Weathering reactions, water chemistry and denudation rates in drainage basins of different bedrock types: I — sandstone and shale

AFIFA A. AFIFI & OWEN P. BRICKER
US Geological Survey, Mail Stop 432, Reston, Virginia 22092, USA

ABSTRACT   This study is a preliminary investigation of a 4.7 km^2 forested drainage basin in Virginia. The main tributary, Mill Run, drains surficial sediments of Cenozoic age and Silurian Massanutten sandstone. Weathering reactions are occurring in the 60 cm soil zone which contains mechanically disintegrated sandstone gravel of the Massanutten sandstone. The streamwater chemistry of Mill Run can be explained by incongruent dissolution of orthoclase, plagioclase, amphibole, and pyrite with precipitation of iron hydroxide, and kaolinite or amorphous materials of similar composition. A chemical denudation rate of 5601 kg $km^{-2}year^{-1}$ was estimated, which is equivalent to the lowering of surface relief by 0.002 mm $year^{-1}$. A secondary tributary receiving water in contact with the Silurian Bloomsburg shale was also investigated. In this case, the water chemistry can be explained by dissolution of feldspars, amphibole, and carbonate minerals and precipitation of iron hydroxide, and kaolinite. A chemical denudation rate of 24 888 kg $km^{-2}year^{-1}$ was estimated, which is equivalent to the lowering of surface relief by 0.010 mm $year^{-1}$.

Réactions d'altération, chimie des eaux et taux d'érosion dans les bassins versants avec différents types des substratum: grès et schiste
RESUME   Ces recherches sont l'étude préliminaire d'un bassin versant de 4.7 km^2 couvert par la forêt, en Virginie. Le tributaire principal, Mill Run, draîne des formations sédimentaires superficielles d'âge cénozoïque et du grès silurien Massanutten. Les réactions d'altération se produisent dans un horizon du sol de 60 cm qui contient des graviers provenant de la désintégration mécanique de grès de la formation Massanutten. La chimie de l'eau du ruisseau de Mill Run peut être expliquée par la dissolution d'orthoclase, de plagioclase, d'amphibole et de pyrite avec précipitation d'hydroxyde de fer, de kaolinite et de matériaux amorphes de composition analogue. On a estimé une érosion chimique de 5601 kg $km^{-2}an^{-1}$ equivalente à un abaissement de la surface du sol de 0.002 mm an^{-1}. On a étudié également un second tributaire en contact avec les schistes de Bloomsburg. Dans ce cas la composition chimique de l'eau peut être expliquée par la dissolution de feldspaths, d'amphibole et de minéraux

carbonates avec précipitation d'hydroxyde de fer et de
kaolinite. Un taux d'érosion chimique de 24 888 kg km^{-2}an^{-1}
a été estimé, équivalent à un abaissement de la surface
du sol de 0.010 mm an^{-1}.

INTRODUCTION

The area of study is located in the Strasburg and Toms Brook
7.5 minute quadrangles in Shenandoah and Warren Counties, Virginia,
USA (Fig.1). The drainage basin is in the temperate climatic zone
and is completely forested by secondary growth, mixed oak-hickory
associations, dominated by Chestnut Oak and Scarlet Oak with
scattered stands of conifer. A forested drainage basin was selected
to minimize recent anthropogenic influences.
   The map by Rader & Biggs (1976) shows the general geology of the
area. The major structural features consist of the Massanutten
Synclinorium and North Mountain fault. The rock strata exposed in
the area range from Lower Cambrian to Devonian in age. A preliminary
field survey combined with the available published data indicate that,
upstream, Mill Run drains surficial sediments of Cenozoic age and
Silurian Massanutten sandstone. A secondary tributary draining
surficial Cenozoic sediments and Bloomsburg shale joins Mill Run at
Veach Gap (Fig.1). Only the drainage basin upstream of Veach Gap,
which consists of approximately 3.2 km^2 drained by Mill Run (MR) and
0.5 km^2 drained by the secondary tributary (MRT), was monitored.
   There are no previous geochemical, hydrological, or geomorphologi-
cal data on the drainage basin under investigation. In the present
study, biomass was assumed to be in dynamic equilibrium with respect
to all chemical elements. Thus, the streamwater chemistry was
considered to be the result of the reaction of atmospheric precipi-
tation with the mineral assemblage of the rocks. The changes in
the chemical composition of the streamwater were related to
dissolution of the primary mineral assemblege of the bedrock and
precipitation of secondary phases. The total dissolved solids were
used to estimate the rate of chemical denudation and the rate of
lowering of the surface relief. These estimates are based on one
year of data collection, and thus are preliminary.

