Rate of chemical weathering of silicate minerals in New Hampshire

NOYE M. JOHNSON
Earth Sciences Department, Dartmouth College
Hanover, New Hampshire

GENE E. LIKENS
Biological Sciences Department, Dartmouth College
Hanover, New Hampshire

F. H. BORMANN
School of Forestry, Yale University
New Haven, Connecticut

and

ROBERT S. PIERCE
Northeastern Forest Experiment Station, U.S. Forest Service, Durham
New Hampshire

Abstract—The losses of dissolved Ca, Na, Mg and K have been determined for six small watersheds in New Hampshire during the period 1963–1967. From the rate at which Ca and Na are lost, the steady-state chemical weathering rate is calculated at 800 kg of bedrock-till per hectare per year. Under podzol weathering conditions, a major part of the K and Mg released by the breakdown of primary minerals is apparently retained in pedogenic clays.

BACKGROUND

OF BASIC interest to the earth sciences are the rate processes which are associated with the geochemical cycling of elements. In this regard, chemical weathering at the earth's surface is one of the decisive rate-determining steps for the activity of the geochemical cycle as a whole (BARTH, 1961). One approach in determining the rate of chemical weathering on a world-wide basis has been to measure the amount of dissolved chemicals discharged by the world's rivers into the sea. However, rivers acquire part of their chemical loads from sedimentary rocks which have been formed by earlier exogenous geochemical processes. The chemistry of "average" river water is, therefore, a composite coming from primary and secondary sources which must be distinguished carefully in the interpretation of the geochemical cycle (LIVINGSTONE, 1963). A chemical weathering rate based on "average" river water is also "average" in the sense that it encompasses all the rock type exposed at the earth's surface. Perhaps the most significant aspect of chemical weathering, however, is the rate at which igneous, silicate minerals are decomposed at the earth's surface. The chemical weathering rate for such minerals may represent or delimit more accurately the activity of the primary geochemical cycle.

A convenient indicator of chemical weathering is provided by the water soluble, lower ionic potential elements, calcium, sodium, potassium and magnesium, which

are abundant in crustal rocks. If time-rate information is available on the removal of these elements from a given area, and the form of the weathering reaction is known, then a quantitative measure of the weathering rate can be calculated.

The weathering of granitic rocks and the relative rates of ion removal have been studied for different natural environments (ANDERSON and HAWKES, 1958; FETH et al., 1964; HARRISS and ADAMS, 1966; and WOLFF, 1967). However, on a small-scale basis, little effort has been directed at the quantitative measurement of chemical weathering rates. Ideally, in a small watershed system with (1) a watertight basement, (2) no through going streams, (3) mature soil colloids, and (4) a climax vegetational regime, it should be possible to measure with considerable precision the characteristic dissolved cation budget of the watershed area (BORMANN and LIKENS, 1967). Implicit in such a determination would be a complete hydrologic study and a systematic chemical sampling of precipitation and runoff. Such a study has been in effect during the past four years in New Hampshire. The cation budgets for the first two years of this study have already been reported (LIKENS et al., 1967). The purpose of this paper is to analyze these cation budgets in terms of their significance as chemical weathering rates.

EXPERIMENTAL

The basis of the present study has been the hydrologic data obtained by the U.S. Forest Service on a series of forested watersheds near West Thornton, New Hampshire. These watersheds, part of the Hubbard Brook Experimental Forest, provide favorable conditions for accurate precipitation and run-off measurements as well as chemical sampling with a minimum of cultural interference. The hydrology, climate and geology of this area has been reported in detail previously (LIKENS et al., 1967). However, the pertinent background material will be summarised here:

Climate. Although the Hubbard Brook area is only 110 airline kilometers from the sea, its climate is dominantly continental. The prevailing wind, on a yearly basis, comes from a westerly direction. It is predominantly from the northwest in winter and from the southwest in summer (LAUTZENHEISER, 1959). Annual precipitation is about 123 cm of which about one-third to one-fourth is snow.

Geology. In the Hubbard Brook area, preglacial weathered rock and soil were removed by the last glacier. Following the glaciation, the ground moraine was disturbed and in part redeposited through frost action, landslides, stream erosion and deposition. Some of these activities have continued to the present day, accompanied by weathering, soil genesis and the accumulation of organic matter. The bedrock of the watersheds is the Littleton formation, which in this area is a sillimanite-zone gneiss. It is medium to coarse grained and consists of quartz, plagioclase and biotite with lesser amounts of sillimanite.

According to MOKE (1949) there is no evidence for significant faulting in the Hubbard Brook area. Most of the watershed is mantled with glacial till which is composed principally of locally-derived lithologies. Soils are predominantly podzols with an interflow drainage system. Because of a thick organic layer overlying the soil, snow protection and tree cover, the soil remains unfrozen throughout the winter (HART et al., 1962).

Hydrology. Although the precipitation of the region is equally distributed among the months streamflow is unequally distributed. By late summer and early autumn, streamflow usually is very low. There is little overland flow, practically all water reaches the drainage streams as subsurface interflow. Snowpack melt causes major streamflow during the spring. Most of the precipitation into the area leaves as streamflow (58 per cent). Loss of water due to deep seepage appears to be minimal in the Hubbard Brook area (LIKENS et al., 1967). The high stream density of the area, high run-off factor and impermeable character of the bedrock-till supports this contention.

The amount of precipitation falling in these watersheds is determined by a network of rain gauges scattered throughout each watershed so that there are about eight for each square kilometer. Automatic recorders register the amount and time of precipitation during each storm. Streamflow is measured continuously at stream-gauging stations at the foot of each experimental watershed (LIKENS et al., 1967).

