Rates of chemical denudation of silicate rocks in tropical catchments

CHEMICAL denudation includes the set of processes which mobilise ions from rocks and carry them to the sea in solution. These processes, and the rates at which they act, are of considerable importance in the development of landforms and soils because they are responsible for weakening rocks which then become susceptible to soil formation and erosion. However, very few adequate measurements of such rates have been made. I report here a set of such measurements from tropical catchments in Kenya. They are the first set of reported values that correctly measure the rate of chemical denudation in the tropics because they include only true denudation components[1] rather than biogenic and atmospheric inputs. Even for temperate regions I am not aware of a set of such data over a range of climate from wet to dry. The data presented here indicate how chemical denudation varies over such a gradient.

Chemical denudation is usually studied by measuring the solute concentration and the water discharge of streams, and the rate is usually expressed in tonnes $km^{-2} yr^{-1}$ of drainage basin. The estimation of chemical denudation rates is complicated by several factors. Both the discharge and the concentration of solutes in streams fluctuate with time; the former over two or more orders of magnitude during a typical year, the latter by two- or threefold. It is necessary, therefore, to have a good record of the two variables over many years. Livingstone[2] has emphasised that such records are not generally available in the tropics. The few rivers for which data are available on a systematic basis (for example, the Amazon[3] and the Mekong[4]) are large, and drain catchments with a variety of rock types, climates and land uses.

Janda[1] has indicated another complication in interpreting chemical denudation rates from streamwater chemistry. The gross solute concentration includes bicarbonate, carbonate, sulphate, and chloride ions, at least part of which must have entered the drainage water either directly from the atmosphere or during the solution of carbon dioxide, for example, in soil pores. These atmospheric and biogenic anions should not be counted as chemical denudation of the rock. Many sedimentary rocks contain these anions and it is not possible to separate the amount that is added to streamwater by chemical denudation. Such a separation is possible with rocks composed entirely of silicate minerals and only silicate rocks are dealt with here.

Precipitation and dry fallout contribute cations to the drainage basin and part of these must be subtracted from the gross solute concentration of streamwater to compute denudation rates. Even if precipitation chemistry were known, however, it is is not clear how much of the cation input should be subtracted from gross solute concentration in continental regions because most of the cations in rainfall and dry fallout there probably originate from dust and burning vegetation and therefore represent a true component of chemical denudation when the cations are leached from the catchment[1].

A few recent investigations have incorporated the necessary corrections[5-12], but apart from Moberly's[13] data for eastern Oahu, tropical data are not amended. The corrected values of chemical denudation rate range from 1.1 to 72.2 tonnes $km^{-2} yr^{-1}$, but because the few measurements sample such a wide range of lithology and climate, it is difficult to generalise about the variation of chemical denudation rate in the same way that Langbein and Dawdy[14] and Meybeck[15] did for gross solute yields.

During two average wet seasons and two dry seasons of a single hydrological year, water samples were collected at monthly or biweekly intervals at 70 river gauging stations throughout the part of Kenya that is drained by perennial
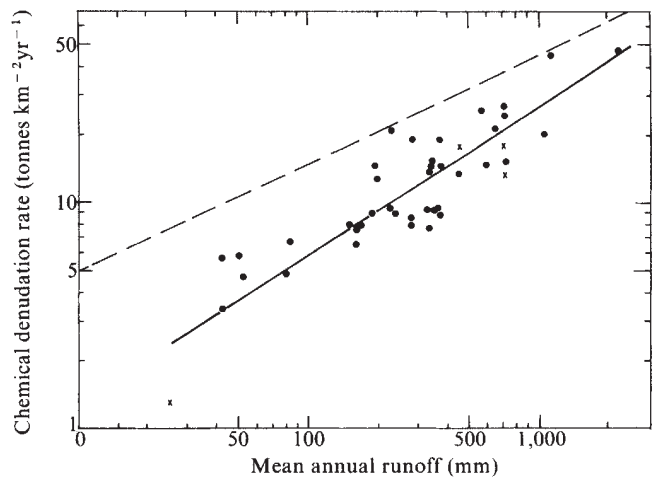

Fig. 1 Relationship between the rate of chemical denudation and mean annual runoff for 43 Kenyan river basins. ●, catchments with a good daily flow record; ×, basins for which the runoff was estimated from other hydrological data. The solid regression line is calculated for only 30 of the basins which are independent of one another; that is, tributary and downstream stations in the same basin were not used together. Chemical denudation rate $= 0.28R^{0.66}$; $n = 30(43)$; $S_{y.x} = 0.13$ log units. Dashed line indicates gross solute yield and is based on measurements at 44 independent stations among the 70 sampled.

