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## Lithologic and climatologic controls of river chemistry\*

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**Abstract**—The chemistries of rivers draining a variety of lithologic and climatic regions have been surveyed for the purpose of quantifying the fluxes of bicarbonate and silica from rivers with respect to bedrock lithology and runoff. In all, 101 different rivers, each draining a primary lithology, were examined across the United States, Puerto Rico, and Iceland. To minimize seasonal effects, only rivers with at least two years of data were used. Basaltic catchments were examined in the greatest detail. In a survey of Hawaiian Island watersheds, the average river chemistries could be related to the distribution of soil associations within each catchment. An analysis of cation activity relationships among rivers draining basaltic catchments shows that the river compositions define slopes which are consistent with an equilibrium (ion exchange) control on cation ratios. Among different lithologies, unique weathering rate relationships were developed with yields at typical present-day runoff rates (1–100 cm/y) increasing in the order sandstones, granites, basalts, shales, and carbonates. The bicarbonate and silica fluxes for each of these lithologies have been quantified for use in global studies of chemical denudation. Our study confirms that the dissolved yield of a given drainage basin is determined by a balance between physical and chemical weathering; thus, a warm, wet climate, or the presence of abundant vegetation cannot guarantee high rates of chemical denudation unless accompanied by high rates of physical removal.

### INTRODUCTION

THIS RESEARCH AROSE OUT of our interests in the global carbon cycle, especially with respect to the bicarbonate flux from the world's rivers. In the global CO<sub>2</sub> budget, the sizes of the atmospheric, oceanic, biologic, and geologic reservoirs are relatively well known; conversely, rates of transfer among the reservoirs and the processes which control these rates are more uncertain. Because the total atmospheric CO<sub>2</sub> content is relatively small, it is most sensitive to changes in the flux rates between the reservoirs. In a simplification of the net global weathering process, atmospheric CO<sub>2</sub> is converted to bicarbonate and, balanced by a dissolved cation from the weathered bedrock, transported to the oceans by rivers. Over million-year timescales, the process of chemical weathering of the continents may shift considerable amounts of CO<sub>2</sub> from the atmosphere to seafloor carbonate sediments via river runoff. Existing models of the global CO<sub>2</sub> cycle include no detailed consideration of global geology, much less a treatment of the rates at which a certain lithologic unit would weather under a given climate (e.g., WALKER et al., 1981; BERNER et al., 1983; ARTHUR et al., 1985; VOLK, 1989; BERNER, 1990). Our objective was to determine the weathering rates of major rock types from the literature, and devise the best method of describing how these various lithologies weather under different climatic regimens.

Unfortunately, published studies of chemical denudation rates lack one or more of the following: separation of catchments into detailed lithologic divisions, calculations of stream

fluxes rather than chemical concentrations (i.e., inclusion of stream discharge data), and diversity of geographic and climatic conditions (temperature, rainfall, runoff, elevation, topography). Most studies do not extend over long enough periods to account for short-term climate and biotic fluctuations, yet it has been repeatedly documented that salts and nutrients are typically stored in the unsaturated zones of drainage basins and washed out during periods of high precipitation and runoff (DREVER, 1988 and references within). In addition, there are conflicts regarding the net weathering result of temperature change (e.g., DAVIS, 1964; HOLLAND, 1978; MEYBECK, 1986; UGOLINI, 1986) and elevation/topography (e.g., GARRELS and MACKENZIE, 1971; REYNOLDS and JOHNSON, 1972; STALLARD, 1985; DREVER, 1988; DREVER and ZOBRIST, 1992). The biota and soils play important roles in determining stream chemistry (LIKENS et al., 1977), yet their effects are inherently more difficult to quantify than mean annual rainfall, temperature, river discharge, or physical properties of the basin. We, therefore, decided to begin our own study using existing data on river chemistry and calculating runoff (area-weighted discharge) using river discharge and catchment area.

Given the current state of knowledge, and our interest in the global cycling of elements by rivers, our goal is to consolidate various physical and chemical parameters of drainage basins and quantify the effects of lithology and climate on river chemistry. The approach to understanding the many complicating factors involved in natural drainage systems is to start from a fairly simple perspective: we begin by examining basins composed of a single lithology (basalt) from a single region (Hawaii) to gain some quantitative insights into the major factors affecting the chemical weathering process. Next, we include regions of varying climate which also drain

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basalt catchments. Lastly, catchment data from a variety of lithologies and climatically diverse regions are surveyed to determine the relationships among rock type, climate, and river chemistry.

## PREVIOUS WORK

### General Conclusions Regarding Chemical Weathering

The numerous influences of different geologic, geographic, climatic, and anthropogenic factors add complexities to quantitative chemical weathering studies of natural systems. However, studies of rock and mineral weathering using actual riverine chemistry consistently conclude what seems intuitively correct: the total dissolved yield from rivers is primarily a function of runoff, while the rates of dissolution are directly related to basin lithology and permeability of the soil and bedrock (e.g., GOLDICH, 1938; more recently GARRELS and MACKENZIE, 1971; STALLARD and EDMOND, 1983; PETERS, 1984; MEYBECK, 1986).

Earlier investigations into the controls of stream chemistry (summarized in PETERS, 1984) generally agreed that both mineral durability and residence time of groundwaters affect surface water quality. For example, the chemical composition of runoff from basins underlain by highly resistant rocks appeared to be far more dependent on precipitation chemistry than that of runoff from more soluble rocks. Basin lithologies were routinely grouped into three relative levels of dissolution tendency or release of cations to stream runoff: low (e.g., sandstones and quartzites); medium (most igneous and metamorphic rocks); and high (carbonates and evaporites).

### Recent Examinations of Climate and Weathering

PETERS (1984) studied relationships among river chemistry, precipitation, stream temperature, human population density, and three types of bedrock (limestone, sandstone, and crystalline). He surveyed fifty-six basins throughout the United States over a three year period using data from the USGS Water Supply Papers. The dominant factor in total dissolved yield was annual precipitation quantity, accounting for 58–71% of the variance in the major dissolved constituents of river runoff for a given lithology. Rock type was secondary in importance. A problem with his investigation was that, although care was taken to select basins composed of a single rock type, the large drainage basin sizes used (>10,000 km<sup>2</sup>) could not strictly adhere to his criterion of monolithology. PETERS (1984) found no conclusive effect of temperature on weathering. He reasoned that although silicate minerals progressively lose cations in warmer climates, regions which seasonally experience subzero temperatures enhance both physical and chemical weathering through frost cracking and wedging. Weathering in temperature climates is further complicated by increased carbonic acid solubility relative to tropical climates, and, therefore, increased dissolution of carbonate rocks at cooler temperatures.

MEYBECK (1986) examined 232 monolithologic watersheds throughout France, comprising fairly uniform land usage, forest cover, and distance from both oceanic and pollutant inputs. However, the streams were sampled only one or two times over the total two year period of study. MEYBECK (1986) assigned a numerical scale of weathering tendency in the general order of increasing susceptibility: granites, sandstones, volcanics, shales, carbonates, and evaporites. In contrast to DAVIS (1964) and PETERS (1984), MEYBECK (1986) found a positive correlation between mean air temperature and dissolved silica (from -2.5 to 11.5°C). The temperature effect was progressively more pronounced from calcareous rocks, to metamorphic lithologies, to basalts. Silica concentration also increased with decreasing elevation, which MEYBECK (1987) asserted was due to accompanying climatic effects. Bolstered by additional data from other water quality studies, MEYBECK (1987) turned to mass-balance calculations for relative concentrations, and computed relative contributions to the global budget from carbonate and silicate rock weathering.

STALLARD and EDMOND (1981, 1983, 1987) investigated the Amazon River basin. In the first paper, a study of precipitation

chemistry in the basin, a scheme was established for determining and correcting for cyclic ocean salt contributions to river dissolved loads. In the second, they used mass balance to evaluate the lithologic, soil, and topographic influences on stream quality. Individual drainage basins and their corresponding stream qualities were analyzed on the basis of denudation rate and relative soil cover. Transport-limited denudation, where the maximum weathering rate exceeds the ability of transport processes to remove material, results in the development of thick soils. Weathering-limited regimes, where transport exceeds generation, produce only a thin soil cover. The third paper concerned chemical and thermodynamic aspects of mineral dissolution. Within the framework of weathering regimes in the Amazon Basin, the carbonate lithologies of the Andes mountains are generally weathering-limited. On the other hand, dissolution of silicates which dominate the relatively low-lying Amazon basin tends to be controlled by transport processes, which leads to the development of thick soils. From his work on the Amazon basin, STALLARD (1985) created a simple model of the balance between soil thickness and mineral dissolution. He proposed that there is an optimal soil thickness for chemical weathering, below which water residence times are too short, and above which the interaction of the waters with fresh mineral surfaces is reduced.

### Biological Factors in Chemical Weathering

It is generally believed that dissolution rates increase in the soil horizon because of root respiration and oxidation of organic carbon, which produces higher levels of CO<sub>2</sub> (and carbonic acid). Bacterial and algal weathering also play large roles in chemical dissolution of near-surface minerals. CAWLEY et al. (1969) studied river runoff from basaltic terrains in central Iceland. They found chemical weathering, in terms of bicarbonate concentration, was 2–3 times higher in areas with plant cover as opposed to barren catchments. These results were repeated qualitatively by JACKSON and KELLER (1970), who compared weathering rinds of Hawaiian basalts between lichen-covered vs. bare rock. The presence of lichens appeared to enhance cation and silica leaching, while increasing iron oxide formation (however, these conclusions have been contested by COCHRAN and BERNER, 1992).

Research at the Hubbard Brook Experimental Forest included balancing nutrient fluxes among the biota, precipitation, soil and rock weathering, and stream runoff. During an 11-year period of study, LIKENS et al. (1977, 1985) found that silica and aluminum were the dissolved solids least affected by biomass uptake. Balanced with the annual input from weathering and precipitation, sodium was taken up only in small quantities, but K (68%), Ca (35%), and Mg (17%) were significantly accumulated by the biomass; the remainder was either stored in the soil as dead matter or removed from the system through stream runoff.