Sampling procedures. Precipitation sampling sites are located in open plots within the watershed area so that precipitation is collected directly from the atmosphere. Precipitation collectors for summer and winter are mounted on a support stand about 1·5 m above ground level. The collectors are not covered during the weekly sampling interval. Rainfall collectors are replaced each week and the precipitation sample is immediately brought back to the laboratory for analysis. Since September, 1965, an automatically opening and closing rain collector (Wong Laboratories, Mark IV) has been used in conjunction with regular collectors. Precipitation chemistry for each week is usually based on two or more distinct samples. Stream waters from each of the six watersheds are sampled weekly on the same day that rainfall is collected.

Cation analyses. All quantitative analyses are done by atomic absorption spectroscopy (LIKENS et al., 1967). Analytic precision is generally better than 1 per cent for the stream samples and better than 5 per cent for the precipitation samples. The reduced precision for the precipitation analyses is because of lower cation concentrations. Sodium, potassium and magnesium interferences were found to be negligible for our samples. Since January, 1966, calcium determinations have been done with a lanthanum additive to dampen chemical interferences inherent in the natural waters. For average Hubbard Brook stream water, the lanthanum treatment has the effect of increasing observed calcium by about 60 per cent. Consequently, the calcium analyses made prior to January, 1966, have been corrected by this factor. Good agreement has been found between our cation analyses and those done by independent labs using various other techniques.

Cation data

A complete chemical analysis of one sample of stream water from the Hubbard Brook area is given in Table 1. This analysis generally exemplifies the composition and ion balance found in the waters of the study area during the period 1963–67

Table 1. Chemical content of watershed No. six stream water, Hubbard Brook Experimental Forest, 26 March 1963. Analysis by Donald M. Fisher, U.S. Geological Survey, Water Resources Division, Washington, D.C.

Hydrogen ion	0·008 ppm
Magnesium	0·45
Chloride	0·10
Sodium	0·79
Calcium	1·54
Potassium	0·26
Sulfate	6·12
Bicarbonate	Not detected
Phosphate (ortho)	0·00
Nitrate	1·54
Silica	3·9
	14·71 ppm
pH	5·11
Specific conductance	23·8 microohms per cm
Ion balance	
Cation	0·16279
Anion	0·15462

(LIKENS *et al.*, 1967; FISHER *et al.*, 1968). The low pH, the small amount of bicarbonate and the predominance of sulfate have been consistently observed over this time. Similar, acidic waters characterise many of the streams in New England which are associated with podzolic weathering and soils. Significantly, in the Hubbard Brook area hydrogen ion and sulfate are also the primary constituents in rain and snow (FISHER *et al.*, 1968).

Table 2 summarises the major cation data for six separate experimental watersheds during four complete annual cycles. The results are compiled from continuous hydrologic data and over 5000 chemical determinations during this time. Two of these water-years, 1963–64 and 1965–66, were about normal hydrologically. 1964–65 was an extreme drought year while 1966–67 was wet. The cation budgets for these years show the changes that were induced by these shifts in hydrologic regimen. In general it may be seen that net cation losses are directly proportional to the amount of water circulated through the system during the year.

Table 2 shows that the chemical input into the watershed systems via precipitation represents a variable but substantial factor in the cation economy. The influx of cations into the study area via precipitation is much more variable than the efflux data both seasonally (LIKENS *et al.*, 1967) and annually (Tables 2 and 3). In calculating the influx budgets, the chemical–analytic errors and precipitation-measuring errors when combined are generally less than 5 per cent. The accuracy of the influx budget is dependent primarily on the validity of the precipitation measurements, the frequency of chemical sampling and sample contamination. To average local variations in precipitation, chemistry samples were taken from different locations over the experimental area. However, no significant variations in rainfall chemistry with location or altitude have been observed (LIKENS *et al.*, 1967). With open-funnel collectors, precipitation samples are intrinsically liable to contamination from infalling leaves, seeds, pollen or insects. The decomposition of this material in place may contribute to the dissolved chemical content of the precipitation sample. Because potassium is readily leached from such biologic materials, the potassium influx budget is perhaps more susceptible to this form of contamination than the other cations. The net gain of potassium during 1963–65 shown in Table 1 is possibly explained on this basis. During the past two years, the use of an automatically opening and closing rain collector has minimised this source of sample contamination.

The mean annual calcium, sodium and potassium concentrations observed in the precipitation for the Hubbard Brook area are consistent with the values published for this location during July, 1955–June, 1956 (JUNGE, 1963). This agreement tends to confirm the over-all accuracy of the influx budgets for these cations. The chloride content of the precipitation which has been determined for the study area also supports the general validity of the sodium influx budget (JUANG and JOHNSON, 1967). Implicit in the precipitation chemistry data in Tables 2 and 3 is that the wet-removal of chemicals from the atmosphere is the sole external process supplying cations to the study area. Another potential source of cation supply is by means of the dry removal of aerosol particles from the atmosphere. For the major cations, however, this process does not appear to be quantitatively significant, at least with regard to the present problem.