streams[16]. Most of the streams drain single rock types which are all igneous and metamorphic silicates, containing only an occasional trace of carbonate, sulphate, or chloride. The lithologies sampled include gneiss, basalt, andesite, trachyte, rhyolite and phonolite, each being represented by at least two basins with a single rock type. Most of the more than 100 chemical analyses of these rocks made by the Kenya Mines and Geology Department showed zero concentrations of carbonate, sulphate and chloride. Mean annual air temperatures varied with elevation from 10°C to 30°C. Annual rainfall also varied with elevation, and ranged from 250 mm to 3,000 mm; the vegetation cover varied accordingly from grass and bush, through cultivated crops to dense evergreen forest, and had been generally stable during the previous decade. The use of chemical fertilisers containing petrological components was limited and runoff processes[17] in most of the fertilised areas were unlikely to carry large quantities of petrological components into streams in solution.

The specific conductance (μS at 25°C) of each of the 850 samples was measured and used with a local empirical relationship between specific conductance and total dissolved solids, to estimate the concentration of dissolved solids. Daily flow records extending over 10–15 yr were available for almost all of the sampling stations, and were used with average concentrations over the one-year sampling period to calculate gross solute yields. These yields increased with runoff, as shown in Fig. 1, and were lower than the average solute yields reported by Langbein and Dawdy[14] for temperate regions. Their data were influenced by solutes from sedimentary rocks and by large inputs of pollutants from agriculture and industry[18].

Analyses of individual solutes were carried out on 175 of the water samples. The constituents measured were dissolved silica (expressed as SiO_2), Na^+, K^+, Mg^{2+} and Ca^{2+}. Silica originates almost solely from the rocks[19], but some of the four cations came from rainfall and from dry fallout. The portion of the atmospheric input that was derived from the ocean had to be subtracted, because solutes derived from terrestrial dust and burning vegetation should be considered as true components of chemical denudation, even when they enter the catchment in solid form from other regions[1].

It was assumed that the atmospheric salt concentrations derived from the ocean retain the same relationship to one another as existed in seawater. This is a reasonable first approximation for the tropics where data on precipitation chemistry are scarce. The only cation value significantly affected by this assumption is the concentration of Na, and Eriksson[18] has shown that chloride is washed from the atmosphere mainly as NaCl, a fact which strengthens the validity of the temporary assumption used here.

The oceanic contribution to streamwater concentrations can then be computed assuming that rain-supplied chloride ions are leached quickly out of a catchment (this has been adequately demonstrated elsewhere[19]). The calculation is based on the equation

$$\frac{[Cl^-]_{stream}[Cation]_{sea}}{[Cl^-]_{sea}} = [Cation]_{evap.\ rain}$$

where the brackets refer to average concentrations and evap. rain indicates the cation concentration in rainwater after it has been concentrated by evaporation.
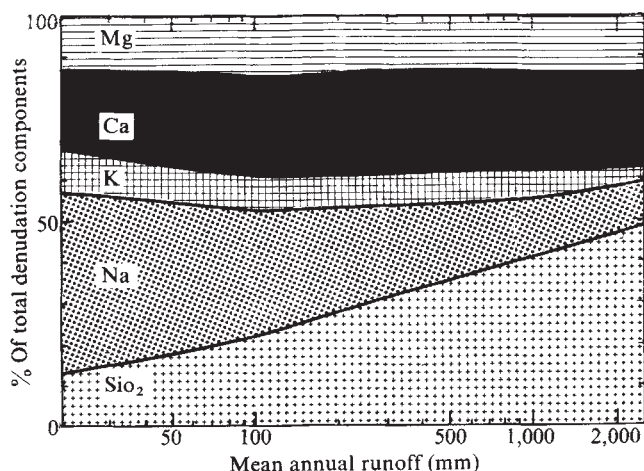

Fig. 2 Proportion of the total denudation contributed by each component in different climates. At each abscissa value the full certicag scale represents 100% of the denudation components dissolved from a catchment. The shaded fields indicate the proportion contributed by the various solutes. The proportions, expressed in terms of equivalents, were calculated from the equation in Table 1.