HYDROLOGY

The annual precipitation in 1982 was 862 mm and the mean annual
temperature was 11.9°C. Assuming that precipitation is the only
source of choride, the increase in chloride concentration in the
discharge was used to estimate the amount of evapotranspiration.
Evapotranspiration was estimated to be 39% and 53% in MR and MRT
respectively. In these calculations, it was assumed that evapotrans-
piration was not accompanied by solid phase precipitation. The amount
of discharge was calculated from the following simplified water
balance equation:

   precipitation = evaporation + discharge   (1)

The hydrological data are listed in Table 1.
   Based on field observation, it appears that infiltration is very
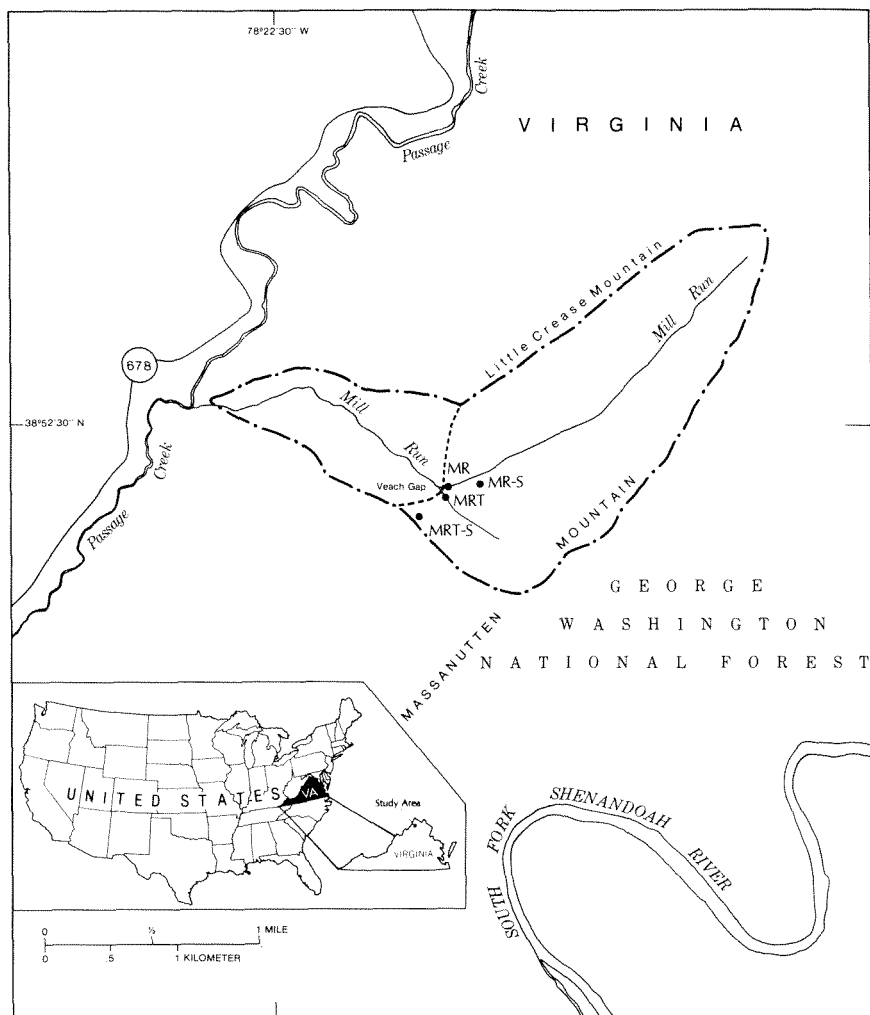
FIG.1   *Location map of Mill Run drainage basin and the
sampling sites (MR and MRT are the locations of the water
samples, MR-S and MRT-S are the locations of the soil
profiles).*