Table 2. Annual budgets for water, calcium, sodium, potassium and magnesium for watersheds 1–6, Hubbard Brook Experimental Forest, West Thornton, New Hampshire. Averages are based on six study watersheds during 1963–65 and five during 1965–67. I hectare (ha) = 10^{-2} km²

June–May	H₂O (cm/area)		Ca (kg/ha)			Na (kg/ha)			K (kg/ha)			Mg (kg/ha)		
	Ppt*	Run-off†	Ppt	Run-off	Net	Ppt	Run-off	Net	Ppt	Run-off	Net	Ppt	Run-off	Net
1963–64	117·1	67·7 ± 1·2	+3·0	−12·8 ± 0·8‡	−9·8 ± 0·8‡	+1·0	−5·9 ± 0·3	−4·9 ± 0·3	+2·5	−1·8 ± 0·1	+0·7 ± 0·1	+0·7	−2·5 ± 0·1	−1·9 ± 0·1
1964–65	94·9	48·8 ± 1·7	+2·8	−6·3 ± 0·4‡	−3·5 ± 0·4‡	+2·1	−4·5 ± 0·3	−2·4 ± 0·3	+1·8	−1·1 ± 0·1	+0·7 ± 0·1	+1·1	−1·8 ± 0·1	−0·7 ± 0·1
1965–66	124·5	72·7 ± 1·5	+2·1	−11·5 ± 0·6§	−9·4 ± 0·6	+1·7	−6·9 ± 0·5	−5·2 ± 0·5	+0·6	−1·4 ± 0·1	−0·8 ± 0·1	+0·6	−2·9 ± 0·1	−2·2 ± 0·1
1966–67	132·5	80·6 ± 1·8	+2·3	−12·3 ± 0·7	−10·0 ± 0·7	+1·2	−7·3 ± 0·6	−8·1 ± 0·6	+0·6	−1·7 ± 0·1	−1·1 ± 0·1	+0·4	−3·1 ± 0·1	−2·7 ± 0·1
4-yr average (1963–67)	117·3 ± 8·1	66·6 ± 2·7	+2·6 ± 0·2	−10·6 ± 0·7	−8·0 ± 0·7	+1·5 ± 0·2	−6·1 ± 0·3	−4·6 ± 0·4	+1·4 ± 0·5	−1·5 ± 0·1	−0·1 ± 0·5	+0·7 ± 0·1	−2·5 ± 0·1	−1·8 ± 0·1

* Average for 1955–1963 is 123·1 cm/area.

† Average for 1955–1963 is 71·7 cm/area.

‡ These values have been increased by a factor of 1·6 over those previously published (LIKENS et al., 1967) to compensate for chemical interferences during analysis (see text for details).

§ Values for the initial 7 months of the water year have been increased by a factor of 1·6 to compensate for analytical interferences.

Table 3. Weighted averages for annual calcium, sodium, potassium and magnesium concentration in precipitation and run-off for watersheds 1–6, Hubbard Brook Experimental Forest, West Thornton, New Hampshire. Based on six study watersheds during 1963–65 and five during 1965–67

June–May	Ca(mg/l)		Na(mg/l)		K(mg/l)		Mg(mg/l)	
	Ppt	Run-off	Ppt	Run-off	Ppt	Run-off	Ppt	Run-off
1963–64	0·26	1·89 ± 0·12*	0·09	0·87 ± 0·04	0·21	0·26 ± 0·04	0·06	0·38 ± 0·01
1964–65	0·30	1·29 ± 0·08*	0·22	0·91 ± 0·06	0·19	0·22 ± 0·02	0·12	0·38 ± 0·02
1965–66	0·17	1·58 ± 0·08†	0·14	0·95 ± 0·07	0·05	0·19 ± 0·01	0·05	0·39 ± 0·01
1966–67	0·17	1·53 ± 0·09	0·09	0·91 ± 0·07	0·05	0·21 ± 0·01	0·03	0·38 ± 0·01
1963–67	0·22 ± 0·02	1·59 ± 0·11	0·13 ± 0·02	0·91 ± 0·05	0·12 ± 0·04	0·22 ± 0·02	0·06 ± 0·01	0·38 ± 0·02

* These values have been increased by a factor of 1·6 over those previously published (Likens *et al.*, 1967) to compensate for chemical interferences during analysis (see text for details).

† Values for the initial 7 months of the water year have been increased by a factor of 1·6 to compensate for analytical interferences.

In calculating the cation efflux budgets shown in Table 2, the experimental error is generally less than 10 per cent. This uncertainty includes the measurement precision of the watershed surveying, chemical analyses and stream gauging procedures. The accuracy of the various efflux budgets is dependent primarily on the frequency and quality of the chemical sampling. Fortunately, this factor is easily accounted for by considering the chemical characteristics of the watershed–ecosystem itself. In view of inherent major hydrologic fluctuations, the cation content of the Hubbard Brook stream water shows a remarkable consistency on a seasonal basis (LIKENS et al., 1967) as well as from year-to-year (Table 3). This attribute of the stream water implies that the cation concentration is effectively buffered against changes in stream discharge (4 orders of magnitude) and precipitation periodicity. The fact of this constancy of cation concentration of stream water simplifies and reinforces the validity of the cation efflux calculations. As a point of further support, the average values found for calcium, sodium, potassium and magnesium concentrations in the run-off (Table 3) agree well with published analyses on other streams in this area (LOVE, 1960, p. 26).

Another form of cation loss from the watershed systems is the physical removal of particulate organic and mineral matter, i.e. mechanical erosion. Because of the heavy mantle of organic litter, the interflow drainage system, and the perennially unfrozen soil, overland drainage is nil in the study area. As a result, there is a notable lack of fluvial erosion in the watersheds studied and this is reflected in the clear "spring-like" water which leaves the area regardless of run-off discharge. Only minor losses of particulate matter have been observed during the past two years. The losses to date have averaged 15 kg/ha-yr of organic matter and 10 kg/ha-yr inorganic matter (BORMANN, LIKENS and EATON, unpublished). These measurements, however, confirm that in the study area the removal of weathering by-products in solid form is quantitatively small.