Watershed mass balance studies have typically accounted for the possible importance of biomass storage and release (e.g., VELBEL, 1985; PACES, 1986) although steady state is often assumed. STALLARD and EDMOND (1983) recognized the potential for biomass storage of silica and nutrients in the Amazon, especially during short-term studies such as theirs, but did not directly account for biological reservoirs in their results. Later, STALLARD (1985) balanced river runoff chemistry with mineral dissolution and concluded that any large-scale biotic effects in the Amazon region must be approximately at steady state. In a quantitative experimental evaluation, ROBERT and BERTHELIN (1986) compared biologic weathering between bare rock and various bacterial or microorganism additions. Microbial attack enhanced dissolution up to 20% in periods typically within only a few months. DREVER (1988) warned of the potential for biomass accumulation of nutrients, especially K, Ca, P, and N for biotic systems which are not at steady state. He suggested that a reference element such as Si may be used to determine the balance of relative solute weathering, because it is often not affected to any great extent by biologic uptake or absorption. However, LOVERING (1959) reviewed a number of studies regarding the effects of plants on rock weathering. Many species, especially those in tropical areas, accumulate silica in their systems. Hardwoods, grasses, palms, and sugar cane may contain as much as 3% of their dry weight in SiO<sub>2</sub> (RODIN and BAZILEVICH, 1965).



### Anthropogenic Effects on River Chemistry

Human activities which add solutes to stream runoff include road salting, mining, industrial waste, and agriculture. Both population density and land use have been used qualitatively as indicators of the impact of pollutants on the concentrations of certain elements (such as Na, chloride, sulfate, nitrate, and phosphate) in rivers. PETERS (1984) was only able to effectively use population density as a predictive tool for sodium and chloride concentrations in U.S. rivers. In general, the major element chemistry of rivers draining highly polluted areas are subject to significant variations, primarily in Ca, Na, Mg, and sulfate concentrations. Notably, the bicarbonate and Si concentration of major rivers (e.g., the Mississippi and Rhine) appear to be much less affected than other ions by increased anthropogenic activity over the last century (BERNER and BERNER, 1987, Table 5.7).

### Use of Bicarbonate and Silica as Indicators of Chemical Weathering

The results of PATTERSON and ROBERSON (1961) demonstrate the relative mobility of cations and silica from the weathering profile of a basalt terrain in Hawaii (Fig. 1). The mobile cations are rapidly depleted; Al (and Ti) oxides are relatively immobile and iron oxides are formed as weathering products. Silica is gradually depleted with degree of weathering. The ratio of mobile cations to silica drops an order of magnitude between fresh rock and the weathered horizons (the slight upward increase of the ratio in the upper portion of the weathered column primarily reflects the continual loss of silica; the cations are almost completely stripped out of the basalt down to the fresh rock). Waters in contact with unweathered rock have a much richer reservoir of cations available for dissolution in comparison to weathered rock (actual ratios in stream waters are modified by the formation of secondary clays such as kaolinite or smectite, which would then lower the available silica).

Other than evaporites and pyrite-bearing units, most rock types contain little natural Cl or S and the dominant anion is bicarbonate. DREVER (1988) showed by charge balance that a large input of sulfuric acid from highly polluted regions could result in reduced bicarbonate ion concentration. However, in typical riverine waters, corrected for ocean salts, the sum of the mobile cations from rock weathering can be assumed to be balanced by bicarbonate. We will, therefore, approximate the net weathering process using the relationships of bicarbonate and dissolved Si to river runoff.

### Consensus of Chemical Weathering Studies

To summarize, previous studies have generally agreed that (1) total dissolved solids in rivers are primarily a function of runoff; (2)

the rates of dissolution are controlled by basin lithology and the permeability of the soil and bedrock; (3) human influences on stream quality are highly variable, but are most likely to affect the Na, chloride, sulfate, and nitrate concentrations; (4) on the long-term, biologic factors may be considered to exist in steady state; that is, any uptake by plants is assumed to be balanced by release to the runoff at comparable rates; and (5) bicarbonate and dissolved Si appear to be the best elements to use to examine chemical weathering, because they give a good idea of the progression of weathering in the bedrock and soil, and are least affected by human activities.

### SOURCES OF DATA

Basin geology was determined primarily from state geologic maps, typically at scales of 1:500,000 or larger. Most sites were chosen by examining the geologic maps, with help from previous work of BEISECKER and LEIFESTE (1975) and PETERS (1984), and matching drainage basin lithology to USGS stream gauging stations. Local geologic maps and individual investigations of regional geology were used to check for accuracy. River sampling sites are listed in the Appendix.

The bulk of river chemistry data used in this study is from the National Water Data Exchange at the U.S. Geological Survey. Icelandic river chemistry data are from ARMANNSSON et al. (1973) and RIST (1974, 1986). The rivers in this study were typically sampled once a month, over a period of at least two years. In addition, there are a wide variety of climatological and topographic sites on the Hawaiian Islands from which to compare river chemistries. In order to test the effects of soil development on chemical weathering, data obtained from the soil maps of FOOTE et al. (1972) and SATO et al. (1973) have been used in conjunction with Hawaiian river chemistry. All river chemistry data have been corrected for concentrations of cyclic sea salts in rainfall using the approach of STALLARD and EDMOND (1981).

### GEOCHEMISTRY OF BASALT CATCHMENTS

A logical and informative starting point is to examine catchments which are similar in lithology. The actual makeup of a carbonate, sandstone, or even granite lithology often varies widely among geographic regions. By comparison, the chemical compositions of basalts collected from different regions are typically quite similar (Table 1). Numerous localities exist in the United States where basalts extend over vast regions, uninterrupted by other rock types. Drainage basins underlain by basalts make a consistent starting point from

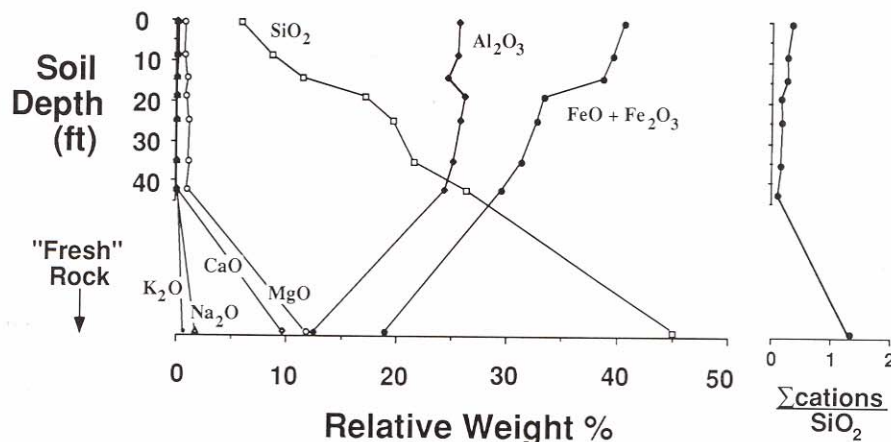


FIG. 1. Soil chemistry, in weight percent, of a weathering sequence above basalt bedrock in Kauai, Hawaii (after PATTERSON and ROBERSON, 1961). Ratios of mobile cation equivalents ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^+$ ,  $Na^+$ ) to silica are balanced on constant  $Al_2O_3$ , calculated at each depth level.

Table 1. Major chemical constituents of basaltic rocks in weight %, and ratio of mobile cation equivalents (Mg + Ca + Na + K) to moles SiO<sub>2</sub>.

	Columbia Plateau		Hawaii		Iceland	
	1	2	3	4	5	6
SiO <sub>2</sub>	50.02	49.08	50.1	48.53	49.70	47.35
Al <sub>2</sub> O <sub>3</sub>	15.43	13.71	13.7	14.26	13.00	13.65
FeO + Fe <sub>2</sub> O <sub>3</sub>	12.51	14.27	12.0	11.94	15.00	16.03
MgO	6.01	4.58	5.6	5.01	5.77	5.03
CaO	9.93	8.44	11.9	11.62	10.50	9.63
Na <sub>2</sub> O	2.38	3.17	2.3	2.60	2.38	3.00
K <sub>2</sub> O	0.50	1.31	0.5	0.66	0.29	0.09
Σcations/SiO <sub>2</sub>	0.90	0.81	0.94	0.94	0.90	0.88

<sup>1,2</sup>WATERS (1961); <sup>3</sup>HAY and JONES (1972);

<sup>4</sup>WASHINGTON and KEYES (1928); <sup>5</sup>GISLASON and EUGSTER (1987); <sup>6</sup>SIGVALDASON (1969).

which to evaluate environmental influences on stream chemistry. The Hawaiian Islands, the Columbia Plateau region, Iceland, and miscellaneous regions in the U.S. provide a number of river sites over a fairly wide range of climatic regimes, and thus were chosen for comparison.

#### Controls of River Chemistry Among the Hawaiian Islands

The Hawaiian Islands can be differentiated by age, from the oldest in the northwest to the youngest in the southeast: from Kauai with a 3.8–3.9 my extinction date, Oahu at 2.2–2.9 my, Molokai at 1.3–1.8 my, Maui at 0.4–1.2 my, to Hawaii which is currently active (CARMICHAEL et al., 1974). A useful relationship would be a correlation between age of the bedrock and resulting chemistry of surface runoff, given a single lithology and climate, assuming that weathering rates decrease with time due to progressive leaching of bedrock

and soil. Figure 2 shows the bicarbonate vs. silica concentration for streams in Kauai, Oahu, Molokai, Maui, and Hawaii. If the age of the rock could be used to indicate the degree of weathering, rivers draining the island of Hawaii should have the highest ratio of mobile cations (bicarbonate) to silica. This age relationship does not occur: ratios ranging from 2:1 to 3:1 for streams draining the island of Hawaii overlap with ratios from 2:1 to 4:1 for Kauai, the oldest island.

The stream concentrations most likely reflect influences of soil development within a particular basin. Among the Hawaiian Islands, extremely high rainfall and intense chemical interaction in windward catchments can rapidly form thick, leached soils. Table 2 summarizes terrain, runoff, and soil characteristics of the Hawaiian catchments used in this study, separated by island. In general, the Hawaiian Islands have extremely high relief. Mean annual rainfall is generally abundant, but highly dependent on geography and thus varies widely among the islands. Runoff varies by an even greater extent, due in part to extensive subsurface drainage that results from the permeable nature of the basaltic bedrock. However, low runoff despite high rainfall may also indicate that only a small portion of the basin area contributes to river runoff. For instance, on the island of Hawaii catchments extend up the flanks of Mauna Loa and Mauna Kea but elevations above ~2000 m receive relatively little rainfall, while the catchment regions at lower elevations may receive over 500 cm during the year (HAY and JONES, 1972).