rapid and ceases shortly after rainfall.   In Mill Run, transport of
water takes place on the steep slopes in the weathering zone, and in
the gravelly sandstone slope deposits at approximately 60 cm depth.
Drainage of the slopes of the secondary tributary occurs from
Cenozoic deposits, sandstone, and from shallow joints in the shales.
The water temperature of a spring in relation to surface temperature
indicates that the spring water has been in contact with the shale
at a shallow depth.

GEOMORPHOLOGY

A preliminary survey suggests that accumulation of slope deposits

TABLE 1   *Precipitation and discharge in Mill Run drainage basin during 1982*

Quarter	Temperature °C	Precipitation mm	Mill Run (3.2 km^2)		Mill Run Tributary (0.5 km^2)	
			Total Input m^3	Total Discharge m^3	Total Input m^3	Total Discharge m^3
First Quarter	7.1*	233*	745 000	455 000	116 000	55 000
Second Quarter	17.0*	268*	858 000	523 000	134 000	63 000
Third Quarter	15.2	135	432 000	264 000	68 000	32 000
Fourth Quarter	8.4	226	723 000	441 000	113 000	53 000
Total		862	2 758 000	1 683 000	431 000	203 000

*The data are from Woodstock, Virginia. There are no data available from Mill Run.

TABLE 2   *Percentages of minerals in the fresh bedrock and the soil profile at different depths determined by X-ray diffraction and petrographic microscope*

Depth	Soil Profile MR-S							Soil Profile MRT-S							
	Quartz	Total Clay	Plagioclase	K-Feldspar	Fe-Oxy-hydroxides	Chlorite, Amphiboles, epidote, Biotite	Pyrite, Fe oxides	Quartz	Total Clay	Plagioclase	K-Feldspar	Fe-hydroxides	Siderite & Calcite	Amphibole & Epidote, pyroxene	Pyrite
0- 5 cm	88	7	1	3	0	0	0	59	34	2	2	2	0	0	0
15-20 cm	74	20	1.8	3.5	trace	trace	trace	56	38	2	1	2	trace	0	0
50-60 cm	72	22	2	4	trace	trace	trace	43	47	4	3	2	0.2	trace	trace
Fresh bedrock	96	1.5	.5	1.0	trace	0.4	0.5	23	54	4	3	10	5*	1	trace

*Determined by x-ray diffraction. However, the dissolution cavities identified by the petrographic microscope suggest that the percentages of the original carbonate mineral were initially much higher.

occurred during the late Pleistocene period. These slope deposits are characterized by a layer of gravel derived from mechanically disintegrated sandstone. The deposits are similar to those previously described by Guillien (1964) as having a grèze-litèe like character. The old slope deposits are overlain by younger deposits containing an argillic horizon that may indicate landscape stability during the Holocene. Soil profiles were partly truncated, possibly due to heavy timbering; however, another period of landscape stability now dominates the forested drainage basin.

BEDROCK AND SOILS

The bedrock of the area under investigation is of sedimentary origin and has been affected by low-grade metamorphic processes. The mineralogical compositions of the bedrock and the top 60cm of the

surface soils are shown in Table 2. The changes in mineral concentr-
ations indicate progressive weathering toward the surface in both
profiles. Profile MR-S has not been formed by *in situ* weathering of
the bedrock; rather it seems to be a result of weathering of slope
deposits that consist mainly of sandstone gravel. The profile MRT-S
has been formed by *in situ* weathering of the shale, but the top 15 cm
are mixed with slope deposits.

