonate weathering inputs as calcium, magnesium, and alkalinity are also produced by silicate weathering. However, since calcium and magnesium are also derived from evaporite dissolution, the preferred tracer for carbonate inputs would be alkalinity. There are two caveats in comparing dissolved silica to alkalinity. First, the ratio of alkalinity to silica resulting from silicate weathering is strongly dependent on whether cation-rich clays are forming. If they are, the ratio will be particularly high, resembling that of carbonate weathering. This situation is present in the Andean rivers [Stallard, 1980]. Second, a number of organisms fix silica. Due to the similarity of Si and K (Table 5), K could be used as an alternative, though less intuitive, parameter.

In the ternary diagram, total cations increase systematically from the Si vertex to the alkalinity vertex, thence to the ($Cl+SO_4$) vertex. This trend appears to be related to the increasing susceptibilty to weathering of evaporites over carbonates over silicates. As discussed earlier, a relationship with respect to susceptiblity would be expected under weathering-limited conditions. Moreover, the most chloride and alkalinity-rich rivers are from the Andes. This is consistent with the observation that the bulk of carbonates and evaporites is found there.

The two less concentrated samples that deviate from the trend are from a river draining black shales (M-05, BPA01, Appendices II, III, and IV). Here, sulfuric acid from the oxidation of reduced sulfur has replaced carbonic acid as a source of protons for rock weathering. The overall process is slow compared to evaporite dissolution. These two samples can be seen as defining a separate trend for black shales, indicated by the insert in Figure 11. However, the trend is not so well defined as it is in graphs of alkalinity versus (Ca+Mg) (Figure 8).

Denudation Regimes and Silicate Weathering

For siliceous rocks, transport-limited and weathering-limited erosional regimes can be distinguished through comparison of the K/(Na+K) ratios in stream waters with those of the bed rock in their catchments. Mg/(Ca+Mg) ratios can also be used, provided that most of the bed rock Mg is in biotite. During transport-limited erosion, cation-poor solid phases are produced, and the K/(Na+K) and Mg/(Ca+Mg) ratios would be the same in solution as in the bed rock. During weathering-limited erosion, cation-rich solids are generated, and cations which remain in the solid products would be depleted in solution relative to their bed rock proportions.

For acid to intermediate rocks, physical transport processes tend to erode the soft saprolite from which Na and Ca bearing minerals have been preferentially leached (Table 1). As a consequence, the K/(Na+K) and Mg/(Ca+Mg) ratios in the dissolved products would be less than those in the bed rock. The Na and Ca enrichment relative to K and Mg, during weathering, is quite unlike the composition trend for common igneous rocks. In the latter, the Mg/(Ca+Mg) ratio decreases and the K/(Na+K) ratio increases, as one goes from basic (uncommon in the Amazon) to acidic rocks.

The Mg/(Ca+Mg) and K/(Na+K) ratios for various rocks and soils have been plotted against one another (Figure 12) along with the same ratios in surface waters, after correction for the cyclic salt component (indicated by a star superscript) and halite dissolution (subtraction of Cl* from