The average bicarbonate to dissolved silica ratio in the rivers varies greatly within each island (Table 2). This variation can be explained by studying the relative distribution of soils within each catchment. The relative proportions of soil types were calculated using the soil survey maps of FOOTE et al. (1972) and SATO et al. (1973). This survey is only for general comparisons as the actual distributions of soil, and

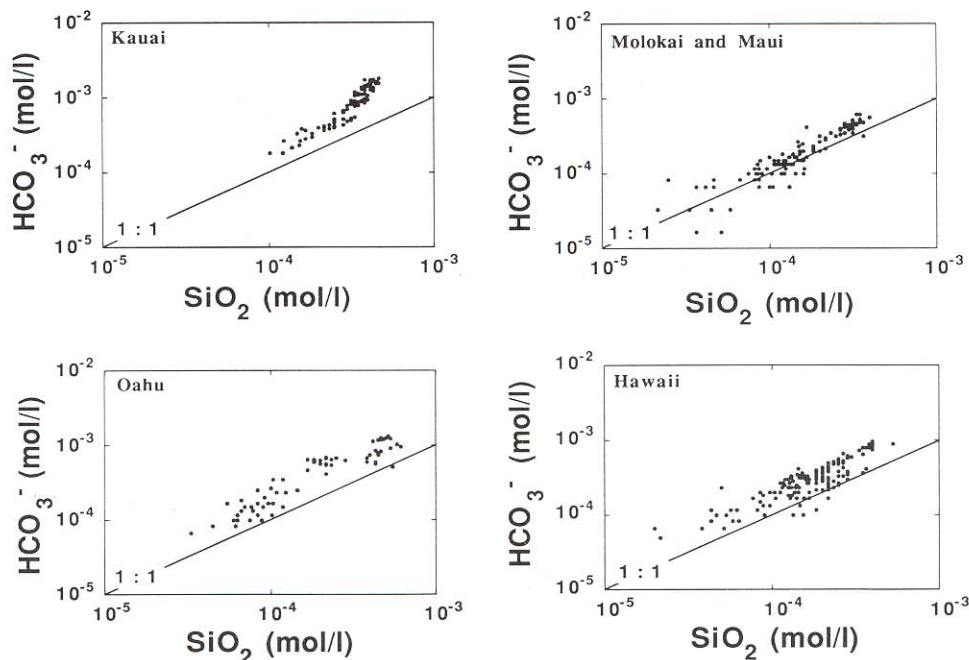


FIG. 2. Bicarbonate vs. silica concentration for selected Hawaiian rivers. The 1:1 lines are plotted for reference.



Table 2. Hawaiian catchments

River Catchment	Relief	Rainfall (cm/yr)	Runoff (cm/yr)	Stream chemistry (HCO <sub>3</sub> <sup>-</sup> /SiO <sub>2</sub> )	Soil weathering associations			
					rock (%)	low-med (%)	high (%)	organic (%)
Hanapepe R., Kauai	high	380	375	2.48	50	25	5	20
Waimea R., Kauai	high - low	190	66	3.03	55	20	5	15
Wainiha R., Kauai	high - low	510	271	1.43	30	20	10	40
Kalihi Str., Oahu	high - moderate	255	52	2.70	40	10	45	5
Kaluanui Str., Oahu	high	255	115	1.66	30	-	70	-
Kipapa Str., Oahu	high - moderate	320	52	1.96	30	30	10	30
Makaha Str., Oahu	high - moderate	130	8	1.59	20	30	35	15
Makawao Str., Oahu	high - moderate	190	127	2.49	10	30	60	-
Halawa Str., Molokai	high - moderate	205	278	1.08	20	20	20	40
Hanawi Str., Maui	moderate	635	394	1.67	15	5	15	65
Kahakuloa Str., Maui	high - moderate	380	148	1.30	25	40	5	30
Hilea Gulch Trib., Hawaii	moderate	195	9	1.06	25	30	-	45
Honolui Str., Hawaii	moderate	400	245	2.10	-	100	-	-
Wailuku R., Hawaii	moderate - low	700	52	1.43	5	80	-	15

Soil data from FOOTE et al. (1972) and SATO et al. (1973)

Rainfall data from STEARNS and MACDONALD (1946); HAY and JONES (1972); WERNSTEDT (1972).

Relief as described in data: High = mountainous, >40% slopes; Low = level, gentle slopes, <15% slopes; Moderate = steep slopes, uplands, 15-40% slopes.

Soil associations: rocky = exposed rock, rocky, ash, cinder, or pre-soil; low-med = inceptisol, mollisol, spodosol; high = ultisol, oxisol; organic = histosol, organic rich soil

their relative influence on each watershed, clearly need more intensive study. However, it appears that among the various islands, rivers which drain basins with high proportions of exposed rock, rocky soils, and relatively less weathered soils, and low proportions of highly weathered or boggy soils, are typically the richest in cations (i.e., have high bicarbonate to silica ratios).

#### Stability Diagrams for River Waters

Previous studies have used mineral stability diagrams in efforts to place thermodynamic constraints on river chemistries. NORTON (1974) analyzed both the dissolved and suspended river load at forty-six locations within the Rio Tanama, Puerto Rico watershed (underlain primarily by hydrothermally altered quartz diorite and andesitic lavas). Using activity-activity ratios, NORTON (1974) found that the river samples plotted along a 2:1 slope in the Ca-Na activity diagram, and along a 1:1 slope in the Ca-Mg diagram. NORTON (1974) concluded from the study that river chemistry was controlled by dissolution of the bedrock and subsequent release of cations in molar proportions. DREVER (1988) re-examined the NORTON (1974) data, and suggested an alternative explanation: cation exchange between the secondary cation-bearing phases (smectites) and river water was responsible for the characteristic position of the data parallel to the Ca-smectite/Na-smectite and Ca-smectite/Mg-smectite boundaries.

Our data for rivers draining basaltic catchments are plotted in activity-activity diagrams comparing Ca, Mg, and Na from rivers draining basalt regions (Fig. 3a-c). The data are from fourteen Hawaiian rivers, nine rivers from the Columbia Plateau, and five rivers from southwest Iceland. For clarity, the figures contain best fit lines through the data (the data were

quite linear, with  $r^2$  values averaging 0.931). The rivers plotted within a narrow range of slopes: the Ca-Mg smectite and the Ca-Na smectite boundaries (DREVER, 1988) are included for reference. Interestingly, the rivers draining the various basalt catchments in this study plot in a nearly identical region to that for rivers draining Rio Tanama andesites/quartz diorites. The main difference observed among the three (basaltic) geographic regions is the relative position of the data on a line which extends from the kaolinite to the Ca-smectite stability regions. The majority of samples from Hawaiian rivers lie in the low activity region, whereas Columbia Plateau rivers plotted mainly in the high activity region; the Icelandic rivers straddled the two.

NORTON (1974) noted that in the Rio Tanama system as one progressed downstream the data plotted further up slope in the activity-activity plots, towards the smectite region. He found this characteristic consistent with that of an initially dilute solution which becomes progressively more concentrated with continued water-rock interaction. But whereas the NORTON (1974) data were from many sampling sites in a drainage system during only a single time period, we observe essentially the same trends in the activity ratios in our spatially and temporally-sampled data (i.e., rivers sampled at one site, but over a period of two years or greater). Within a given watershed, the river compositions plotted towards the kaolinite field during periods of high river discharge, and towards the smectite field during low discharge. MILLER and DREVER (1977) observed a similar trend in their study of the North Fork Shoshone River, Wyoming watershed (underlain by andesitic lavas): when groundwater discharge dominated the drainage system during the wintertime the water samples plotted in the smectite field, while waters collected during the high spring-runoff season plotted in the kaolinite field.

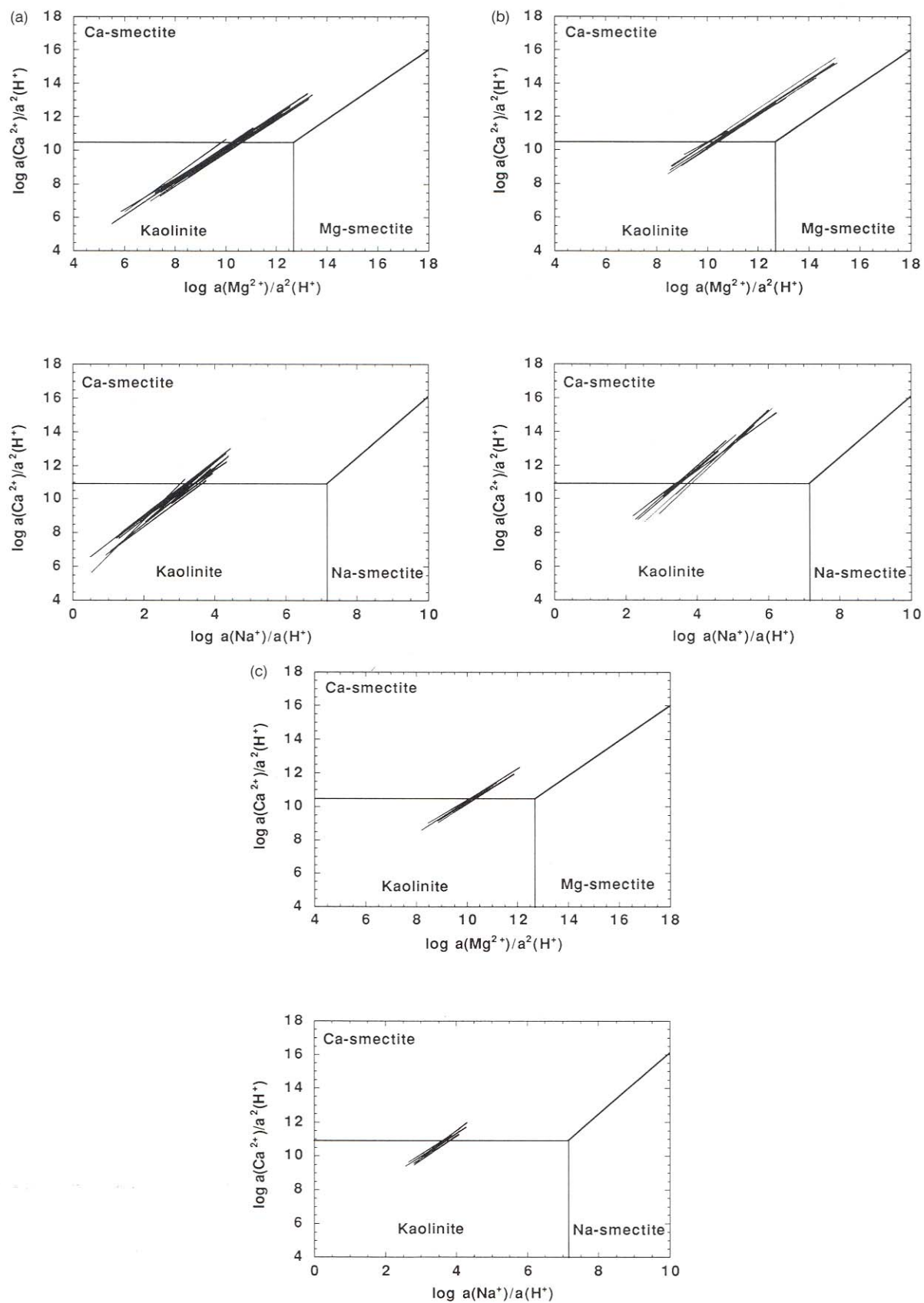


FIG. 3. Activity diagrams of the Ca-Mg and Ca-Na smectite-kaolinite systems.  $T = 25^\circ\text{C}$ ,  $a_{\text{SiO}_2} = 10^{-3.7}$ . Phase boundaries from DREVER (1988). (a) Hawaiian Islands; (b) Columbia Plateau region; (c) southwest Iceland.