Feldspars, amphiboles and pyrite are the reactive minerals common
to both rock types. Other reactive minerals are chlorite in the
sandstone, and calcite and siderite in the shale. The chlorite is of
retrograde origin. Other interesting diagenetic features in the
sandstone include formation of clays, epidote, gedrite and mica
filling between grains (Fig.2(a)). Quartz overgrowth also acts as a
cementing agent and reduces permeability. It is noteworthy that
rutile and magnesium silicate phases are abundant inclusions in the
K-feldspar and quartz (Fig.2(b)). Small amounts of calcite and siderite
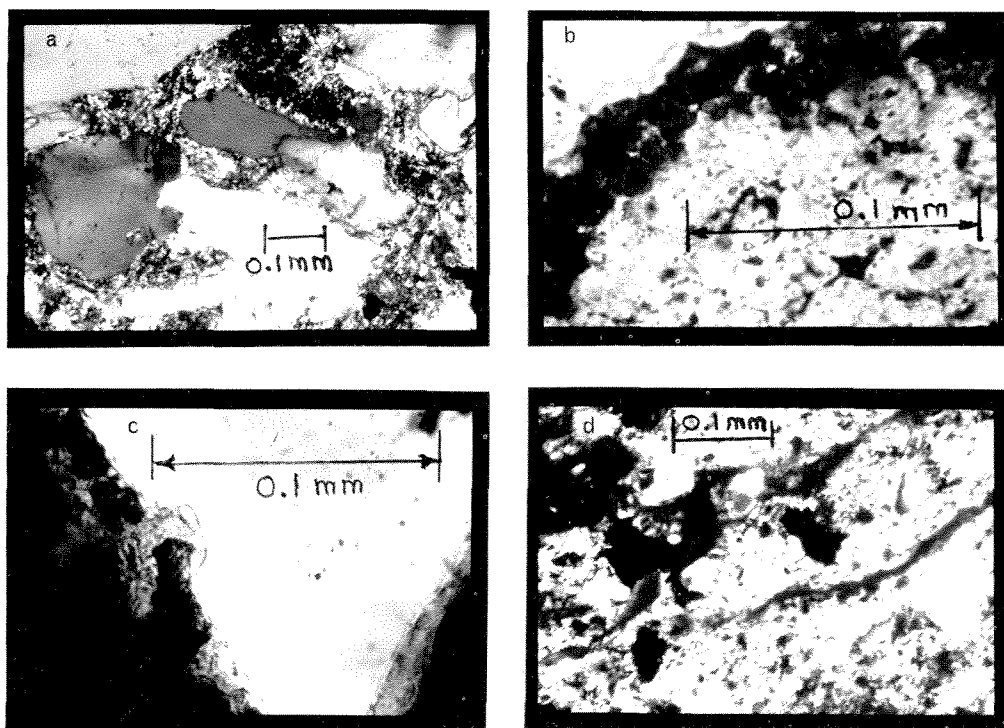were detected in the shale by X-ray diffraction methods. In addition,

FIG.2 *Photomicrographs of polished thin sections in*
Massanutten sandstone and Bloomsburg shale under crossed
Nichols showing retrograde chlorite, epidote, gedrite,
mica, and clays filling interstices in sandstone (a);
framboidal rutile marginally replacing K-feldspar in sand-
stone, inclusions rich in Mg and Ti in the K-feldspar and
quartz, and quartz overgrowth (b); rhombic shaped dissolu-
tion cavity with small crystals lining the walls in shale
(c); residual clay seams between quartz crystals and
rhombic shaped dissolution cavities (d).

rhombohedron shaped cavities (Fig.2(c)) and microfissures, that
possibly were produced by dissolution of carbonate minerals, were
observed in thin sections. The dissolution is accompanied by
leaching of the red colour which characterizes the Bloomsburg shale
(Fig.2(d)). Petrographic identification of the carbonate minerals in
the shale was not possible.