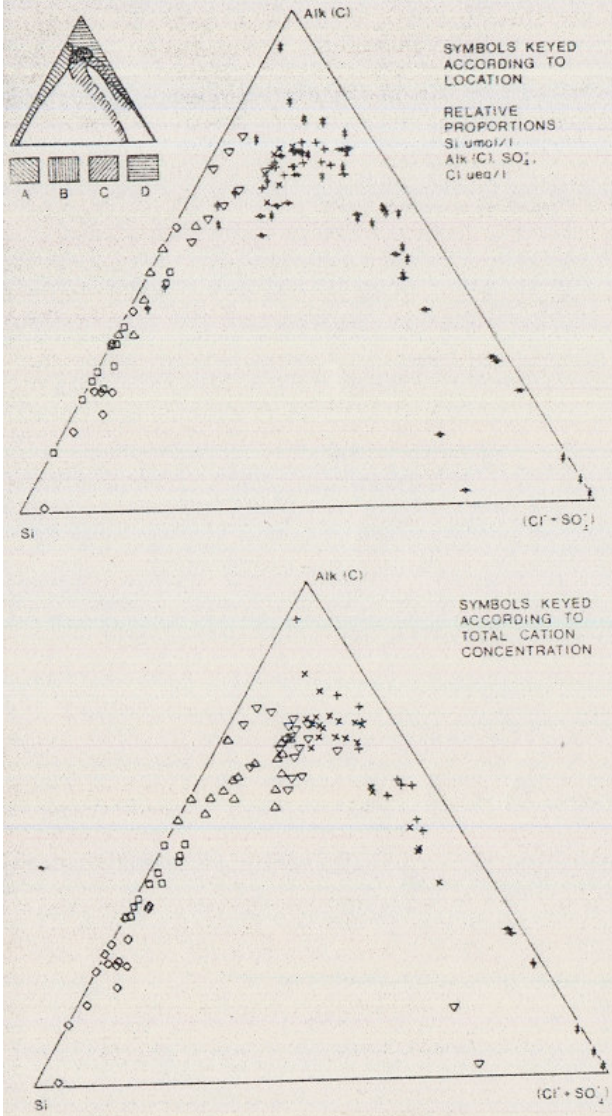

Fig. 11. Two ternary diagrams relating relative amounts of silica, carbonate alkalinity, and chloride plus sulfate. The data have been corrected for cyclic salt inputs. In the upper diagram samples are keyed according to sample location. In the lower diagram, samples are keyed according to their total cation concentration (TZ+). Rivers falling near the silica vertex drain cation-poor siliceous rock types; rivers falling near the alkalinity vertex drain areas of carbonates and to a lesser extent locations where cation-rich soils are forming on silicates, and rivers falling near the chloride-sulfate vertex drain evaporites (higher TZ+ samples) or reduced shales (lower TZ+ samples). For the lower diagram, symbols (refer to numbers and symbols in Table 4) correspond to the following ranges in total cations (μeq/l): 6, <100.; 9, 100.-215.; 8, 215.-464.; 7, 464.-1000.; 10, 1000.-2154.; 1, 2154.-4642; 5, 4642.-10000.; 4, 10000.-21544.; 3, 21544.-46416.; 2, 46416.-100000.. On the small insert, the fields stand for a, lowland rivers; b, main channel; c, Madeira drainage; d, Peruvian Andean rivers..

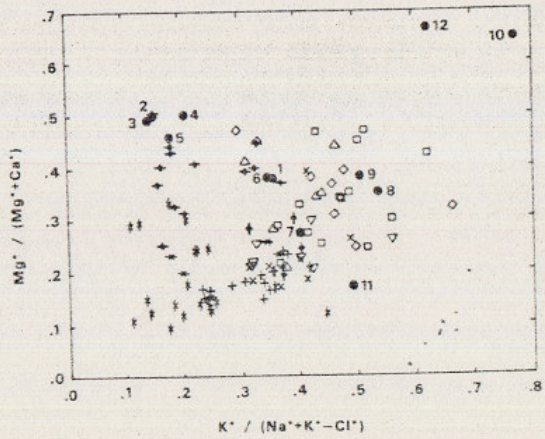

Fig. 12. Mg*/(Mg*+Ca*) versus K*/((Na*-Cl*)+K*). Ratios for samples from Amazon surface waters are included along with ratios predicted for transport-limited erosion of siliceous lithologies. Numbers refer to 1, average shield; 2, gabbro; 3, continental basalt; 4, diorite; 5, andesite; 6, granodiorite; 7, sodic granite; 8, potassic granite; 9, average shale; 10, black shale; 11, fresh granite, and 12, weathered granite [cf., Stallard, 1980]. Note that all of the lowland samples fall into a grouping, consistent with lithologies known to be in their drainages. In contrast, Andean samples are strongly sodium and calcium enriched compared to any reasonable silicate lithologies in their drainages.

