

GEOCHEMICAL MASS BALANCES AND WEATHERING RATES IN FORESTED WATERSHEDS OF THE SOUTHERN BLUE RIDGE. III. CATION BUDGETS AND THE WEATHERING RATE OF AMPHIBOLE

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ABSTRACT. The geochemical mass balance of alkali and alkaline-earth elements in a southern Blue Ridge watershed underlain by amphibolite (Carroll Knob Complex; Watershed 3 of the U.S. Forest Service Coweeta Hydrologic Laboratory, Otto, North Carolina) can be explained by weathering of plagioclase (oligoclase-andesine), hornblende (ferroan pargasite), biotite, and calcite, and elemental uptake by forest biota. Feldspar and biotite weathering rates (calculated from geochemical mass balance) in the amphibolitic watershed are similar to previously calculated rates for compositionally similar minerals in the surrounding gneissic/schistose watersheds. However, the similarity of feldspar weathering rates despite significant differences in modal abundance suggests that feldspar in the Carroll Knob Complex is somewhat less reactive per unit modal abundance than is plagioclase in the surrounding rocks. Textural differences between the Carroll Knob Complex and the surrounding rocks (smaller surface-area-to-volume-ratio of coarser crystals in the Carroll Knob Complex) could be responsible. Hornblende and plagioclase weathering rates in Coweeta Watershed 3 are approximately equal (when normalized for differences in modal abundance of the two minerals), consistent with experimentally determined rates and empirical weathering series.

INTRODUCTION

Silicate-mineral weathering reactions are fundamental processes in the reaction of acid precipitation with susceptible landscapes (Cosby and others, 1985; Reuss, Cosby, and Wright, 1987; Binkley and others, 1989; Turner and others, 1990; Kaufmann and others, 1991) and in the contributions of continental crustal weathering to global geochemical cycles (Berner and Berner, 1987). Different geological substrates differ widely in their abilities to "buffer" atmospherically deposited acidity; the reactivity of different geological materials determines, to a considerable degree, the sensitivity of landscapes, soils, and surface- and groundwaters to acid precipitation (Edmunds and Kinniburgh, 1986; Bricker and Rice, 1989; Binkley and others, 1989; Webb and others, 1989; Turner and others, 1990). Landscapes developed on carbonate bedrock (limestone, dolostone, marble), calcareous sandstones or shales, or carbonate-rich glacial materials contain sufficient reactive mineral matter in the form of calcite to mitigate the effects of acid deposition (Edmunds and Kinniburgh, 1986; Bricker and Rice, 1989; Messer and others, 1988) and are not considered further here. The most sensitive landscapes to acidification are those underlain by crystalline silicate bedrock, especially granitic and gneissic (felsic) bedrock. This is because the silicate minerals

of which these rock types are composed do not react with throughgoing solutions quickly enough to neutralize the added acidity or to contribute base cations and acid-neutralizing capacity to the soil exchange complex and natural waters, respectively (Johnson, Reynolds, and Likens, 1972; Johnson, 1979, 1984; Edmunds and Kinniburgh, 1986; Schnoor and Stumm, 1986; Reuss, Cosby, and Wright, 1987; Binkley and others, 1989; Turner and others, 1990; Stauffer, 1990a; Kaufmann and others, 1991).

The role of feldspars in supplying cations is widely studied, because feldspar is the most abundant mineral in the Earth's crust, and because feldspar is the only abundant reactive mineral in acid-sensitive felsic rock types. However, ferromagnesian silicate minerals play a large role in global geochemical cycles and in neutralizing excess acidity and supplying base cations, because the (typically less abundant) ferromagnesian minerals weather more readily (and perhaps more quickly) than the more abundant but less reactive aluminosilicates (Goldich, 1938; Wilson, 1975; Lasaga, 1984; Sverdrup, 1990). For example, weathering of Mg-silicates (pyroxene, amphibole, biotite, chlorite, and olivine) is responsible for 54 percent of the Mg^{2+} in global dissolved river fluxes (Berner and Berner 1987). Furthermore, silicate weathering is responsible for over half (58 percent) of the carbonic acid consumption by continental weathering (Berner and Berner, 1987). Of the silicate portion, 35 percent is from Ca-silicates (including calcic plagioclase, pyroxene, and amphibole), and 41 percent from Mg-silicates (including pyroxene, amphibole, biotite, chlorite, and olivine) (Berner and Berner, 1987). Because carbonic acid is formed from carbon dioxide, this means that weathering of Ca- and Mg-silicates (including the ferromagnesian silicates emphasized here) accounts for 44 percent of the carbon dioxide consumption by continental geological processes. Weathering of ferromagnesian silicates is therefore a major factor in the greenhouse effect.