The X-ray diffraction pattern for the <1 μm size oriented clays
is shown in Fig.3. Both soil profiles contained 7 Å clays which
could not be attributed solely to weathering because the bedrock also
contained a 7 Å peak. However, in these soils, an increase in the
intensity of the 7 Å peak associated with a decrease in the amount of
amorphous material towards the surface was observed, which may
indicate the formation of kaolinite. A nonexpandable 14 Å clay, that
upon heating to 300°C collapsed to a diffuse 10-12 Å spacing which
persisted on heating to 500°C, was found in the <1 μm fraction of the
MR-S profile. This interstratified chlorite-vermiculite/illite clay
mineral is believed to be inherited from the sandstone. The occurrence
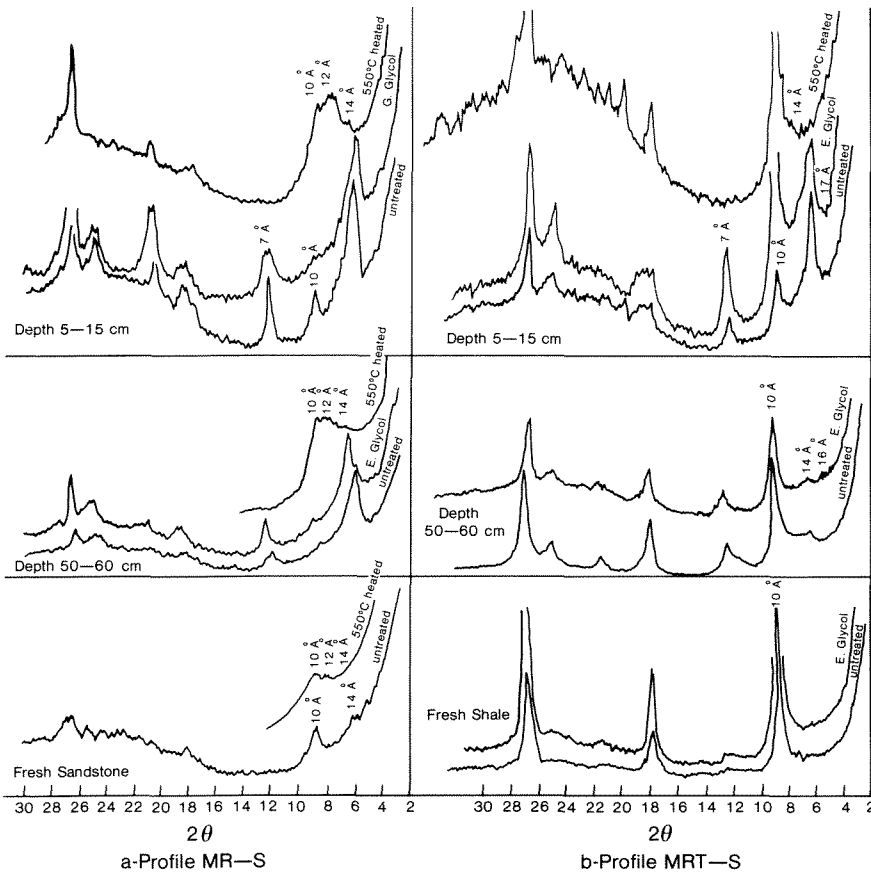of this mixed-layer clay in Mill Run soils resembles that described by

FIG.3   X-ray diffraction pattern for oriented clays of
less than 1 μm size (the clays in the fresh sandstone were
not size-separated).

Rabenhorst *et al.* (1982) in Maryland soils. The predominant clay in
the MRT-S profile is a 10 Å clay which is inherited from the shale.
The top 15 cm of the profile contained nonexpandable 14 Å clay which
may come from mixing with slope deposits. This profile also
contained trace amounts of 16 Å mixed-layer clay, possibly
vermiculite-smectite.