Na*). The K*/((Na*-Cl*)+K*) ratio represents inputs solely from silicate weathering, while the Mg*/(Ca*+Mg*) ratio also includes contributions from carbonates and sulfates. Three features can be seen: (1) samples from particular regions plot as distinct groupings; (2) samples from lowland rivers plot in a general field which encompasses intermediate to acidic igneous rocks, "average" shield and "average" shale compositions (reflecting transport-limited conditions); and, (3) Andean samples are sodium and calcium enriched compared to typical igneous and shale compositions (reflecting preferential weathering-limited inputs in the case of Na).

The chemistry of the dissolved and solid loads of lowland rivers is consistent with erosion under transport-limited conditions. Most of the cation load is in solution. Denudation rates are exceedingly low [Stallard 1980], in agreement with the diminution of weathering rates with the developement of thick soils. This is exemplified by the Negro River, which drains Precambrian shield, and is volumetrically the largest tributary (Figure 1). After cyclic salt correction, the dissolved metals in the Negro, normalized to silica, have proportions similar to average shield rocks (Table 6). The enrichment of K and Mg in the Negro and some other lowland rivers probably reflects the reweathering of soils and fluvial-lacustrine sediments that have been enriched in K and Mg. Such reweathering has been described by Irion [1976, 1978].

In the Andean samples, calcium enrichment is largely due to contributions from limestones and evaporites; however, the (Na*-Cl*) enrichment can

TABLE 6. Comparison of Dissolved Solids in the Upper Negro River, With Average Shield

Element	Upper Negro	Average Shield
Sodium	0.095	0.122
Potassium	0.119	0.062
Magnesium	0.035	0.042
Calcium	0.073	0.069
Silicon	1.000	1.000
Iron	0.057	0.067
Aluminum	0.067	0.313

only be a result of the partitioning of potassium, during silicate weathering, into solid phases in soils and river suspended loads. This partitioning is particularly pronounced in the case of the Madeira tributaries which drain micaceous, black shales. The Na to K ratio of these rivers is much greater than that of the rocks in their catchments, probably reflecting the stability of potassium-bearing micas.

Terrestrial Biological Effects

There is no direct way to identify the effects of terrestrial biological reservoirs on the chemical budgets of the Amazon Basin without a detailed time-series sampling from lowland rivers. If biogeochemical budgets were constant and balanced, there would be no sensible effect on geochemical fluxes; however, if there are seasonal gains and losses of elements in the biomass, one-time sampling would not detect the effects. Elements for which a large proportion is found in the biomass compared to the soils are Ca, Mg, K, N, and S. Nitrate and sulfate showed substantial variations in lowland rivers between 1976 and 1977 samplings. Precipitation data suggest that these are in part recycled through the atmosphere [Stallard and Edmond, 1981]. All rivers which were sampled twice and which do not have marine sediments or red beds in their catchments (Negro, Tefé, Coari, Jutai, Nanay) show a factor of 2 variations in calcium (the Coari also shows a factor of 2 variation in Mg). Other species do not show such effects. This variability may reflect changes in biological reservoirs.

Factor Analysis

The above forms of data representation do not necessarily portray all of the relationships between samples in this data set. The presence of additional relationships, however, can be tested with Q-mode factor analysis. Factor analysis transforms the original data to a new set of variables or factors, fewer than the number of items being compared. When expressed as the amount of variance accounted for, the information content of these factors is almost as great as that of the original data. For the sake of argument, the factors can be taken as reflecting the underlying processes controlling the original data. For a set of geological data, factor analysis can be used both to determine the number of specific interrelationships between variables (degrees of freedom) in the data set and to describe them in light of some model [Joreskog et al., 1976]. A common geologic application of Q-mode factor analysis is to indentify source end members in a suite of sediment samples. For dissolved conservative phases in water, it would be expected that end members (in this case, specific water sources or characteristic weathering processes) could be similarly identified.