Combining the errors previously mentioned yields an uncertainty of 10–15 per cent in the precision of the net cation budgets. With the exception of potassium, the observed net losses of cations from the study area exceed this experimental error by a substantial amount. The error limits expressed in Tables 2 and 3 are the standard deviations of the mean for the six individual watersheds and/or the four separate years. As such, these errors represent the reproducibility of the chemical budget determinations over-all. The cation losses summarised in Table 2 may be used to circumscribe the form and amount of chemical weathering that has been in effect during the observation period.

Chemical mass balance

The net cation losses shown in Table 2 cannot continue indefinitely without depleting the entire supply of free cations in the soil and biologic system. An obvious source of cation supply to offset these losses is chemical weathering of the inorganic substrate. However, if the cation budgets of Table 2 are to relate simply to chemical weathering, certain operational conditions must be satisfied. Specifically, the cation budget should reflect the weathering reaction and not intermediate or transient effects. An example of such interferring reactions may be various seasonal biologic or pedologic processes. It follows that for a meaningful analysis

of chemical weathering, the whole system must have a dynamic balance between the hydrologic, biologic and geologic forces which add to or draw on the chemical content of the system (the vegetational climax steady state, BORMANN and LIKENS, 1967). In order to justify the assumption of steady-state chemical conditions within the Hubbard Brook system, the following three conditions may be considered.

1. *Constancy of stream water chemistry.* A strong argument for a steady-state release of chemicals from the Hubbard Brook watersheds is the observed constancy of the water chemistry (see above). This stability implies that some continuous and self-perpetuating buffering process is in effect. The immediate cation retention and exchange function is most likely performed by the humic and clay colloids found in the local podzol soils. The soils in the study area, however, are generally low in clay abundance, and because of low pH conditions, these clays are usually low in the amount of exchangeable bases they hold. The humic compounds are, therefore, more important than clay in the chemical interaction between soil and co-existing water (LUTZ and CHANDLER, 1959, p. 213). The interflow water drainage which characterises the study area assures an intimate and ubiquitous contact between incoming water and all components of the soil.

2. *Biologic activity.* Perhaps the major process drawing upon the soluble cation reservoir of the Hubbard Brook area is the present-day biological activity of the area. The evidence suggests that the biological fraction of the Hubbard Brook ecosystem is more or less in a steady-state regarding cation uptake and release.

The northern hardwood forest which typifies Hubbard Brook is an immature climax forest in which notable changes in species composition are not expected to occur under the existing climatic regime. The forest was partially cut about 50 years ago and is now slowly accumulating additional biomass. This probably does not result in a decisive diversion of cations into the biomass since rates of accumulation are slow and are likely to be in the form of low-cation-content wood.

In the Hubbard Brook area, a major part of the organic matter is concentrated in the form of 8-cm thick organic layer of the soil (HART et al., 1962). The organic layer (A1 horizon) is a complex mixture of humic materials with varying degrees of chemical stability in the soil regime (Fig. 1). This layer represents the long-term accumulation and transformation of living biomass back into an elemental, nutrient form. Assuming, on a dry-weight basis, that the litter layer has a density of 0.3 g/cm^3, the mass of humus in the Hubbard Brook area averages 2.4×10^5 kg/ha. The rate at which litter is added to the humus layer averages 3.2×10^3 kg/ha/yr (HART et al., 1962) while additions of root material may be assumed to be about 0.8×10^3 kg/ha/yr, making a total of 4×10^3 kg/ha/yr.