The average atmospheric inputs were subtracted from the average concentration of each cation in the streamwater to obtain the average concentration released by rock weathering. This last value for each component correlated significantly with mean annual runoff from each basin (see Table 1). The yields of silica, sodium, potassium, calcium and magnesium were then calculated from their average concentration and mean annual runoff. The sums of these yields, shown in Fig. 1, indicate that the rate of chemical denudation increased approximately as the two-thirds power of runoff. As Janda[1] predicted, using gross solute transport to estimate denudation rate led to an exaggeration of ~1.5-2.5 times the true value.

Runoff is the dominant variable affecting solution rates. It is associated with the general level of biological activity in the soil and therefore the partial pressure of carbon dioxide in solutions that percolate through rocks and soils, as well as the volume of water available for dissolution. Runoff, in turn, is

affected by precipitation, net radiation, air temperature and vegetation cover. Differences in annual solution rate between rock types for any value of runoff in Fig. 1 are minor and sometimes contradictory. The wide range of lithology (from basalt to rhyolite, for example) does not have a major effect on the denudation rate.

In addition to controlling the absolute amount of dissolution in a catchment, the amount of available moisture affects chemical weathering processes in ways which release varying amounts of solutes in different climates. The effect of these processes is shown in Fig. 2, in which the proportion that each solute contributed to the total denudation is expressed by a shaded fraction of the graph at each runoff value. The proportions were calculated from the equations in Table 1. In dry climates, Na is the most common solute and the SiO_2 : Na ratio (in terms of equivalents) is 0.30 where the mean annual runoff is 20 mm. As the climate became wetter, the SiO_2 : Na ratio increased to 4.33 at 2,000 mm. The proportions of other cations remained relatively stable through the range of climate, and the ratio of silica to total cations increased from 0.15 to 0.91 over the same range of runoff.

These field variations can be explained by interpreting laboratory investigations of clay mineral stability[20-22] in the light of hydrological conditions in Kenya. In the wet highland regions, weathering of primary silicates, particularly Na-feldspar and ferromagnesian minerals from phonolite, the most common rock, releases cations and dissolved silica (H_4SiO_4). Leaching is relatively rapid, and the residence time of water in the soil is too short to allow high concentrations of silica or metal cations to build up in the matric solution[23]. In these conditions, kaolinite is the most common stable product of weathering, and the streamwaters of wet regions in Kenya plot within the kaolinite field on stability diagrams[20,21,23] based on activities of H_4SiO_4, various cations, and pH (5.5-7 in groundwaters of these regions). In these conditions most of the silica and almost all of the Na^+ (for example) are leached from the profile.

In drier climates, the residence time of water in the regolith is greater, allowing time for the development of higher solute concentrations in the matric solution. Further concentration takes place by evaporation during the dry season. These two processes also lead to high pH values (7-8.5), and the drainage waters of regions with 20 mm of runoff plot in the stability field of Mg-montmorillonite[22], and close to the kaolinite-montmorillonite boundary for sodium and calcium clays[20,21]. Montmorillonites become common on the poorly drained footslopes in regions of Kenya with 20 mm of runoff per year, and occur even more extensively in the drier regions where extrapolation of the equations in Table 1 predicts the occurrence of montmorillonites. For Na-montmorillonite to form (for example) SiO_2 and Na^+ must be immobilised in the ratio of 11 : 1 (ref. 21), allowing a relatively small amount of dissolved silica to escape in the streamwater.

Table 1 Regression equations relating mean annual runoff to average concentrations $(mg\ l^{-1})$ of solutes from rock weathering in Kenya

Solute	Equation*
Silica	$[SiO_2] = 51.9R^{-0.16}$
Sodium	$[Na^+] = 380R^{-0.74}$
Potassium	$[K^+] = 77.8R^{-0.54}$
Calcium	$[Ca^{2+}] = 57.2R^{-0.41}$
Magnesium	$[Mg^{2+}] = 23.2R^{-0.43}$
Total denudation components	$[TDC] = 258R^{-0.33}$

The sample size for each regression was 30 independent catchments. All of the correlations are significant at the 0.01 level.
* R is the annual runoff in mm.