The major dissolved species, Na, K, Mg, Ca, Alk, Cl, SO_4, and Si were examined with Q-mode analysis. Concentrations were expressed in equivalents, except for silica, which was expressed as moles. This approach is different from that of the Mackenzie study, where log-transformed data were used. The data were processed with Imbrie Q-mode analysis [Imbrie and Van Andel, 1964; Joreskog et al., 1976], using a varimax rotation. The varimax factor matrix was then rotated obliquely such that all factor scores were greater than or equal to zero. Three factors account for 96.5% of the variance (Figure 13). Inclusion of a fourth accounts for 99.1%. These results indicate that three or four major distinguishable end members or processes could explain the relative concentration of major species in the samples.

The ternary diagram of Si-alkalinity-(Cl + SO_4) (Figure 11) and the ternary diagram of the three largest Q-mode factors are almost identical. This demonstrates that these three chemical paramenters are reasonably unique in terms of their information content and are effective at discriminating between characteristic types of samples. Those Madeira Basin samples which depart from the trend of (Ca+Mg) versus alkalinity (Figure 8) are those which exhibit high values of (the unplotted) factor 4. High values of factor 1 are related to rivers which drain marine deposits, factor 2 to siliceous terrains, factor 3 to evaporites, and factor 4 to reduced sediments.

Conclusion

In the Amazon Basin, substrate lithology and erosional regime exert the most fundamental control on the chemistry of surface waters within a catchment. Secondary effects, such as the precipitation of salts within soils and in stream beds, biological uptake and release, and cyclic salt inputs, are more difficult to discern, especially in more concentrated samples.

Erosional regimes provide the framework within which one can examine the role of substrate lithology. Two extreme cases can be defined: transport-limited and weathering-limited denudation. In the former, weathering inputs by a given lithology (at geomorphological equilibrium) should be proportional to the area exposed. For major cations, little fractionation would occur between bedrock and the dissolved weathering products, and solid products would be cation depleted. In the latter, weathering inputs by a given lithology should be proportional to both its area exposed and its susceptiblity to weathering. In addition, for dissolved phases, considerable fractionation relative to bed rock would occur, and solid products would be cation-rich. As is observed for Andean Rivers, Na and Ca are partitioned into solution, and K and Mg into solids, during weathering-limited erosion of siliceous rocks.