From the above it may be seen that a large reservoir of cations within the watershed system is contained in the humus layer as readily decomposable biologic matter or as exchangeable cations. The importance of the humus layer in controlling cation distribution may be illustrated by calculating the residence times for the various cations in the humus layer; that is, the average time necessary to turn over all the cations of one type in the humus layer. Assuming that the mass of the humus layer, H, is in dynamic balance between the opposing rate processes of
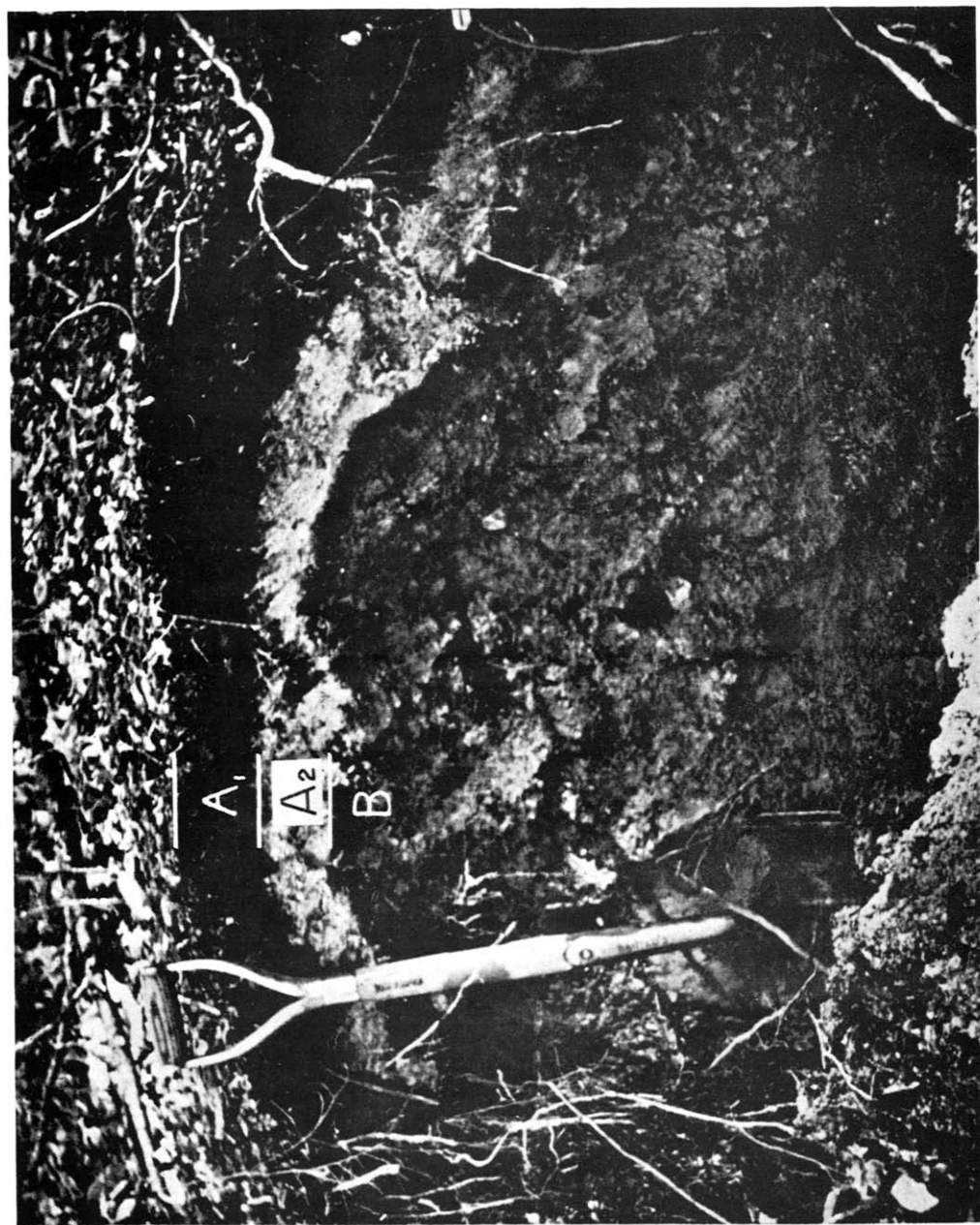
Fig. 1. Cross-section through podzol soil developed on till in Hubbard Brook Experimental Forest, New Hampshire. The uppermost dark layer (A1) is composed of organic litter and humus. The bleached and chemically leached horizon (A2) immediately underlies the humus layer.

accumulation and decay (decay rate = accumulation rate = $\partial H/\partial t$), the residence time τ for any element i within the humus layer is then;

$$\tau_i = \frac{H}{\partial H/\partial t} \times \frac{n_i}{m_i} \tag{1}$$

where n is the concentration of i in the humus layer itself and m is the concentration of i in the material entering or leaving the humus layer. In the present case m is taken as the concentration of i in the annual litter fall. Taking H as $2 \cdot 4 \times 10^5$ kg/ha/yr and $\partial H/\partial t$ as 4×10^3 kg/ha/yr equation (1) becomes:

$$\tau_i = 60 \times \frac{n_i}{m_i} \text{ yr.} \tag{2}$$

Table 4 lists the residence times calculated from equation (2) for various cations in the study area. The values for n_i/m_i for average humus and litter have been calculated from the data of OVINGTON (1958a, Fig. 1; 1958b, Fig. 2).

Table 4. Residence times (equation 2) for various components of the humus layer $(F + H)$ of the soil at Hubbard Brook Experimental Forest, West Thornton, New Hampshire

	(n/m)	T(yr)
Litter $(F + H)$	1·0	60
Ca	0·5	30
Na	0·5	30
K	0·3	20
Mg	0·7	40

The length of residence time within the humus layer for a given cation indicates the extent to which the humus layer chemically stabilises that cation from temporal shifts in biologic activity. By virtue of this stabilising effect, the chemical impact of seasonal biologic events may be sufficiently damped to permit a meaningful determination of average chemical conditions. During the present study, the most stable cation in the run-off waters with regard to chemical concentration has been magnesium; the least stable has been potassium (LIKENS et al., 1967). Significantly, these cations also have the longest and shortest residence times in the humus layer (Table 4).

3. *Stable mineral phases.* As mentioned above, the bedrock of the study area is the Littleton formation, the major mineralogy of which is quartz, plagioclase and biotite. Since the last period of glacial erosion, a weathering rind from 2·5 to 25 cm thick has developed on the Littleton wherever it has been exposed. The bulk chemical composition of both the fresh and the weathered Littleton are given in columns 1 and 2, Table 5. Overlying about 85 per cent of the study area is a glacial till which averages 1·4 m in thickness but ranges up to 6·1 m thick. Significantly, where the till is greater than 1·5 m thick the underlying Littleton is virtually unweathered showing ideally preserved fine-structured glacial striae and no iron staining. In most of the watershed areas, therefore, the boulder content and groundmass of the till is the material that is undergoing active chemical weathering and

Table 5. Bulk chemical composition of various lithology types and weathering
products found in the Hubbard Brook study area*

	(1) Unweathered Littleton fm. (%)	(2) Weathered Littleton fm. (%)	(3) Till groundmass (%)	(4) Unweathered Kinsman fm. (%)	(5) Weathered Kinsman fm. (%)	(6) A2 soil horizon (%)
SiO_2	64·8	70·8	70·5	64·5	69·2	80·8
Al_2O_3	16·2	14·3	14·1	16·1	15·7	9·6
FeO	5·4	1·2	1·5	4·3	0·44	0·64
Fe_2O_3	0·86	3·4	3·4	1·7	3·3	0·16
CaO	1·1	0·87	0·98	2·6	0·17	0·60
Na_2O	1·8	1·5	1·8	2·4	1·6	1·3
K_2O	3·6	3·1	3·3	3·5	5·5	2·9
MgO	2·4	1·1	0·98	1·8	0·42	0·13
TiO_2	1·2	1·0	1·0	1·4	1·1	1·0
MnO	0·14	0·07	0·19	0·12	0·07	0·09
P_2O_5	0·23	0·32	0·12	0·22	0·12	0·02
H_2O^-	0·16	0·49	0·46	0·13	0·31	0·36
H_2O^+	2·1	1·7	1·6	1·3	1·9	1·5
CO_2	<0·05	<0·05	<0·05	<0·05	<0·05	<0·05
Sum	100	100	100	100	100	99