WATER-MINERAL RELATIONS

The quarterly average of the stream composition and the average
composition of 1982 precipitation are shown in Table 3. These data
combined with those in Table 1 were used to calculate the total input
in the drainage basin. The difference between the input and the
output was attributed to the chemical weathering of minerals.
Organic chelates, adsorption/desorption processes and the role of the
biomass were not considered.

The chemical composition of the reactive minerals, identified in
the previous section, were determined by electron microprobe and/or
optical properties. The mineral-water mass balance was calculated
and is tabulated in Table 4. The results show that the streamwater
chemistry of Mill Run can be explained by incongruent dissolution of
orthoclase, albite, chlorite and amphibole in proportions that agree
reasonably well with the sandstone mineralogy in Table 2. Precipita-
tion of iron oxyhydroxide, aluminium trihydroxide, and amorphous
silica satisfies the mass balance. Non-stoichimetric dissolution
that leaves behind some of the aluminosilicates and iron oxides also
satisfies the mass balance. The mineral-water mass balance required
larger amounts of amphiboles and chlorite than their proportions in
the shale and sandstone to explain the tributary water chemistry
(Tables 2 and 4). One reason for the discrepancy is the
assumption that amphiboles and chlorite are the only sources of
magnesium. However, siderite, Mg-calcite, or dolomite contain
magnesium and also satisfy the mineral-water mass balance. Another
reason for the discrepancy is that the proportions of the water
draining the Cenozoic sediments and sandstone relative to those
draining shale are not known.

The concentrations of HCO_3^- predicted by the weathering reactions,
assuming that the H_2CO_3 was the only source of H^+, were 163.5 and
1107.5 $\mu mol\ l^{-1}$, respectively, in MR and MRT (Table 4). These values
exceed the measured concentrations of 26.7 $\mu mol\ l^{-1}$ in MR and
987.6 $\mu mol\ l^{-1}$ in MRT. The deficit of HCO_3^- in the water indicates
that another source of H^+, for example atmospheric deposition of
H_2SO_4 and HNO_3, is required for the weathering reactions in addition
to the carbonic acid. Carbonate dissolution in Bloomsburg shale
coupled with carbonic acid of atmospheric origin make HCO_3^- the
dominant anion in MRT. The strong positive correlation between
cation concentration and alkininity indicates that CO_2 is the most
important weathering agent in MRT (Table 3). The relationship
between cation concentrations and alkininity (Table 3) indicates that
CO_2 is not the most important weathering agent in MR. In addition to
atmospheric input of H_2SO_4, HNO_3, and CO_2, internal H^+ production by
sulphide oxidation may also be occurring. Oxidation of 8.4 μmol of
pyrite per litre of water satisfies the sulphate balance in MR

TABLE 3 Chemical composition of the streamwater and precipitation in Mill Run drainage basin

| Elements	Precipitation Average Composition $\mu mol\ \ell^{-1}$	Mill Run — Quarter 1	Quarter 2	Quarter 3	Quarter 4	Average Output–Input $\mu mol\ \ell^{-1}$	Mill Run Tributary — Quarter 1	Quarter 2	Quarter 3	Quarter 4	Average Output–Input $\mu mol\ \ell^{-1}$
Sodium	6.83	32.2	27.6	23.8	28.4	17.2	53.6	44.3	48.6	57.8	36.5
Potassium	4.18	32.8	26.3	26.4	32.9	22.9	43.5	34.4	32.8	42.0	29.7
Calcium	12.63	29.9	26.4	24.5	28.0	6.6	480.3	146.1	377.0	711.1	393.7
Magnesium	2.26	55.6	53.8	46.4	48.2	47.9	185.1	75.2	167.8	277.6	167.6
Aluminum	0.2	6.7	8.4	5.7	4.0	7.8	1.1	1.6	1.4	0.9	0.8
Iron	0.0	1.7	1.0	0.9	1.35	1.1	0.36	0.7	0.4	0.02	0.3
Manganese	0.0	0.6	1.0	0.8	0.6	0.8	0.16	0.35	0.2	0.015	0.2
Silica	0.0	91.0	92.5	97.0	96.2	93.7	134.5	119.6	156.6	172.0	143.2
Chloride	22.76	40.0	31.9	34.6	42.5	0.0	43.6	44.4	53.2	54.9	0.0
Bicarbonate	0.0		10.4	26.2	44.6	26.8	1277.2	375.8	1046.2	1947.7	987.6
Sulfate	37.95	82.7	89.4	73.0	66.4	16.8	68.4	65.0	56.2	59.6	-17.4
Nitrate	29.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ammonia	22.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hydrogen Ions	72.44	8.6	12.9	9.0	4.6	-109.8	0.03	0.055	0.03	0.01	-153.8