If the river chemistry depended only on bedrock composition and weathering stoichiometry (NORTON, 1974), we would expect a much greater variation among the cation activity ratios. Our data are consistent with both the DREVER (1988) suggestion that cation exchange between secondary phases and river waters, and the MILLER and DREVER (1977) idea that kinetic dissolution rates of the bedrock mineralogy act as limiting factors in controlling river chemistry. However, if cation exchange among clays and solution is the controlling mechanism of river chemistry, our data imply that the clay exchange sites must be compositionally similar from region to region, a possibility which could be tested in a more detailed investigation. In summary, as DREVER (1988) has stated it is not clear that a single interpretation exists for all river systems, and this study can only, at this time, add information from a wider variety of environments.

#### Comparison of River Chemistry from All Basalt Catchments

Figure 4(a-b) shows the trends of bicarbonate and silica concentrations for basaltic terrains as functions of runoff. During short periods of increased rainfall, such as during storms, the dissolved load of river waters may show little sign of dilution if old waters stored in the unsaturated and saturated zones of catchments are washed out (e.g., CLEAVES et al., 1970; JANDA, 1971; KENNEDY and MALCOLM, 1977; MILLER and DREVER, 1977; SKLASH et al., 1986). However, over a longer-term seasonal basis, chemical denudation (and riverine dissolved load) does not correspondingly increase with increased runoff. Rather, chemical denudation rates begin to approach a plateau as the effects of dilution become important. Different catchment lithologies have unique values of maximum chemical denudation; eventually a maximum dissolved yield from the basin is reached, and stream chemistry is controlled by simple dilution. Thus, the trend of the plotted data approaches a dilution slope (negative unity).

At low runoffs, bicarbonate concentrations appear to be limited by calcium carbonate solubility. Typical groundwaters in carbonate terrains ( $T = 10^{\circ}\text{C}$ ,  $p_{\text{CO}_2} = 10^{-2.0}$  atm) would be saturated with respect to calcite at bicarbonate concentrations of  $10^{-2.44}$  mol/L (after HOLLAND, 1978). Bicarbonate concentration begins to decrease at runoff rates of 1–10 cm/y. For reference, the world's twenty largest rivers have average runoff rates ranging from 14–120 cm/y; the world average is about 30 cm/y (HOLLAND, 1978).

At a mean annual air temperature of  $25^{\circ}\text{C}$ , the upper limit of silica values is well above quartz saturation ( $10^{-4}$  mol/L), yet below that of amorphous silica at  $10^{-2.7}$  mol/L (KRAUSKOPF, 1956). The upper limit of silica concentration suggests that silica is buffered by equilibrium with a silica phase of intermediate solubility such as chalcedony (ROGERS, 1987), or by secondary clay minerals such as kaolinite and smectites. In contrast to the bicarbonate content of rivers, silica concentrations do not begin to demonstrate dilution until much higher runoff rates, around 100 cm/y.

The dilution trends in these plots of basaltic terrains are similar to those of HOLLAND (1978), who used average river compositions and drainage basins of mixed lithology. HOLLAND (1978) found the range of bicarbonate and silica con-

centrations at runoffs greater than 15 cm/y is much broader than the range at lower runoff values, and noted similar trends for Ca, Mg, and silica. Holland (1978) attributed this difference to large rivers with high runoff rates; these rivers drain a wider variety of lithologies, and the different proportions of carbonate rocks in the drainage basins produce the spread of data. The other major ions tend to plot uniformly along negative slopes throughout the range of runoff. We observe a similar, apparent scatter at high runoff values. However, we cannot invoke variations in catchment lithology to explain these trends because our watersheds are all in basalt terrains. Also, we have found that there is no obvious tendency for large watersheds to have the largest runoffs; indeed, large drainage basins tend to average out the extreme runoffs periodically observed in smaller catchments. Some of the scatter can be attributed to the relative rates of physical to chemical weathering within the given watershed (this concept is discussed in the following section). In our dataset however, the scatter at high runoff in silica and bicarbonate concentrations is largely due to differences in the position of dilution trends for the various watersheds analyzed.

#### RELATIONSHIPS OF STREAM FLUXES TO BASIN LITHOLOGY

In this section, we will address (1) our use of relationships among river runoff and elemental fluxes; (2) the unique weathering rates of carbonate and noncarbonate lithologies; and (3) in light of these results, the effects that climate change may impart on continental denudation.

##### River Runoff and Elemental Fluxes

Stream chemistries, while useful for understanding weathering processes, cannot describe the intensity of weathering or rates of material loss from a drainage basin. Flux rates are essential for denudation estimates and models of  $\text{CO}_2$  cycling. The relationships among runoff, silica, and bicarbonate concentrations have established that increased runoff will increase the denudation rate only to a finite extent, until dilution becomes dominant. Fluxes, which are simply the product of the concentration and runoff, directly represent denudation rates while not introducing any new variables (i.e., trends which are evident in concentration-runoff plots appear in flux-runoff plots as well).

River runoff, as used in this study, represents the net flow of water out of a watershed, averaged over the surface of the catchment. Factors which affect the ultimate discharge of water by river drainage include topography, vegetation, soil, temperature, and rainfall: in other words, river runoff can be considered a function of both long- and short-term regional climate. At this stage of our investigation only runoff and lithology are used as variables: runoff as a proxy for climate and lithology representing the starting material in the catchments.

In a simple sensitivity experiment, BLUTH (1990) calculated the global bicarbonate flux from chemical denudation for times in the geologic past, by estimating the geographic distribution of geologic exposures and using climatic regimens derived from global climate models. This spatially resolved

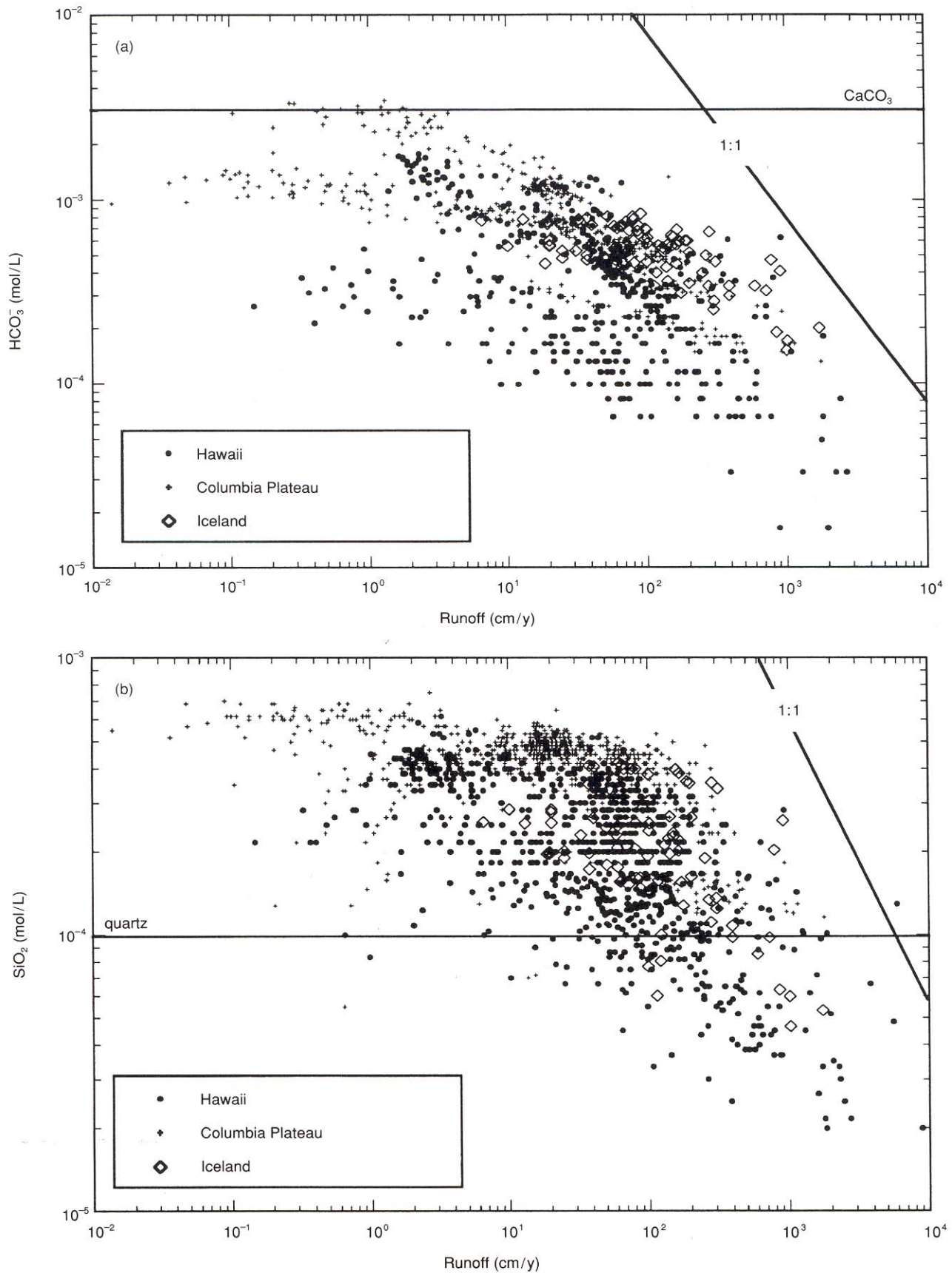


FIG. 4. Concentration vs. runoff for rivers draining basaltic terrains in Hawaii, the Columbia Plateau region, and Iceland. (a) Bicarbonate.  $\text{CaCO}_3$  solubility boundary is shown at  $10^\circ\text{C}$ ,  $p\text{CO}_2 = 10^{-2}$  atm; (b) Silica. Quartz boundary shown at  $25^\circ\text{C}$ .



Table 3. Chemical compositions in weight % of some major rock types, and ratio of mobile cation equivalents (Mg + Ca + Na + K) to moles SiO<sub>2</sub>.