The significant contribution of ferromagnesian silicates to geochemical budgets is also well illustrated by small-watershed studies. For example, in a mafic watershed in Minnesota, feldspar and olivine weather at equal bulk rates, despite a feldspar:olivine ratio in the parent material of 25:1 (Siegel and Pfannkuch, 1984a). In the southern Blue Ridge, bulk garnet weathering rates are in some instances equal to the bulk feldspar weathering rate, in systems where the parent material has a feldspar:garnet ratio of about 4:1 (Velbel, 1985a, 1986a; Taylor and Velbel, 1991). Similarly, in the Adirondacks, hornblende weathering contributes significantly to dissolved elemental budgets and hydrogen ion consumption, despite the fact that hornblende makes up less than 3 percent of the sand-size fraction of the soils (April and Newton, 1983a,b, 1985; Newton and April, 1982; April, Newton, and Coles, 1986). Numerous papers report similar results (Miller and Drever, 1977; Katz, Bricker, and Kennedy, 1985; Bricker, 1986; Hornung and others, 1986; Drever and Hurcomb, 1986; Rochette, Drever, and Sanders, 1988; Katz, 1989). This may be especially significant in landscapes of mixed reactive (mafic) and

unreactive (felsic) rock types, in which cation budgets may be strongly influenced by small abundances of more highly reactive rock types (Drever and Hurcomb, 1986; Hornung and others, 1986; Rochette, Drever, and Sanders, 1988; Psenner, 1989; Stauffer, 1990a).

Chain-silicates (pyroxenes and amphiboles) are the most common ferromagnesian silicates in the Earth's crust (Deer, Howie, and Zussman, 1963). Despite their significance in geochemical budgets, little is known about the effects of compositional variation on chain-silicate weathering rates. A compositional influence on amphibole weatherability has been suggested in some previous studies (Eggleton, 1986). Secondary amphiboles (formed by uralitization) may be more stable in the weathering environment than amphiboles of direct igneous origin (Creasey and others, 1986), but specific compositional variations responsible for this behavior have not been reported. Actinolite and glaucophane appear to weather simultaneously in a study area in France (Proust, 1985); unfortunately, it is impossible to establish from the petrographic descriptions and sketches the relative extents or rates of weathering of the different amphiboles.

This study investigates the geochemical mass balance of a watershed underlain by amphibolite in the southern Appalachians. Previous studies of weathering rates in watersheds immediately adjacent to the present study area (Velbel, 1985a; Taylor and Velbel, 1991) have all involved rock types that do not contain any minerals of the amphibole group. The watershed examined here is also unique among watersheds in the study area in that its streamwater has the highest Ca/Na ratio of any watershed in the study area (table 1). The purposes of this study are (1) to determine the weathering rate of an amphibole-group mineral in nature, (2) to compare the weathering rates of mafic and felsic minerals in the southern Blue Ridge, and (3) to compare the amphibole weathering rate determined here with experimentally determined amphibole weathering rates.

THE STUDY AREA

The study area is in the Coweeta Hydrologic Laboratory of the United States Department of Agriculture Forest Service, located in the Nantahala Mountains 15 km southwest of Franklin, North Carolina (fig. 1). Bedrock in the area consists predominantly of high-rank (amphibolite facies) metasedimentary schists and gneisses (the Coweeta Group and the Tallulah Falls Formation), with local pods of mafic-ultramafic lithologies (Hatcher, 1979, 1980, 1988). Slopes are steep (avg 27°), annual average rainfall is high (approx 2 m), and temperatures are moderate (mean annual temperature at 685 m elevation is 12.8°C). The hydrology of Coweeta saprolites is discussed by Velbel (1985b).