* Through courtesy of the U.S. Geological Survey, analysts: P. Elmore, L. Artis, H. Smith, D. Taylor, S. Botts, G. Chloe, J. Glenn.

not the underlying bedrock. The groundmass of the till is chemically identical to weathered Littleton (columns 2 and 3, Table 5) and suggests that it may be an accumulation of pre-existing weathered Littleton. The boulder content of the till is of local lithologies, predominantly the Kinsman quartz monzonite. The Kinsman outcrops less than a mile to the north and west of the study area, the direction from which the last glacier advanced. To a first approximation, therefore, immediately after the last glaciation, the surface of the study area consisted of fresh Littleton bedrock exposed as glacially scoured prominences and glacial erratics, Kinsman quartz monzonite as glacial erratics, and a till groundmass. This combination of materials was then subjected to chemical weathering, biologic action and soil development which has evolved to the present state. The time interval involved in this history is most likely 13–14,000 yr (SCHAFER, 1967).

In podzolic soils like those which have formed over the study area, the A2 horizon (Fig. 1) represents the zone where the maximum hydrolysis, chelation and chemical dissolution may be expected (LUTZ and CHANDLER, 1959, p. 393). The A2 horizon lies immediately below the A1 layer (Fig. 1) and is directly subject to the acids and various organic solutions which drain from the humus. Consequently, the A2 horizon is strongly leached of its iron and bases and is generally high in silica (LUTZ and CHANDLER, 1959, p. 394). The bulk chemistry of the A2 horizon as sampled from the Hubbard Brook area (column 6, Table 5) shows this acid-leaching effect. The B horizon of podzolic soils (Fig. 1) is a zone of chemical precipitation of various inorganic and organic compounds that have been introduced from the upper levels of the soil. Included in these precipitates may be colloidal

metal–organic complexes and clays (DUBACH *et al.*, 1964). The deep brown coloration of the B horizon indicates the deposition of iron.

Assuming for the Hubbard Brook area that the starting material in the weathering process has been a mixture of Littleton, Kinsman and till, and that the maximum amount of chemical leaching is given by the A2 horizon, then the relative amounts of cations which are being leached from the system may be predicted (Table 6).

Table 6. Chemical composition of composite bedrock and changes induced by podzolic weathering, Hubbard Brook Experimental Forest, New Hampshire

	Composite bedrock*		Weathered residue†		Change due to weathering	
	% Oxide	% Metal	% Oxide	% Metal	% Oxide	% Metal
SiO_2	65·8	30·7	80·8	37·7	+15·0	+7·0
Al_2O_3	15·7	8·3	9·6	5·1	−6·1	−3·2
Fe_2O_3	1·9	1·3	0·2	0·1	−1·2	−1·2
FeO	4·0	3·1	0·6	0·5	−3·4	−2·6
CaO	2·0	1·4	0·6	0·4	−1·4	−1·0
Na_2O	2·2	1·6	1·3	1·0	−0·9	−0·6
K_2O	3·5	2·9	2·9	2·4	−0·6	−0·5
MgO	1·8	1·1	0·1	0·1	−1·7	−1·0

* Assuming that the volume of material subject to weathering is 20% Littleton fm., 20% till groundmass and 60% Kinsman fm.

† Assuming that present day A2 horizon typifies the weathering residue.

On this basis, approximately one part by weight of sodium and potassium and two parts of calcium and magnesium should be released per unit of rock weathered. If this were the total extent of the steady-state weathering process, these ratios should be reflected in the losses of these elements in the drainage waters from the watershed. During the present study, the losses of calcium and sodium in drainage water from the study do approximate the 2:1 ration, e.g. 8·0 kg Ca/ha-yr:4·6 kg Na/ha-yr (Table 2). Potassium and magnesium, however, are being removed in much lesser amounts than anticipated on this basis (Table 2). This relative deficit in the amount of potassium and magnesium that is removed may predicate the existence of other reactions in the weathering process besides the simple hydrolysis and leaching that is exemplified by the A2 horizon. A reaction that must be considered in this regard is the formation of pedogenic compounds, including clays, notably in the B horizon of the soil.

The soils of New Hampshire are characterised by illite–vermiculite or illite–montmorillonite assemblages depending on soil type (GAMBLE, 1954). In the Hubbard Brook area illite (mica)–vermiculite are the dominant clays throughout the soil profile. Also, traces of kaolin are found especially in the A2 horizon. The vermiculite is involved in mixed-layering, probably with biotite (ROBERT C. REYNOLDS, personal communication). This evidence suggests that muscovite is stable in the ambient weathering regime while biotite is going to vermiculite. Significantly, illite (mica)–vermiculite clays are composed in part of potassium and magnesium. If these clays are being formed or reacting somewhere below the A2 horizon, the associated potassium–magnesium will not be removed from the system during weathering. The existence of stable illite (mica)–vermiculite in the weathering zone and the relative deficit in the potassium–magnesium budget,

when considered together, suggests that the study area is probably in a state of dynamic equilibrium with respect to its inorganic chemical cycling.