	Basalt <sup>1</sup>	Granite <sup>1</sup>	Sandstone <sup>1</sup>	Shale <sup>2</sup>	Limestone <sup>2</sup>
SiO <sub>2</sub>	51.55	70.77	78.66	55.43	5.19
Al <sub>2</sub> O <sub>3</sub>	14.95	14.59	4.78	13.84	0.81
FeO + Fe <sub>2</sub> O <sub>3</sub>	11.65	3.37	1.38	5.74	0.54
MgO	6.63	0.89	1.17	2.32	7.9
CaO	10.0	2.01	5.52	1.41	42.61
Na <sub>2</sub> O	2.35	3.52	0.45	1.01	0.05
K <sub>2</sub> O	0.89	4.15	1.32	3.60	0.33
Σcations/SiO <sub>2</sub>	0.91	0.27	0.23	0.50	7.3

<sup>1</sup>HOLLAND, 1978

<sup>2</sup>CLARKE, 1924

case resulted in a significantly different global bicarbonate flux compared to a spatially unresolved model (e.g., those using global average runoff and silicate/carbonate distribution). Thus, we believe current models can be improved by the addition of a spatial dimension of rock weathering. BLUTH and KUMP (1991) used records of sedimentary and volcanic rock deposition to approximate the geographic distribution of rock exposures through each period of the Phanerozoic. The next step, described here, is to examine the actual rates of weathering of each rock type and determine the best method of describing how these various lithologies weather under a given climate.

The chemical compositions of the catchment rock types used in this study are compared in Table 3. In typical river

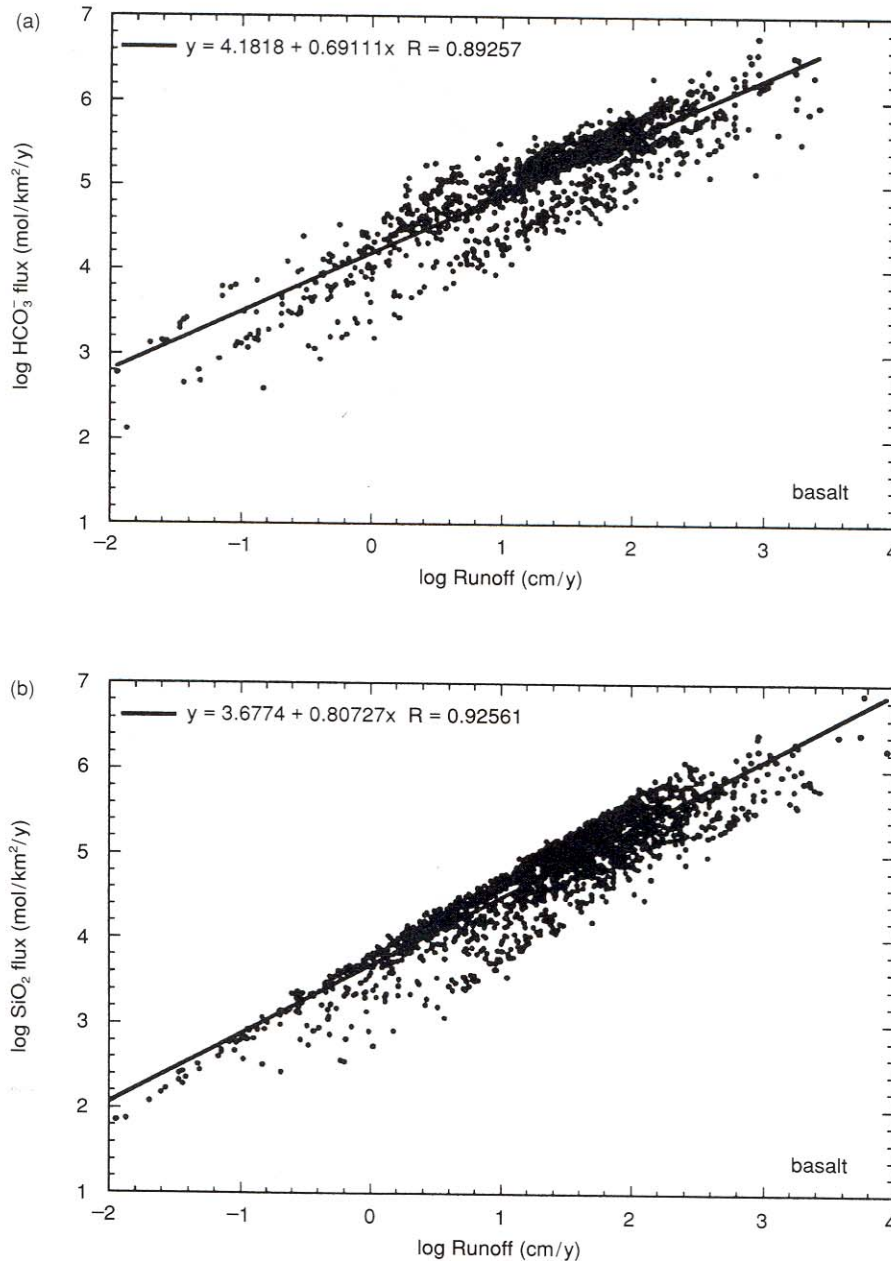


FIG. 5. Elemental fluxes vs. runoff for all streams draining basaltic lithologies. (a) Bicarbonate; (b) Silica.

waters, the dissolved cations (chiefly Mg, Ca, Na, and K) are balanced by bicarbonate and, to a much lesser extent, sulfate. Whether river chemistry of catchment lithologies is strongly dependent on dissolution tendencies, or is affected by cation exchange with secondary phases, rivers which drain basalts, granites, sandstones, shales, and limestones should show unique trends in bicarbonate and dissolved silica flux rates.

The chemistry data for rivers draining basalt, granite, sandstone, carbonate, and shale catchments have each been

used to calculate bicarbonate and silica flux rates (Figs. 5–9, and Table 4). Not surprisingly, rivers draining carbonate catchments produce higher bicarbonate fluxes throughout the range of runoff. Carbonate terrains also yield a large amount of dissolved silica during chemical denudation. At runoff rates below approximately 100 cm/y, rivers which drain silicate catchments yield more silica than do carbonate drainage basins. However, at runoff rates higher than 100 cm/y, carbonate rocks produce relatively higher yields of dissolved sil-

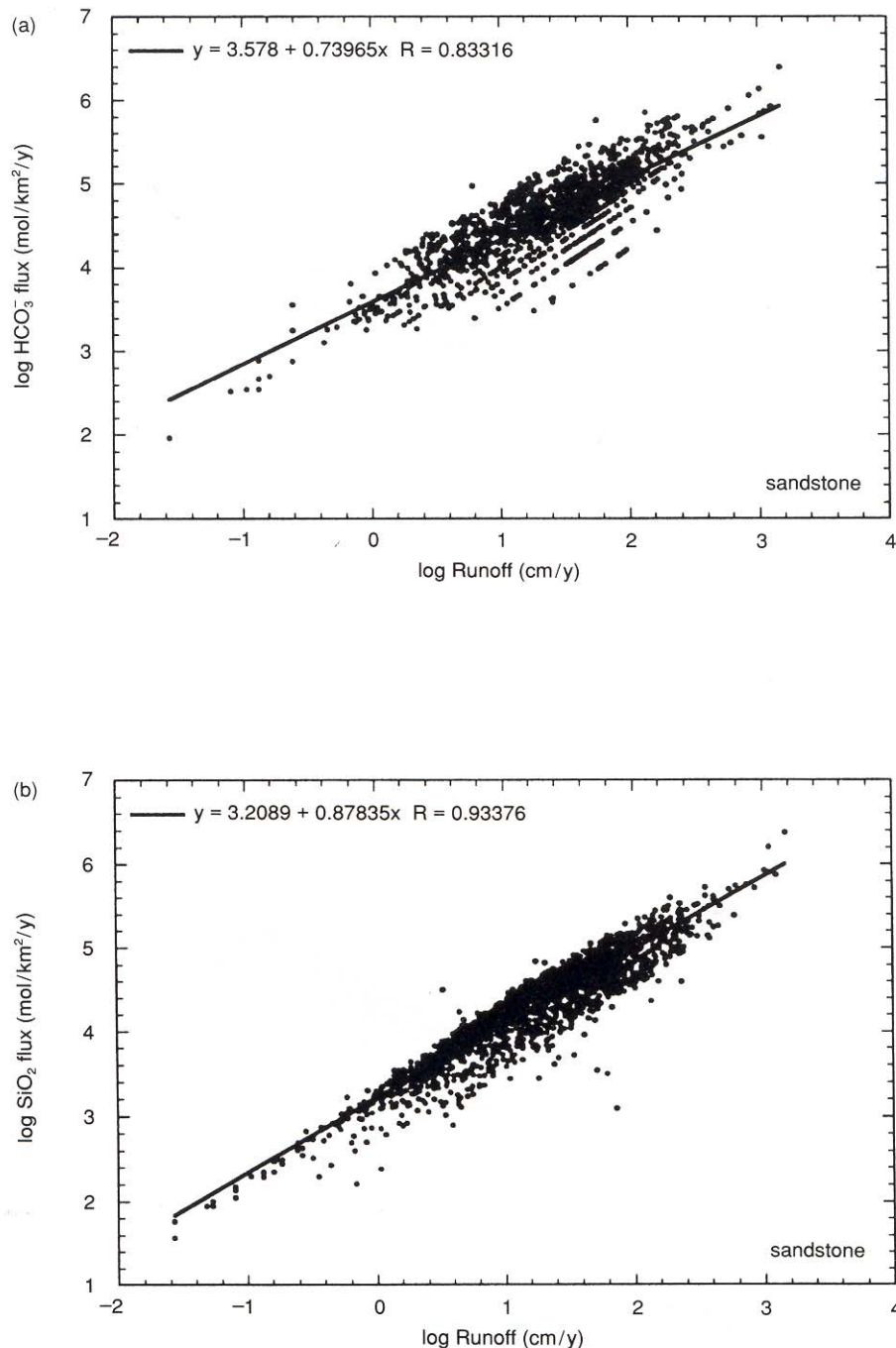


FIG. 6. Elemental fluxes vs. runoff for all streams draining sandstone lithologies. (a) Bicarbonate; (b) Silica.