n.d.=not determined.

TABLE 4 Weathering reactions controlling the streamwater chemistry at Mill Run drainage basin

μmol Reactants per one liter Water		μmol Products per one liter Water										
		Dissolved Species								Solids		
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	Fe^{3+}	HCO_3^-	$H_4SiO_4^{\circ}$	$Al(OH)_3$	SiO_2	$FeOOH$
A-Mill Run 23.0 orth + 13.9 alb + 3.3 amph + 7.6 ch + 163.5 CO_2 + 319.5 H_2O		17.2	23.0	6.6	47.9	7.8	1.1	163.5	93.7	54.2	56.5	5.5
B-Mill Run Tributary 29.7 orth + 15.6 alb + 21.0 amph + 21.0 ch + 352 cal + 755.55 CO_2 + 980.2 H_2O		36.6	29.7	394.0	168.0	0.8	0.4	1107.5	143.2	149.5	160.8	41.6

Orthoclase(orth)=$KAlSi_3O_8$, Albite(alb)=$NaAlSi_3O_8$, Amphibole(amph)=$NaCa_2Mg_3Fe_2Al_3Si_5O_{22}(OH)_2$, Chlorite(ch)=$Mg_5Al_2Si_3O_{10}(OH)_8$, and Calcite(cal)=$CaCO_3$

according to the reaction:

$$8.4 \ FeS_2 + 31.5 \ O_2 + 21 \ H_2O \rightarrow 16.8 \ SO_4^{2-} + 8.4 \ FeOOH + 33.6 \ H^+ \quad (2)$$
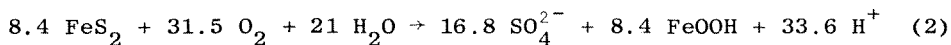
This reaction agrees with the mineralogical constituents. The H^+ produced satisfies the H^+ deficit if atmospheric H_2SO_4 and HNO_3 (Table 3), in addition to 26.7 $\mu mol \ l^{-1} \ H_2CO_3$, were the sources of the H^+ predicted by the weathering reactions in Table 4.

The mineral–water mass balance suggests the precipitation of $Al(OH)_3$ and formation of a SiO_2-rich residue. The aluminium solubility data suggest that aluminium solubility in these systems may be controlled by an $Al(OH)_3$ phase (Fig.4). These data in conjunction with the mineralogy of the soils suggest formation of a metastable phase of Al, less stable than gibbsite, during early
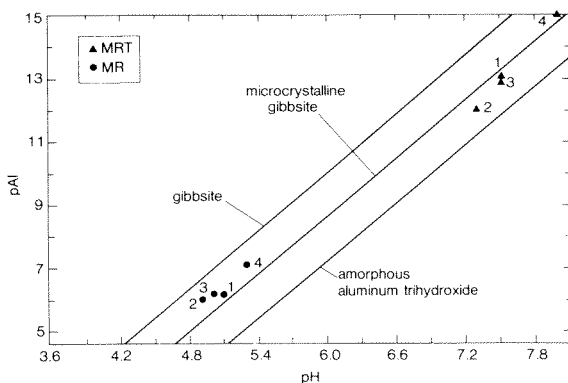