Calculated weathering rate

According to BARTH (1961, p. 6) if steady-state conditions are realized in the geochemical cycle, then the rock-weathering equation is given by:

$$W = \frac{D_i}{c_i - s_i},$$ (3)

where W is the amount of rock chemically weathered per unit time, c_i and s_i are the concentration of element i in the original rock and the weathered product

Table 7. Calculated chemical weathering rates (equation 3) in Hubbard Brook study area during 1963–1967

	D (4-yr mean) (kg/ha-yr)	c*	s†	W (4-yr mean) (kg/ha-yr)	W (max. yr)	W (min. yr)
Ca	8.0 ± 0.7	0.014	0.004	800 ± 70	1000 ± 70	350 ± 40
Na	4.6 ± 0.4	0.016	0.010	770 ± 70	1000 ± 100	400 ± 50
K	0.1 ± 0.5	0.029	0.024	20 ± 100	220 ± 20	0
Mg	1.8 ± 0.1	0.011	0.001	180 ± 10	270 ± 10	70 ± 10

* Assuming that the volume of material subject to weathering is 20% Littleton fm., 20% till groundmass and 60% Kinsman fm.

† Assuming that the present-day A2 soil horizon typifies the weathering residue.

respectively, and D_i is the amount of element i removed in solution per unit time. Assuming that (1) the Hubbard Brook watershed area is chemically in a steady-state condition (previous section), (2) the bulk composition of the original rock-till surface can be approximated (Table 6), (3) the net sodium and calcium budgets (Table 2) are representative, and (4) limiting concentrations of sodium and calcium in the weathered product can be assigned (Table 6), then equation (3) can be applied to the Hubbard Brook area. Solutions to equation (3) are presented in Table 7. Average and extreme values of D_i were used to delimit the spectrum of weathering rates that were encountered during average, drought and wet years. The minimum amount of chemical weathering occurred in the driest year (1964–65) and generally increased as the annual hydrologic activity increased. The 4-yr average activity of the local hydrology was slightly below normal (Table 2).

The composition of the original bedrock-till surface (c_i) as used in Tables 6 and 7 has not been uniquely determined. The values chosen for c_i purport to show the best combination bedrock-till distribution as determined at 208 stations in one watershed of 13 hectare. Significantly, any values for c_i based on a reasonable permutation of bedrock-till, involving only the Littleton formation, Kinsman formation and the till, will yield approximately the same solution for W. The values selected for s_i assume that the A2 soil horizon shows the true amount of primary mineral decomposition during chemical weathering. However, this assumption is necessarily qualified when applied to the removal of potassium and

magnesium because of reactions that may occur deeper in the weathering zone (see preceding section). Nevertheless, the A2 horizon will probably best characterise the maximum amount of cation mobilisation during the overall weathering process.

Because of the apparent involvement of potassium–magnesium in stable phases, the weathering rates calculated from the potassium–magnesium data are decidely lower than those from the calcium–sodium data (Table 7). Under the given premises the observed losses of potassium and magnesium require considerably less rock to be weathered each year than do the losses of calcium and sodium. Calcium and sodium do not appear to be associated with any distinctive inorganic reaction products during weathering. With respect to calcium–sodium, therefore, the assumption of the A2 composition for s_i is probably valid. In addition sodium is notably clear of extensive involvement in the biologic cycle. Consequently sodium probably affords the most reliable index of weathering rate while calcium provides a convenient check.

Assuming that the weathering rate W calculated from the calcium–sodium data is correct, and that c_i and D_i from Table 7 are also correct, then s_i for potassium and magnesium can be calculated from equation (3). In effect, this calculation is a means for obtaining a reasonable stoichiometry for the complete weathering reaction. The calculated s_i for potassium and magnesium on this basis then becomes 0·029 and 0·009 respectively for 4-yr average weathering conditions for the weathering zone overall. As mentioned, the key premise in this calculation is that the A2 horizon accurately depicts s_{Ca} and s_{Na}.

If $W = 800$ kg/ha-yr (W_{Ca} and W_{Na} of Table 7) is typical for the chemical weathering rate in the Hubbard Brook area since the last glaciation, 11×10^6 kg/ha of bedrock-till should have been completely weathered. In other words, the depth that complete weathering should have reached in hard-till is about 50 cm. This depth, however, is not too meaningful since chemical weathering proceeds as a transitional profile and not as a distinct boundary. Also, the upper surface of the weathering zone is subject to erosion which would minimise the apparent depth of weathering. In the Hubbard Brook area, however, the nominal depth of weathering observed on exposed, glacially striated bedrock is generally less than 25 cm. It would appear, therefore, that over the past 14,000 years the major chemical weathering in the study area has been concentrated on the volume of the till.

Given $W = 800$ kg/ha-yr for the average weathering rate and the values for c_i and s_i in Table 7, about $5·6 \times 10^4$ kg/ha of potassium and $11·2 \times 10^4$ kg/ha of magnesium should have been chemically removed from silicate minerals since the last glacial event. Of this amount approximately $5·5 \times 10^4$ kg/ha of potassium and $8·7 \times 10^4$ kg/ha of magnesium should have been re-deposited lower in the soil, if our analysis of the potassium–magnesium geochemistry is correct. On the average, therefore, 4 kg/ha potassium and 8 kg/ha magnesium are produced each year by chemical weathering of silicate minerals, but only 0·1 kg/ha-yr potassium and 1·8 kg/ha-yr magnesium leave in solution.