Crystalline rocks of the study area are extensively weathered to saprolite. Saprolite developed on metasedimentary schists and gneisses averages 6 m in thickness, with a range from 0 to 20 m. Soils are classified as Ultisols and Inceptisols; as is common in the Blue Ridge (Graham,

TABLE 1
Ca/Na flux ratios in Coweeta low-order streams

	Watershed number	Parent rock type	Net output kg/ha/yr		Ca/Na mole ratio	
			Ca	Na	Output	Plagioclase
Control	2	TFF	1.82	8.26	0.13	0.47
	14	CG/TFF	1.45	4.22	0.20	0.33/0.47
	18	TFF	3.03	6.75	0.26	0.47
	27	CG	3.49	3.91	0.51	0.33
	32	CG	4.00	5.94	0.37	0.33
	34	TFF	4.92	7.44	0.38	0.47
	36	TFF/CG	6.40	9.90	0.37	0.47/0.33
Manipulated	1	TFF	0.91	3.49	0.15	0.47
	3	CKC	59.0	6.8	4.98	0.43
	6	TFF/CG	6.31	6.69	0.54	0.47/0.33
	7	TFF	6.94	7.99	0.50	0.47
	13	CG	1.54	3.44	0.26	0.33
	17	TFF/CG	-0.06	2.69	<0	0.47/0.33
	28	CG	13.47	9.33	0.83	0.33
	37	CG	10.03	7.58	0.76	0.33
	40	TFF	10.49	10.15	0.59	0.47

Parent rock-types (TFF = Tallulah Falls Formation; CG = Coweeta Group; CKC = Carroll Knob Complex) from Hatcher (1980); plagioclase compositions from Velbel (1985a) and this study. Where two parent rock types are present in subequal amounts, both are indicated, with the areally dominant shown first. Stream flux data (output - atmospheric input) for control watersheds from Swank and Waide (1988); for all manipulated watersheds except WS3, from Swank (1988); for WS3, this study (see text).

Daniels, and Buol, 1990), the former occur primarily on slopes, whereas the latter are developed on transported colluvial parent materials (Velbel, 1988).

Despite the thick saprolites and mature soils, even the uppermost (oldest) soil horizons on the thickest (oldest) saprolites in the Blue Ridge landscape still contain weatherable primary minerals. Feldspar (Velbel, 1983, 1986b; Daniels, Zelazny, and Everett, 1987; Norfleet and Smith, 1989), almandine garnet (Velbel, 1984; Graham and others, 1989a), biotite mica (Graham and others, 1989a,b; Norfleet and Smith, 1989; Graham and Buol, 1990; Velbel, in preparation), and hornblende (Berner and others, 1980; Velbel, 1989) are common in the upper parts of weathering profiles at Coweeta and elsewhere in the Blue Ridge and in sediments derived from these profiles (Grantham and Velbel, 1988). Consequently, even subtle differences in bedrock lithology are discernable in the dissolved loads of streams leaving the study watersheds (Velbel, 1985b). This is also true of groundwaters in the surrounding Blue Ridge and Piedmont landscapes (LeGrand, 1958). Weathering of bedrock minerals controls surface water chemistry at larger spatial scales in the southern Appalachians as well (Stauffer, 1990b; Kaufmann and others, 1991); however, because of the overall uniformity (at large spatial scales) of high-grade metasedimentary bedrock in the southern Blue

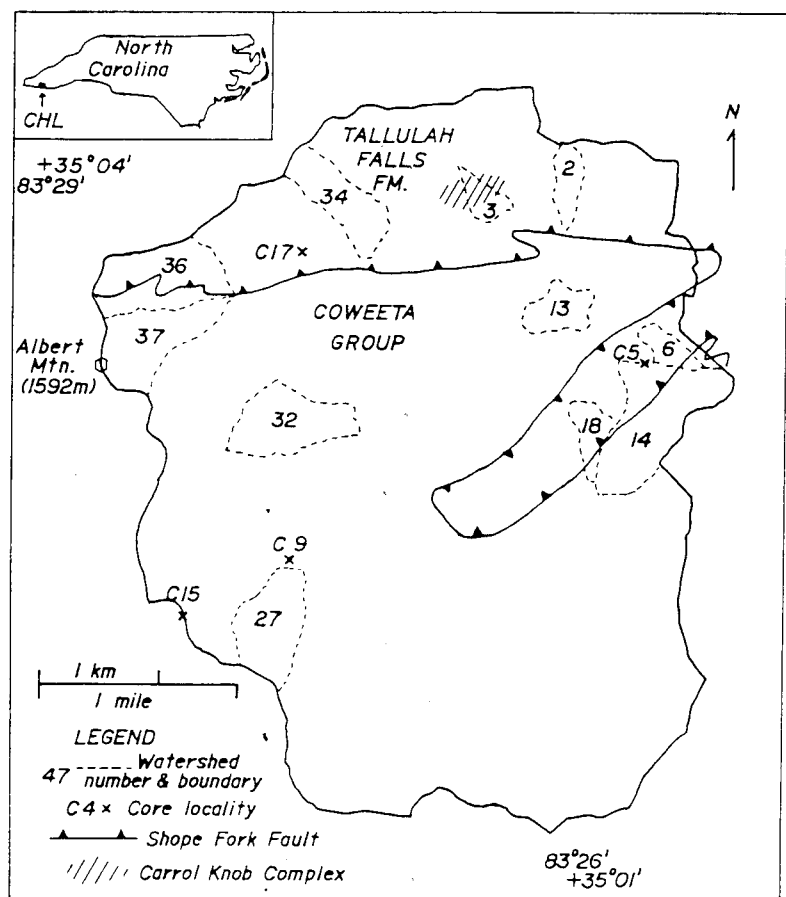


Fig 1. Map of study area.