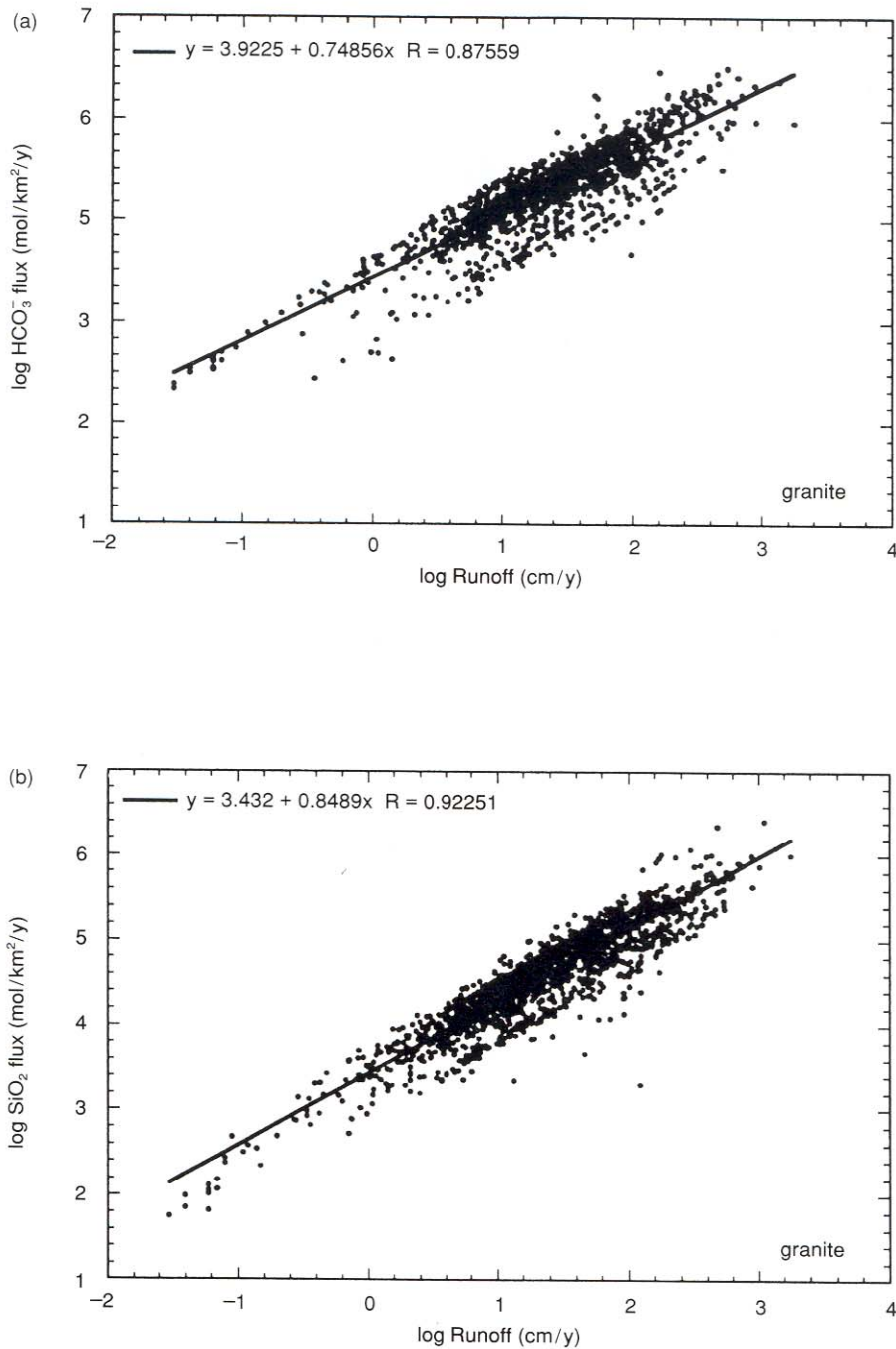


FIG. 7. Elemental fluxes vs. runoff for all streams draining granitic lithologies. (a) Bicarbonate; (b) Silica.

ica. These high proportions of dissolved silica in rivers draining carbonates can be explained by the presence of biogenic silica in carbonate rocks (either disseminated or interbedded), which is easily dissolved along with the carbonate material.

Shales also produce high yields of both silica and bicarbonate; as suggested by HOLLAND (1978), high bicarbonate fluxes for shale lithologies are most likely due to dissolution of interbedded carbonates. Shales in the United States typically contain from about three to ten weight percent carbon-

ates (using data of CLARKE, 1924, and calculations from HOLLAND, 1978).

The similarity of river compositions, especially at runoffs  $> 100$  cm/y, draining granitic and basaltic rocks contradicts the MEYBECK (1986, 1987) results. However, BEISECKER and LEIFESTE (1975) and the data from PETERS (1984) both indicate chemical denudation in granitic watersheds proceeds at the same or higher rate as in basaltic watersheds. BEISECKER and LEIFESTE (1975) explained the trend in their data by

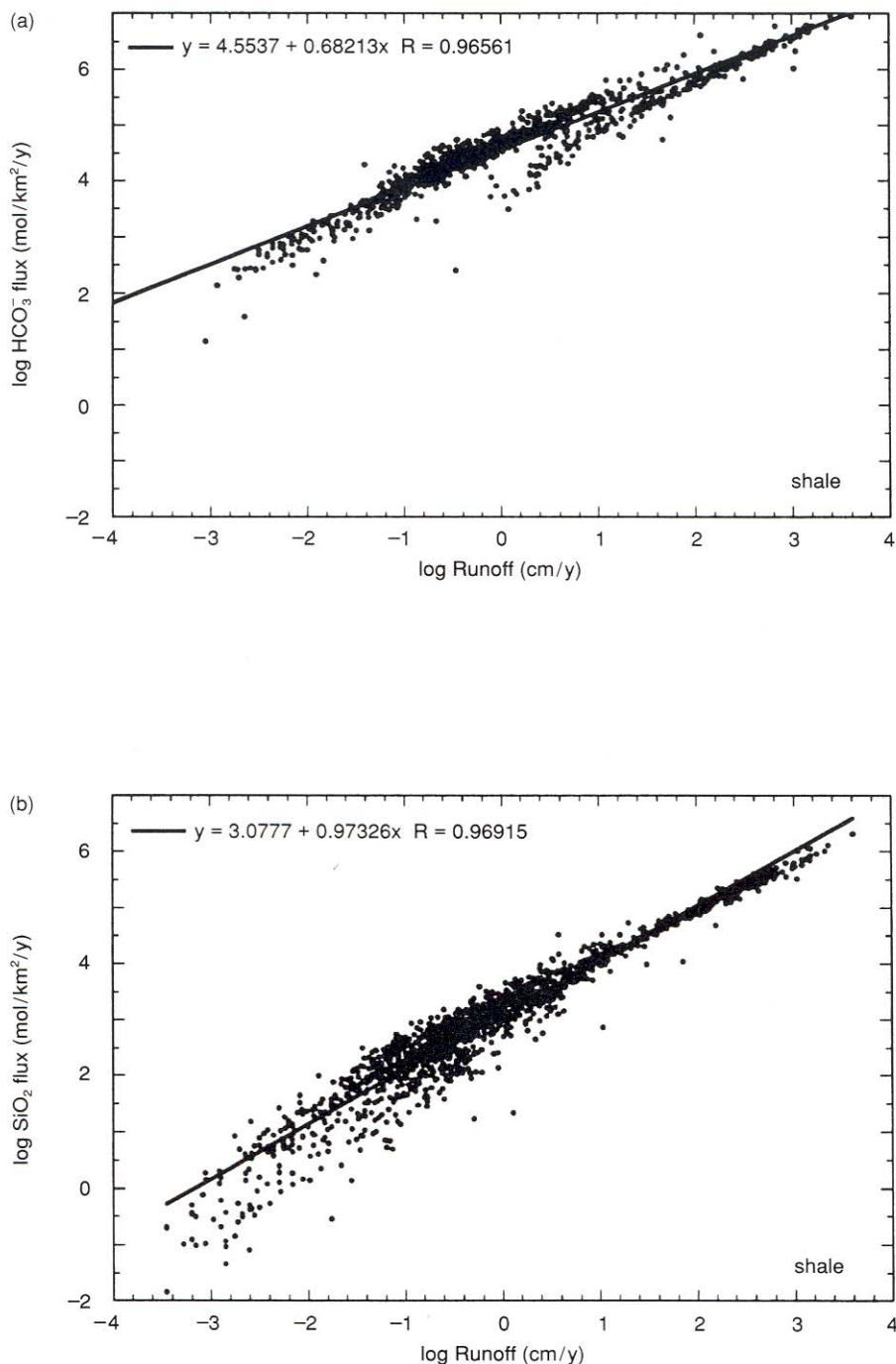


FIG. 8. Elemental fluxes vs. runoff for all streams draining shale lithologies. (a) Bicarbonate; (b) Silica.

reasoning that the residence time of groundwaters in granitic bedrock is typically greater than that of basalts, due to the lower permeability of granite. The waters are, therefore, able to react with the rock for a longer time in the granitic terrains.

Figures 5–9 show that slopes of silica flux vs. runoff are closer to unity than are those for bicarbonate flux to runoff. This trend represents the different effects of dilution on elemental transport (as previously observed for basaltic terrains), whereby bicarbonate is affected by dilution at much lower

runoff rates than is silica. Thus, it appears that silica buffering is occurring to some extent among all the lithologic types.

GARRELS and MACKENZIE (1971) calculated the rates of chemical denudation for each continent, based on the relative proportions of bicarbonate and silica in the rivers which drain them. They concluded that the continental denudation rate increased as a function of the proportion of carbonate rocks, reflected in the bicarbonate/silica ratio. In Fig. 10, we have plotted the total flux rates (bicarbonate + silica) at the global