Fisher et al. (1968) have found that the amount of hydrogen ion that is deposited into the Hubbard Brook area from precipitation each year corresponds well with the amount of equivalent bases that are removed in the effluent streams. The fact

that the rate of chemical denudation (Table 2) is directly proportional to the amount of water, or more correctly, the amount of hydrogen ion that is flushed through the system, suggests that the entire weathering reaction obeys a simple mass-action rule with relatively fast kinetics.

The weathering rate data which are described in this work may reasonably characterise much of the mid-latitude, glaciated region of the world. However, whether or not these data are representative for other latitudes and for past geologic times is problematical. The fact that glacial till is more amenable to chemical weathering than hard bedrock equivocates the problem. In the geologic past, however, fragmental material of various sorts has very likely been a large part of the earth's dry-surface and has been subject to chemical weathering. If the 800 kg/ha-yr value for W is generally applicable for glaciated regions, then it may be useful in the dating of certain paleosols and "gumbotil" intervals.

The weathering rates shown in Table 7 are consistent with the value of 270 kg/ha-yr predicted on general grounds by Barth (1961, p. 7). The comparison is particularly striking by considering that Barth's value is based on a whole-earth surface that has been weathered throughout geologic time. Assuming that two-thirds of the earth's surface has always been submerged below sea level and not subject to weathering, Barth's effective weathering value becomes 810 kg/ha-yr. In this connection it is interesting to consider the systematic errors that may affect the validity of the weathering rates calculated from equation (3). As used in this study, the values for ion removal rate (D_i) are less likely to be in serious error than the choice of c_i and s_i. For example, as an extreme case we could assume that chemical weathering with respect to the removal of calcium–sodium is complete, that is $s_i = 0$. Under such conditions the apparent weathering rate (W) based on sodium data alone could be slower than shown in Table 7 by a factor of $2 \cdot 7$ at most. At the other extreme, we could assume that only minimal removal of calcium–sodium prevails during weathering, that is c_i is low and/or s_i is high. In this case the apparent weathering rate based on calcium data alone could be faster by a factor of $2 \cdot 5$. In either of these limiting cases, however, the values for W on an order of magnitude basis still concur with Barth's generalisation. In essence, therefore, the central findings of this work present a specific, quantitative support for Barth's concept of the activity of the geochemical cycle.

References

Anderson D. H. and Hawkes H. E. (1958) Relative mobility of the common elements in weathering of some schist and granite areas. *Geochim. Cosmochim. Acta* **14**, 204–210.

Barth T. F. W. (1961) Abundance of the elements, areal averages and geochemical cycles. *Geochim. Cosmochim. Acta* **23**, 1–8.

Bormann F. H. and Likens G. E. (1967) Nutrient cycling. *Science* **155**, 424–429.

DUBACH P., MEHTA N. C., JAKAB T., MARTIN F. and ROUTLET N. (1964) Chemical investigations on soil humic substances. *Geochim. Cosmochim. Acta* **28**, 1567–1578.

FETH J. H., ROBERSON C. E. and POLZER N. L. (1964) Sources of mineral constituents in water from granitic rocks, Sierra Nevada, California and Nevada. *U.S. Geol. Surv. Water-Supply Paper* 1535-I.

FISHER D. M., GAMBELL A. W., LIKENS G. E. and BORMANN F. H. (1968) Atmospheric contributions to the water quality of Hubbard Brook, New Hampshire. In preparation.

GAMBLE J. F. (1954) *An Introductory Study of the Clay Minerals in New Hampshire soils.* Master's Thesis, University of New Hampshire, Durham, New Hampshire.

HARRISS R. C. and ADAMS J. A. S. (1966) Geochemical and mineralogical studies on the weathering of granitic rocks. *Amer. J. Sci.* **264**, 146–173.

HART G., LEONARD R. E. and PIERCE R. S. (1962) Leaf fall, humus depth, and soil frost in a northern hardwood forest. *Forest Res. Note* 131, Northeastern Forest Experiment Station, Durham, N. H.

JUANG F. H. F. and JOHNSON N. M. (1967) Cycling of chlorine through a forested watershed in New England. *J. Geophys. Res.* **72**, 5641–5647.

JUNGE C. E. (1963) *Air Chemistry and Radioactivity, International Geophysics Series*, 4. 365 pp. Academic.

LIKENS G. E., BORMANN F. H., JOHNSON N. M. and PIERCE R. S. (1967) The calcium, magnesium, potassium and sodium budgets for a small forested ecosystem. *Ecology* **48**, 772–785.

LIVINGSTONE D. A. (1963) The sodium cycle and the age of the ocean. *Geochim. Cosmochim. Acta* **27**, 1055–1069.

LOVE S. K. (1960) Quality of surface waters of the United States, (1957) Part 1–4, *U.S. Geol. Surv. Water Supply Paper* 1520.

LUTZ H. J. and CHANDLER R. F. (1959) *Forest Soils*, 514 pp. Wiley.

MOKE C. B. (1949) *Geology of the Plymouth Quadrangle, New Hampshire.* Doctoral Thesis, Harvard University.

OVINGON J. D. (1958a) Studies of the development of woodland conditions under different trees, VI. Soil sodium, potassium and phosphorus. *J. Ecol.* **46**, 127–142.

OVINGTON J. D. (1958b) Studies of the development of woodland conditions under different trees, VII. Soil calcium and magnesium. *J. Ecol.* **46**, 391–405.

SCHAFER J. P. (1967) Retreat of the last ice sheet in New England (abstract). *Program.* 1967 Meeting, Northeastern Section, Geol. Soc. Amer. p. 55.

WOLFF R. S. (1967) Weathering of Woodstock Granite near Baltimore, Maryland. *Amer. Sci.* **265**, 106–117.