Ridge, subtle bedrock-controlled stream-solute variations like those demonstrable at Coweeta are not readily discernable at present elsewhere in the region (Eshleman and Kaufmann, 1988; Messer and others, 1988). The solute chemistry of Blue Ridge lakes is likewise remarkably homogeneous (Ellers, Landers, and Brakke, 1988), but this is apparently due to the fact that most Blue Ridge lakes are reservoirs with large watersheds (Ellers, Landers, and Brakke, 1988; Lee and others, 1989). These large drainage areas likely encompass within their boundaries a large variety of Blue Ridge bedrock types. Thus, southern Blue Ridge lake chemistry spatially averages solute contributions from numerous small streams, the solute compositions of which are bedrock controlled.

The amphibolite examined in this study is from the Carroll Knob Complex¹ in Watershed #3 (W3) of the Coweeta Hydrologic Laboratory (fig. 1). The Carroll Knob Complex consists of a large body of amphibolite which encloses small bodies of metagabbros, ultramafic rocks, epidiosites, hornblendites, and soapstone (McSween and Hatcher, 1985; Walter, ms). The mafic bodies are severely deformed, and the outcrop pattern is a complex fold interference pattern (McSween and Hatcher, 1985). Crosscutting relationships have not been observed, and it remains uncertain whether the Carroll Knob Complex was emplaced by faulting or by intrusion (McSween and Hatcher, 1985).

The small exposure of the Carroll Knob Complex in W3 is not among those studied by Walter (ms) but is less than 1 km from samples she analyzed (compare her fig. 2 with fig. 1, or Hatcher, 1980). The Carroll Knob Complex in W3 consists of hornblende, plagioclase, quartz, and some biotite. It thus closely matches Walter's (ms) amphibolite assemblage 3 (hornblende + plagioclase + quartz + biotite \pm chlorite \pm epidote), which is distinguished from five other amphibolite assemblages by the presence of biotite and the absence of garnet, clinopyroxene, staurolite, and anthophyllite (Walter, 1990, p. 19–20). Biotite-bearing amphibolites usually occur near contacts with metasediments, suggesting late-stage metasomatism and retrogression (Walter, ms, p. 22); the Carroll Knob "outlier" in W3 is consistent with this, in that it is so small that all of it is near the Carroll Knob-Tallulah Falls contact. Carroll Knob amphibolites also contain some calcite fracture fillings (Walter, ms, p. 21). Although both epidote (which forms distinctive rims partially replacing plagioclase) and scapolite (replacing plagioclase) occur elsewhere in Carroll Knob amphibolites (Walter, ms, p. 21), neither was observed in material from W3.

Three petrographic thin sections of fresh Carroll Knob samples (one from within W3, two others from another body of the Carroll Knob Complex several hundred meters to the northwest) were polished for electron microprobe analysis of plagioclase compositions (replicate analyses of 6 grains per sample). Microprobe analyses of the 18 plagioclase grains from the Carroll Knob Complex at Coweeta give compositions of $An_{30\pm 4}$ (oligoclase/andesine), essentially identical with the plagioclase in the surrounding Tallulah Falls Formation (An_{32} ; Velbel, 1985a). The sodic nature of plagioclase in W3 probably reflects modification of the bulk-rock composition by elemental mass-transfer between the small amphibolite body in W3 and the surrounding metasediments during late-stage metasomatism and retrogression (Walter, ms, on the distribution and inferred origin of the biotite-bearing amphibolite assemblage). Point counts (300 random points per sample) to determine modal hornblende abundances averaged 19.2 percent (individual modes: 16.7,

¹ In previous papers on weathering at Coweeta, I have misspelled this unit's name, omitting the second "l" in "Carroll."

19.3, and 21.7 percent). This abundance corresponds to the low end of the range of hornblende abundances reported for the Carroll Knob Complex as a whole (20–70 volume percent; Walter, ms, p. 20).