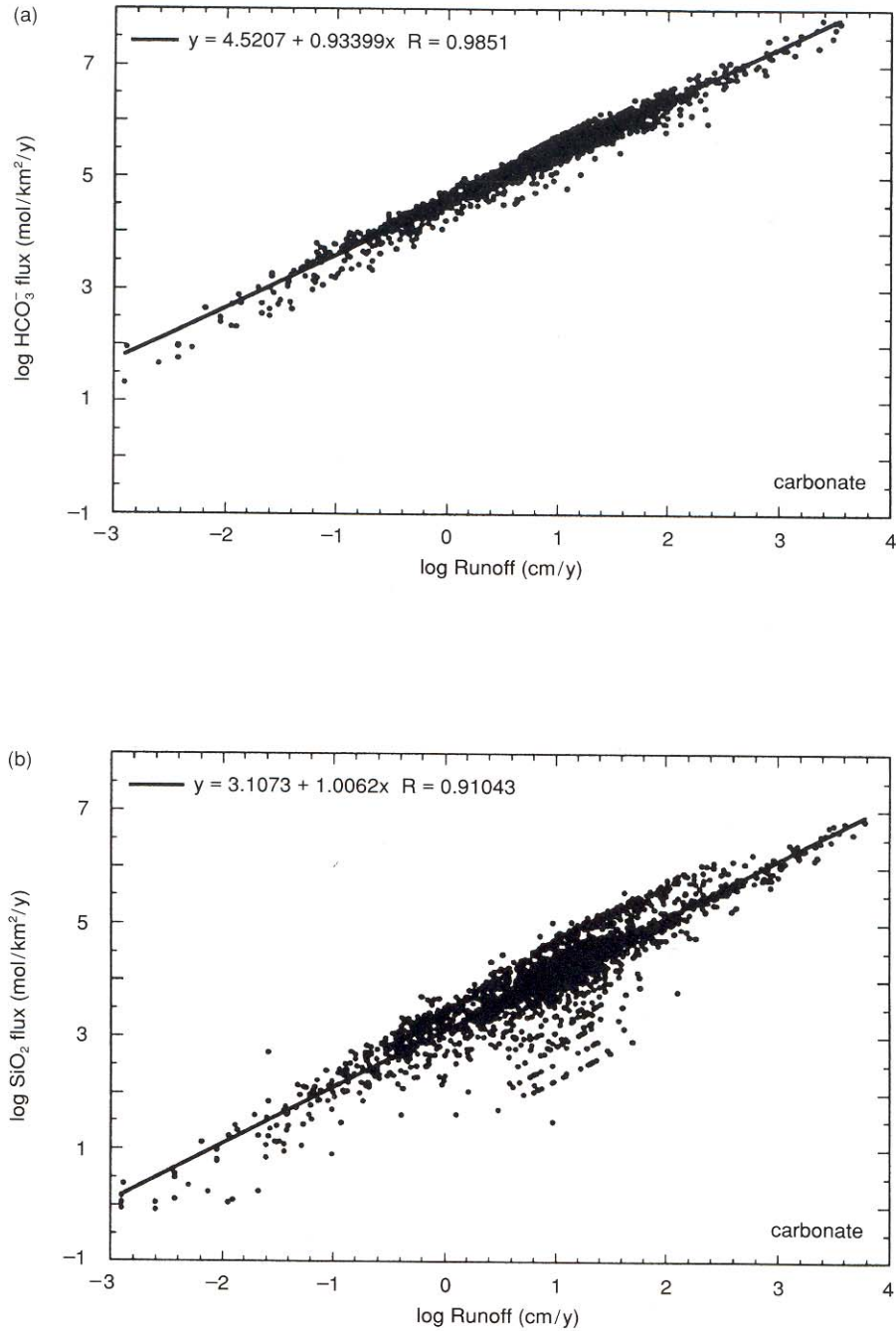


FIG. 9. Elemental fluxes vs. runoff for all streams draining carbonate lithologies. (a) Bicarbonate; (b) Silica.

average runoff of 30 cm/y for each lithology with respect to the ratio of bicarbonate and silica concentrations in the rivers. The data from GARRELS and MACKENZIE (1971) are included for comparison; note that their denudation rates are based on total dissolved material, while our rates are based on bicarbonate and silica only. This plot clearly illustrates the differences in yield from each lithology, and indeed, under comparable conditions of climate and physical denudation, continental exposures composed mainly of carbonates and shales would have a much higher chemical denudation rate

compared to a continent rich in igneous and sandstone exposures.

It is interesting to compare the relative denudation rates of each lithology with their original compositions of cations and silica (Table 3). As a first approximation, the cation/silica ratios of the major rock types may be categorized as either carbonate or non-carbonate. The same distribution is essentially true for chemical denudation of monolithologic watersheds, with basalt, granite, and sandstones grouped together at relatively low denudation rates, carbonates at high

Table 4. Empirical bicarbonate and silica flux relationships for chemical denudation calculations.

Basin Lithology	Equation	Correlation ( $r^2$ )
Basalt	$\log(\text{HCO}_3^- \text{ flux}) = 4.182 + 0.691(\log R)$	0.7967
	$\log(\text{SiO}_2 \text{ flux}) = 3.677 + 0.807(\log R)$	0.8567
Sandstone	$\log(\text{HCO}_3^- \text{ flux}) = 3.578 + 0.7396(\log R)$	0.6942
	$\log(\text{SiO}_2 \text{ flux}) = 3.209 + 0.878(\log R)$	0.8720
Granite	$\log(\text{HCO}_3^- \text{ flux}) = 3.922 + 0.749(\log R)$	0.7667
	$\log(\text{SiO}_2 \text{ flux}) = 3.432 + 0.849(\log R)$	0.8510
Shale	$\log(\text{HCO}_3^- \text{ flux}) = 4.554 + 0.682(\log R)$	0.9324
	$\log(\text{SiO}_2 \text{ flux}) = 3.078 + 0.973(\log R)$	0.9393
Carbonate	$\log(\text{HCO}_3^- \text{ flux}) = 4.520 + 0.906(\log R)$	0.9512
	$\log(\text{SiO}_2 \text{ flux}) = 3.080 + 1.020(\log R)$	0.8409

Flux units are in mol/km<sup>2</sup>/yr; R = runoff in cm/yr.

denudation, and shales falling in between. The denudation rate of shale catchments is much higher than would be predicted by the bedrock composition, reflecting the high proportion of interbedded carbonates.

### Biological Effects on Continental Denudation

Biological processes affect chemical weathering in a number of ways, for instance by supplying acidity to the subsurface, by the transfer of nutrients from the soil to the surface during growth cycles, and by physically working the soil through root growth (e.g., see DREVER, 1994). KNOLL and JAMES (1987) concluded from experimental and laboratory studies that vascular land plants must promote weathering of soil minerals, regardless of plant type. BASU (1981a) discussed the differences in chemical dissolution between pre- and post-Silurian sandstones. He noted that there has been apparently no loss of K feldspars in pre-Silurian sediments. Since K is a highly processed nutrient in present-day regions, weathering must have occurred to the extent that Ca and Mg feldspar was dissolved, but high K activity sustained through lack of biological uptake favored the preservation of K-feldspars (however, see the comments of GRAUSTEIN and VELBEL, 1981, and reply by BASU, 1981b). SCHWARTZMAN and VOLK (1989) favor microbial activity as the primary force of chemical weathering rather than higher forms of vegetation, thus suggesting that pre- and post-Silurian weathering were relatively unaffected by the introduction of land plants.

The biological effect on chemical denudation likely depends to a great extent on weathering regime (following the terminology of STALLARD and EDMOND, 1987). In tropical, stable, or subsiding basins, thick soils may develop whether or not an active soil biota exists, creating a transport-limited denudation regime. At the other extreme, thick soils and a transport-limited regime are unlikely to develop on steep slopes even with biological acceleration of chemical weathering. Between these extremes, and in regions prone to weathering limitations, the effect of organisms on chemical denudation rates could be significant.

The basalts which comprise the watershed bedrock of Iceland and Hawaii are of similar composition (see Table 1). Intuitively, Hawaiian streams draining basins with an average rainfall of 200–400 cm/y and mean annual temperatures of 16–23.5°C (WERNSTEDT, 1972) should have higher chemical

dissolution rates than those of southwest Iceland (average rainfall 75–150 cm/y, mean annual temperatures 3.0–3.5°C; EYTHORSSON and SIGTRYGGSSON, 1971). However, comparison of dissolved load of silica and bicarbonate to runoff (Fig. 5a–b) reveal that this is clearly not the case. Of the two regions, Icelandic streams plot among the highest flux to runoff values.

This trend can be explained by comparison of the different soil characteristics of the Hawaiian and Icelandic catchments. The warm, wet tropical climate of Hawaii has formed drainage basins containing soils which are relatively thick, acidic, and low in available nutrients (FOOTE et al., 1972; SATO et al., 1973). In contrast, southwest Icelandic soils are relatively thin, less acidic, and more nutrient-rich (HELGASON, 1963, 1968). Both physical and chemical denudation rates for southwest Iceland are 2–3 times higher than the world average (GISLASON et al., 1990). Although temperature and soil biota do directly affect chemical weathering, it appears that over time the magnitude of that influence probably depends on rates of physical removal. If rates of physical weathering are equal to or greater than chemical removal (e.g., southwest Iceland, a weathering-limited regime), the chemical weathering rate remains high. If chemical dissolution is faster than the rate of physical removal (Hawaii, a transport-limited regime), a leached soil can rapidly form and accumulate to the point of shielding the bedrock and reducing the rate of chemical weathering.

The results of our comparison of different climatic regions suggest that over geologic time, the combination of climate, vegetation, and uplift are the controlling mechanisms of continental denudation rates. While the presence of plants both directly and indirectly favor mineral weathering, an excess of soil formation will greatly retard further dissolution. Thus, a warm global climate and abundant vegetation alone should not be equated with high long-term rates of chemical weathering; without physical removal over geologic time the denudation rate may be no different with a cooler, drier climate, or on lifeless continents. Optimum, long-term weathering conditions consist of a balance between chemical dissolution

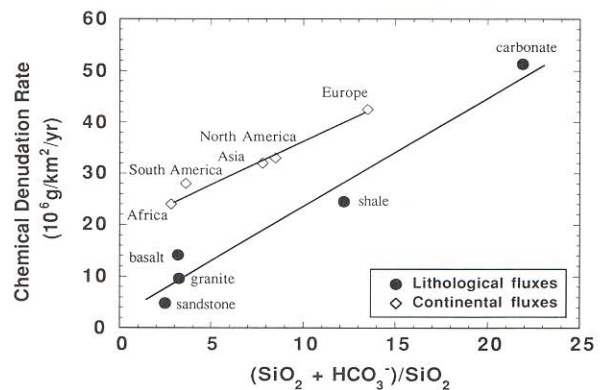


FIG. 10. Comparison of continental vs. lithological chemical denudation rates, as functions of silica and bicarbonate contents of rivers. Continental denudation relationships from GARRELS and MACKENZIE (1971). Lithological denudation rates are the total of bicarbonate and silica fluxes in this study, using the global average runoff rate of 30 cm/y (after HOLLAND, 1978).



and physical removal, a goal achieved episodically over geologic time by rapid uplift.

#### SUMMARY AND CONCLUSIONS

We have undertaken a study of small drainage basins composed of a single lithology to develop relationships among rock type, climate, and chemical denudation. For rivers which drain most rock types, the sum of cations are balanced largely by bicarbonate. The denudation rates among the different lithologies in this study were similar, in a general sense, to the relative proportions of cations and silica in the original rock compositions, with silicates at low denudation rates and carbonates at high rates. Shale catchments plot at intermediate denudation levels as a result of their high carbonate content. Of all the major elements in river waters, bicarbonate and silica are relatively unaffected by human influences. Therefore, bicarbonate and silica appear to be good indicators of chemical weathering, even under present-day conditions.

A survey of basalt catchments was undertaken using thirty-three rivers from Hawaii, Iceland, the Columbia Plateau region, and other regions in the U.S.A. Among Hawaiian Island watersheds, the average river chemistries could be related to the relative distribution of soil units within each catchment. Using activity-activity diagrams, the river compositions consistently fall along slopes that are consistent with an equilibrium (ion exchange) control on cation ratios. During periods of high runoff, the activities of Ca, Mg, and Na are low, and vice-versa; nevertheless, the data follow a 1:1 slope for Ca/Mg and 2:1 slope for Ca/Na at all values of runoff.