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Zooplankton fecal pellets and element residence times in the ocean

THE concept of oceanic residence time has been used widely in marine chemistry; element residence times[1] range from 10^8 to <100 yr, and provide a useful measure of the reactivity of an element in the ocean. The residence time of an element is defined as the average time an element spends in ocean water between introduction into the ocean and incorporation into the sediments. Between introduction and incorporation transport mechanisms must exist; a relationship between residence time and a property associated with a particular transport mechanism is, therefore, a logical possibility. A transport mechanism which has received increasing attention and which is discussed here involves zooplankton fecal pellets. These pellets sink fairly rapidly[2–4], at rates ranging from 50 to ~950 m per day, and they decompose relatively slowly. They seem to have the potential to reach the sea bottom in most areas, and have been identified in sedimentation traps[3] placed at depth in the ocean; moreover, a model for particle settling in the equatorial Atlantic Ocean[4] indicated that 99% of the vertical mass flux through 388 m is carried by fecal matter and fecal pellets. As far as specific elements are concerned, fecal pellets have been shown to be important in the vertical oceanic transport of zinc[5], cerium[6], polonium[7] and plutonium[8].

Determinations of element concentrations in the fecal pellets from a common zooplanktonic species, the euphausiid *Meganyctiphanes norvegica*, are now available for 18 elements[9]. When we plotted the log of the concentration factor of each element in fecal pellets relative to seawater against the logarithm of the oceanic residence time of the element a clear relationship was obtained. The relationship was linear, of the form:

$$\log F = \alpha + \beta \log T \tag{1}$$

where $F = C_f/C_{sw}$, C_f being the element concentration in wet fecal pellets in μg per kg and C_{sw} the concentration in seawater in $\mu g \, l^{-1}$ and T the oceanic residence time in years. C_f values were taken from published data[9] plus our unpublished value for uranium; a wet to dry ratio of 4.4 was used for fecal pellet material[8,9]; C_{sw} values were taken from Goldberg *et. al.*[1]

The residence time, T, is calculated from the formula:

$$T = A/(dA/dt) \tag{2}$$

where A is the total amount of the element in the oceans and dA/dt is the amount introduced into the oceans per unit time. The residence time concept assumes a steady-state system in which the amount of an element entering the marine environment is compensated by the transfer of an equivalent amount from seawater to the sediment; dA/dt is, therefore, the amount precipitating per unit time as well as the amount introduced per unit time. Residence times can accordingly be calculated in two ways. Goldberg *et al.*[1] used data for dissolved element concentration in river waters to calculate the input dA/dt and hence T; alternatively, one can use element concentrations in marine sediments to calculate T from output dA/dt. It is important to check whether or not the fit to equation (1) is sensitively dependent on the method used for calculating T; accordingly, we calculated the fit twice: the first time using the Goldberg *et al.*[1] ('river input') log T values, and then using 'sediment output' log T values calculated by rewriting equation (2):

$$T = \frac{C_{sw}}{C_{sed}} (3.8 \times 10^5) \, \text{yr} \tag{3}$$

In equation (3) C_{sed} is the element concentration in sediment in μg per g and the numerical factor 3.8×10^5 comes from assuming a total mass of seawater in the oceans of 1.4×10^{21} kg, an average density of seawater of $1.028 \, \text{kg} \, l^{-1}$ and a mass output to the sediment of $3.6 \times 10^{15} \, \text{g} \, \text{yr}^{-1}$. Values for C_{sed} were taken from Chester and Aston[10] for deep-sea clays, and values for C_{sw} are from Goldberg *et al.*[1] Both calculations were performed for the same 15 elements which represented all the elements for which the necessary data were available, in the references cited, for all four of fecal pellets, seawater, river water and sediments. In equation (1) there is no *a priori* reason why one of the two variables log F and log T should be designated as the independent variable; moreover, neither are known without error. Classical regression cannot therefore be used to quantify the linear relationship[11], and we have instead calculated the reduced major axis line[12]. The parameters α and β thus obtained are given in Table 1. If log T is calculated from the sediment output data the correlation is less satisfactory than if it is calculated from the river input data. Furthermore, the two lines are significantly different at the 5% significance level. Figure 1 shows the reduced major axis fit to the river input data points.

At this stage we should draw attention to an inherent inconsistency between the two methods we have used for calculating T. The residence time concept is usually assumed to apply to dissolved elements, and dissolved element concentrations in river waters were used by Goldberg *et al.* to calculate the river input T. On the other hand, the total element concentration in the sediment represents dissolved and particulate contributions and it is not possible to distinguish between the two fractions. Bewers and Yeats[13] have taken account of nearshore element precipitation and of the particulate as well as the dissolved river discharges of elements, and were able to obtain improved agreement between river input and sediment output T for seven metals. Six of these seven were elements which were included amongst the 15 used in Table 1; recalculating these fits after substituting the Bewers-Yeats data for T and C_{sw} for these six elements, adding in the seventh Bewers-Yeats element (Cd) as well, and retaining the original data for the other nine elements results in the α, β and