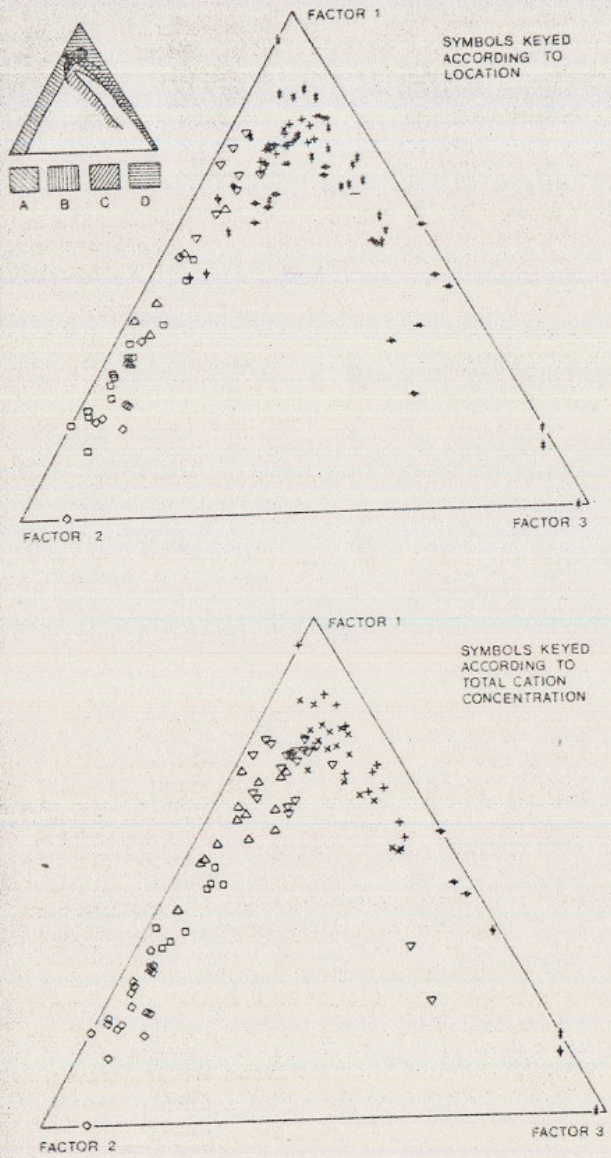

Fig. 13. Graphs of Q-mode factor analysis results showing the relative contributions made by the three obliquely rotated Q-mode factors. Symbols in the top and bottom diagrams are the same as in Figure 11.

Samples can be separated into four principal groupings based on relationships between total cation charge (TZ+) and geology: (1) Rivers with 0<TZ+<200 μeq/l drain the most intensely weathered materials formed in transport-limited regimes (Upper Tertiary sediments, soils of the Negro Basin and similarly weathered regions). These rivers show high levels of Fe, Al, H^+ and coloration and are enriched in Si relative to other major species; cation ratios are similar to those of substrate rocks. (2) Rivers with 200<TZ+<450 μeq/l drain siliceous terrains. These rivers are also rich in silica relative to other species. Rivers draining weathering-limited siliceous terrains tend to exhibit the highest TZ+ (even a little higher than 450 μeq/l), and their cation load is preferentially enriched in Na over K and Ca over Mg when compared to the rocks in their catchments. (3) Rivers with 450<TZ+<3000 μeq/l drain marine sediments or red beds with high cation concentrations (resulting from the presence of carbonates and minor evaporites in the Peruvian Andes and reduced shales and minor carbonates in the Bolivian Andes). These rivers exhibit relatively high levels of Ca, Mg, alkalinity, and SO_4 (in rivers draining reduced shales and minor evaporites). (4) Rivers with TZ+>3000 μeq/l drain massive evaporites. These rivers are rich in Na and Cl. In the third and fourth categories, rivers tend to have 1:1 (equivalent) ratios of Na:Cl and (Ca+Mg):(alkalinity+SO_4), caused primarily by the weathering of carbonates and evaporites.

The relationships between chemistry and geology are perhaps best illustrated by a ternary diagram relating silica, alkalinity, and sulfate plus chloride (Figure 11). Rivers that drain siliceous rock types are relatively high in silica and low in total cations. Those that drain carbonates are relatively high in alkalinity and possess intermediate levels of TZ+, while those that drain evaporites are rich in sulfate and chloride and are highest in TZ+. This is consistent with the weathering susceptibility trend for minerals in a tropical environment (Table 1), and indicates that susceptibility to weathering has a significant role in determining overall input rates, provided that the reactive lithologies are found in a weathering-limited region, such as the Andes.

The contribution by evaporites along the lower Amazon valley is observed to be minor. This is in accord with the observation that these deposits exist in a region of transport limited denudation.

The results from the ternary diagram are almost identical to the results of a Q-mode factor analysis. This is expected, since the ternary parameters were chosen to be as independent as possible based on observations of sample chemistry and basin geology.

The relatively simple relationships seen between major species in the Amazonian samples probably are not reflected in global surface waters as a whole, at least to the same degree. The basin lies entirely within the humid tropics, a situation amenable to the formation of cation depleted soils in a geologically short time. In the Amazon Basin, evaporative concentration of water and the associated precipitation of soil salts is unimportant, and massive seasonal uptake of plant nutrients does not appear to occur. Large regions are extremely flat and low lying. Silica uptake by organisms is insignificant in most samples, although it is detectable in some of the floodplain lakes (large scale silica consumption would of course completely alter some of the major observed trends). Finally, there is a deficency of some common lithologies, with two not being found extensively: namely, platform marine sediments and basic igneous rocks. As a consequence, concentrations in many large rivers which drain the shields are exceptionally low. This is in major contrast to systems like the Mississippi, Chiang Jiang, and Mackenzie.

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