FIG.4   Streamwater quality data superimposed on aluminium trihydroxide solubility diagram, after Driscoll (1980) (1, 2, 3, and 4 represent the quarterly average composition of the stream during 1982).
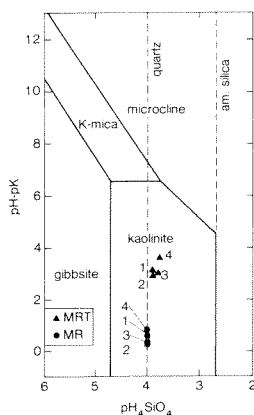

FIG.5   Streamwater quality data superimposed on K_2O-Al_2O_3-SiO_2 solubility diagram, after Feth et al. (1964)(1, 2, 3 and 4 represent the quarterly average composition of the stream during 1982).

weathering of the sandstone and shale. Formation of a phase less
stable than gibbsite in these systems agrees with the work of Hem
et al. (1973), Johnson (1979), and Driscoll (1980). Mineral
equilibria diagrams, for example the system $K_2O-Al_2O_3-SiO_2$ in Fig.5,
indicate that the cation concentrations in the streamwater even at
low flow conditions are controlled by dissolution-precipitation
kinetics rather than equilibrium with primary minerals.

CHEMICAL DENUDATION

Chemical denudation for 1982 (Table 5) was calculated as equal to
output minus input, using data in Tables 1 and 3. The dissolved load
in MR includes the amount of sulphate, as sulphur, derived from the
weathering of pyrite. In MRT, the amount of carbonate derived only

TABLE 5   *Chemical denudation (kg) in the study basin*
in 1982

	MR $(3.2\ km^2)$	MRT $(0.5\ km^2)$
Na_2O	901	229
K_2O	1 819	284
CaO	631	4 484
MgO	3 252	1 371
Al_2O_3	674	9
Fe_2O_3	159	6
MnO	100	3
SiO_2	9 484	1 773
Cl	0	0
CO_3	0	4 288
S	903	0
TOTAL	17 923	12 444

from the weathering of calcite was considered. Thus, chemical
denudation rates of 5601 $kg\ km^{-2}year^{-1}$ for MR and 24 888 $kg\ km^{-2}year^{-1}$
for MRT were estimated. If the removed material has an average
specific gravity 2.5 $g\ cm^{-3}$, the chemical denudation may be assumed
to lower the surface relief 0.002 $mm\ year^{-1}$ in MR and 0.010 $mm\ year^{-1}$
in MRT.

CONCLUSIONS

Dissolution of orthoclase, plagioclase, chlorite, amphibole and
pyrite; precipitation of microcrystalline gibbsite and FeOOH, and the
formation of SiO_2-rich residue during weathering appear to control
the streamwater chemistry in Mill Run. These weathering reactions
are occurring in the soil zone, which contains mechanically
disintegrated members of the Massanutten sandstone. In the Mill
Run sandstone, carbonic acid is not the most important weathering

agent since sulphuric acid of atmospheric origin augmented by that produced by pyrite oxidation is more important. Sulphate ion is the dominant anion in these waters. The denudation rate and resultant lowering of the surface relief by chemical solution in Mill Run is small.

Dissolution of carbonates from the Bloomsburg shale and neutralization of the carbonate alkalinity by carbonic acid of atmospheric origin make bicarbonate the dominant anion in the Mill Run tributary discharge. MRT is fed by water that has been in contact with shale bedrock. This water is diluted bt water draining sandstone and the highest dilution occurs during high-flow conditions. In addition to carbonate dissolution, dissolution of orthoclase, plagioclase, amphibole, and chlorite probably controls the chemistry of the MRT waters. Because the dissolution rate of carbonate is very high, the denudation rate and consequent lowering of the surface relief by chemical solution in MRT is larger than in MR.

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