The bicarbonate and silica fluxes from each rock type were determined as a function of runoff. At the typical present-day range of runoff from 1–100 cm/y, the order of increasing weathering susceptibility is sandstone, granite, basalt, shale, then carbonate lithologies. Our comparison of rivers draining basaltic terrains shows that the optimum climatic conditions do not necessarily produce the highest rates of chemical denudation; while the presence of abundant vegetation and tropical climate favor chemical dissolution, an excess of soil formation (e.g., low rates of physical weathering) will greatly reduce chemical weathering. For a given continental mass, the balance between chemical weathering and physical removal acts as a negative feedback against either high, long-term chemical weathering under a tropical climate, or preservation of the bedrock under a temperate climate. Thus, changes in climate, continental position, and uplift rates are vital components of the global weathering budget.

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## Appendix A1. Basalt Catchments

Station Number	River	Location	Period of Record	Basin Area (km <sup>2</sup> )
4014500	Baptism R.	Beaver Bay, MN	4/68 - 8/89	363
5124480	Kawashiwi R.	Ely, MN	7/66 - 8/89	656
10237000	Beaver R.	Adamsville, UT	7/50 - 10/89	785
10346000	Truckee R.	Farad, CA	10/60 - 4/81	2416
10356500	Susan R.	Susanville, CA	10/60 - 3/90	477
10396000	Donner und Blitzen R.	Frenchglen, OR	3/75 - 8/86	518
13169500	Big Jacks Cr.	Bruneau, ID	1/67 - 7/89	656
13342450	Lapwai Cr.	Lapwai, ID	12/74 - 1/90	609
14048000	John Day R.	Mcdonalds Ferry, OR	8/60 - 2/90	19647
14103000	Deschutes R.	Biggs, OR	12/52 - 3/90	27216
14113000	Klickitat R.	Pitt, WA	9/47 - 7/86	3362
14123500	White Salmon R.	Underwood, WA	8/60 - 6/80	1000
14143500	Washougal R.	Washougal, WA	10/64 - 9/70	280
14223500	Kalama R.	Kalama, WA	10/61 - 7/70	513
16031000	Waimea R.	Waimea, Kauai	2/71 - 4/90	150
16049000	Hanapepe R.	Eleele, Kauai	2/71 - 9/88	48
16108000	Wainiha R.	Hanalei, Kauai	8/71 - 9/88	26
16211600	Makaha Str.	Makaha, Oahu	12/67-10/86	6.0
16212800	Kipapa Str.	Wahiawa, Oahu	1/68 - 9/86	11
16229000	Kalihi Str.	Honolulu, Oahu	4/69 - 2/90	6.8
16254000	Makawao Str.	Kailua, Oahu	12/67 - 6/86	5.3
16304200	Kaluanui Str.	Punaluu, Oahu	5/70 - 8/86	2.9
16400000	Halawa Str.	Halawa, Molokai	6/69 - 1/90	12
16508000	Hanawi Str.	Nahiku, Maui	1/72 - 8/88	9.0
16618000	Kahakuloa Str.	Honokohau, Maui	12/74 - 4/90	9.0
16704000	Wailuku R.	Piihonua, Hawaii	10/71 - 9/88	596
16717000	Honolooi Str.	Papaikou, Hawaii	9/69 - 2/90	30
16764000	Hilea Gulch Trib.	Honuapo, Hawaii	10/71 - 4/88	24
127	Fossa	Jadar, Iceland	2/72 - 12/73	29.0
65	Grimsa	Fossatun, Iceland	7/73 - 12/74	313.0
n.a.	Floka	Pjodvegur, Iceland	7/73 - 12/74	155.0
n.a.	Pvera	Pjodvegur, Iceland	7/73 - 12/74	480.0
128	Noroura	Stekkur, Iceland	7/73 - 12/74	500.0

## Appendix A2. Sandstone Catchments

Station Number	River	Location	Period of Record	Basin Area (km <sup>2</sup> )
1362198	Esopus Cr.	Shandaken, NY	8/63 - 10/89	154
1545600	Young Womans Cr.	Renovo, PA	5/65 - 4/89	120
2176500	Coosawatchie R.	Hampton, SC	4/58 - 5/86	526
2197300	Upper Three Runs	New Ellenton, SC	11/67 - 9/89	225
2202500	Ogeechee R.	Eden, GA	5/37 - 10/89	6860
2203000	Canoochee R.	Claxton, GA	12/37 - 9/70	1437
2225500	Ohoopee R.	Reidsville, GA	12/37 - 9/70	2874
2226500	Satilla R.	Waycross, GA	5/37 - 8/70	3107
2228000	Satilla R.	Atkinson, GA	11/37 - 10/89	7223
2231000	St. Mary's R.	McClenny, FL	2/58 - 8/86	1812
2264100	Bonnet Cr.	Vineland, FL	5/61 - 7/84	145
2266480	Davenport Cr.	Loughman, FL	4/68 - 5/81	60
2327500	Ochlockonee R.	Thomasville, FL	12/37 - 8/70	1424
2329000	Ochlockonee R.	Havana, FL	8/57 - 11/89	2955
3237280	Upper Twin Cr.	McGaw, OH	8/67 - 2/90	33
3460000	Cataloochee Cr.	Cataloochee, NC	10/62 - 11/89	128
3497300	Little R.	Townshend, TN	8/63 - 8/87	275
7026000	Obion R.	Obion, TN	3/75 - 8/87	4800
8041500	Village Cr.	Kountze, TX	10/62 - 9/85	2230

## Appendix A3. Granite and Gneiss Catchments

Station Number	River	Location	Period of Record	Basin Area (km <sup>2</sup> )
1054200	Wild R.	Gilead, ME	9/64 - 9/89	180.2
2052000	Meherrin R.	Emporia, VA	10/52 - 8/89	1936
2075500	Dan R.	Paces, VA	10/52 - 7/89	6610
2212600	Falling Cr.	Juliette, GA	10/67 - 10/89	187
2223000	Oconee R.	Milledgeville, GA	5/37 - 2/67	7638
2331000	Chattahoochee R.	Leaf, GA	6/41 - 5/76	389
2344500	Flint R.	Griffin, GA	3/37 - 9/69	704
2412000	Tallapoosa R.	Heflin, AL	5/65 - 8/83	1160
6623800	Encampment R.	Encampment, WY	10/64 - 10/89	188
7311200	Blue Beaver Cr.	Cache, OK	2/65 - 7/89	64
8431700	Limpia Cr.	Ft. Davis, TX	8/67 - 10/81	136
9196500	Pine Cr.	Fremont Lake, WY	5/75 - 4/88	196
9352900	Vallecito Cr.	Bayfield, CO	3/63 - 12/89	187
11187000	Kern R.	Kernville, CA	10/74 - 3/90	2615
11208630	Atwell Cr.	Hammond, CA	7/68 - 9/71	1.7
11208650	Redwood Cr.	Hammond, CA	7/68 - 9/71	3.5
11208680	Squirrel Cr.	Hammond, CA	7/68 - 9/71	15
11218500	Kings R.	Trimmer, CA	10/55 - 1/90	3478
11264500	Merced R.	Yosemite, CA	3/68 - 7/89	469
12392300	Park R.	Colburn, ID	10/74 - 10/81	321
12416000	Hayden Cr.	Hayden Lake, ID	11/66 - 11/89	57
12447390	Andrews Cr.	Mazama, WA	12/71 - 2/90	57
12452500	Chelan R.	Chelan, WA	10/64 - 9/72	2395

## Appendix A4. Shale Catchments

Station Number	River	Location	Period of Record	Basin Area (km <sup>2</sup> )
2450250	Sipsey Fk.	Grayson, AL	10/66 - 8/89	238
6175540	Prairie Elk Cr.	Oswego, MT	10/75 - 9/79	911
6177500	Redwater Cr.	Circle, MT	10/74 - 8/85	1416
6177825	Redwater R.	Vida, MT	10/75 - 9/85	5111
6178150	Poplar R.	Scoby, MT	8/75 - 8/89	1553
6436800	Horse Cr.	Vale, SD	9/64 - 2/82	1372
6470500	James R.	La Moure, ND	1/58 - 7/87	11366
6471000	James R.	Columbia, SD	3/51 - 11/89	15164
9213500	Big Sandy R.	Farson, WY	10/62 - 9/78	8334
9216000	Big Sandy R.	Eden, WY	10/61 - 5/81	4168
9306410	Evacuation Cr.	Dragon, UT	11/74 - 8/83	259
12039300	N Fork Quinalt R.	Amanda Park, WA	9/65 - 8/86	192
12041200	Hoh R.	Forks, WA	11/61 - 6/80	655



## Appendix A5. Carbonate Catchments

Station Number	River	Location	Period of Record	Basin Area (km <sup>2</sup> )
1634000	N Fork Shenandoah R.	Strasburg, VA	3/68 - 6/86	1991
2313000	Withlacoochee R.	Holder, FL	1/50 - 7/89	4730
3276700	S Hogan Cr.	Dillsboro, IN	10/68 - 9/85	99
3427500	E Fork Stones R.	Lascassas, TN	3/65 - 6/68	679
4085000	Fox R.	Wrightstown, WI	6/60 - 11/89	16096
5376000	N Fork Whitewater R.	Elba, MN	8/67 - 7/89	262
6867000	Saline R.	Russell, KS	10/45 - 9/75	3893
6897950	Elk Cr.	Decatur City, IA	10/45 - 9/89	136
6898000	Thompson R.	Davis City, IA	2/68 - 9/73	1815
7060710	N Sylamore Cr.	Fifty Six, AR	6/66 - 2/90	151
7343000	N Sulphur R.	Cooper, TX	1/67 - 3/90	715
8069200	Cypress Cr.	Humble, TX	10/71 - 5/83	826
8155300	Barton Cr.	Austin, TX	1/79 - 6/89	301
8158600	Walnut Cr.	Austin, TX	4/76 - 3/90	133
8158640	Walnut Cr.	Austin, TX	1/75 - 8/86	133
10244950	Steptoe Cr.	Ely, NV	3/68 - 4/89	29
50143000	R. Grande de Anasco	Lares, P.R.	2/59 - 9/86	68
50146000	R. Grande de Anasco	Anasco, P.R.	3/60 - 9/86	251
50147600	R. Culebrinas	San Sebastian, P.R.	11/79 - 9/86	151
50149100	R. Culebrinas	Aguado, P.R.	4/58 - 9/86	251