Hornblende (ferroan pargasite) of the Carroll Knob Complex weathers by etching, stoichiometric dissolution, and precipitation of Al and Fe (neoformation), producing a microboxwork of ferruginous and aluminous products (goethite, gibbsite, and kaolinite; Velbel, 1989). Although transformation of biotite to vermiculite is common in weathering profiles of the southern Blue Ridge (Daniels, Zelazny, and Everett, 1987; Graham and others, 1989a,b; Norfleet and Smith, 1989; Graham and Buol, 1990; Velbel, in preparation), and mechanical abrasion of soil grains during colluvial transport breaks down coarse primary 2:1 phyllosilicates into the clay-size fraction of Blue Ridge colluvial soil horizons (Graham and others, 1989b), intense leaching in the southern Appalachians prevents neoformation of 2:1 clay minerals in the weathering profiles (Velbel, 1985b, 1989; Daniels, Zelazny, and Everett, 1987; Norfleet and Smith, 1989; Graham and Buol, 1990; Stauffer, 1990b). Weathering of Carroll Knob plagioclase is similar to plagioclase weathering in the surrounding gneisses and schists, which was described by Velbel (1983). Plagioclase from saprolites and corestones developed on the Carroll Knob complex in W3 shows typical weathering features, including prismatic etch pits. Kaolinite and gibbsite are common weathering products of plagioclase feldspar in the study area (Velbel, 1983, 1985a,b; Daniels, Zelazny, and Everett, 1987; Norfleet and Smith, 1989; Graham and Buol, 1990; Stauffer, 1990b).

Vegetation on Coweeta W3 was cut and completely removed in 1940, and two-thirds of the watershed area was used for farming (including application of agricultural lime) and grazing for 12 yrs (Swank and Crossley, 1988). Thus, the land-use history of W3 is markedly different from that of the watersheds studied by Velbel (1985a,b) and Taylor and Velbel (1991), which are control watersheds with no anthropogenic disturbance of the forest ecosystem since 1927. Watershed #3 is not gauged, but mean annual discharges from the two nearest control watersheds (W2 and W34) are 93 and 128 cm, respectively (Swank and Waide, 1988). The discharge of W3 almost certainly falls between these two values, because rainfall and discharge decrease from west to east in the Coweeta basin (Swift, Cunningham, and Douglass, 1988), and W3 is situated between W2 and W34 (fig. 1). Because W3 is closer to W2 than to W34, its hydrologic characteristics are more similar to the former. For the purposes of the mass balance and associated weathering rate calculations, a mean annual discharge of 100 cm is assumed for W3. This is probably within 10 to 20 percent of the actual value.

METHODS

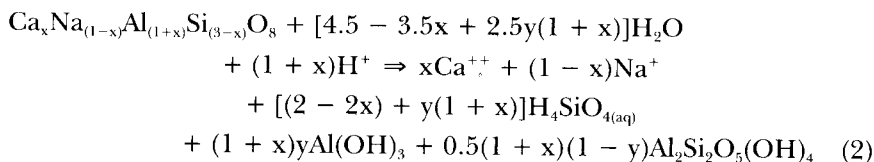
Mineral weathering rates are calculated by geochemical mass balance (Garrels and Mackenzie, 1967), following the method of Velbel (1985a, 1986a). Weathering rates are calculated by solving a system of

simultaneous linear equations which represent the steady-state input-output behavior of the watershed (Plummer and Back, 1980, eq 3),

$$\sum_{j=1}^{\phi} \alpha_j \beta_{c,j} = \Delta m_c \quad c = 1, \dots, n \quad (1)$$

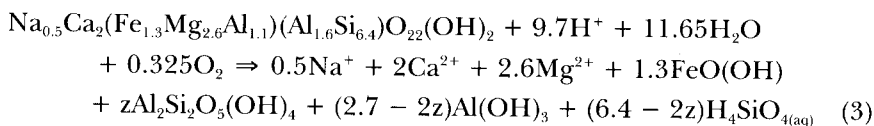
where ϕ (ϕ) is the number of (mineral) phases j whose transformations account for the change of mass of species c within the system; Δm_c is the total (known) change in mass of species c across the boundaries of the system (output minus input); $\beta_{c,j}$ is the stoichiometric coefficient of species c released to solution by the weathering of phase j ; and α_j is the weathering rate of phase j . Where multiple mass balance equations are stoichiometrically linked to one another through one or more phase(s) j containing more than one species c , a system of n equations results. If the number of mass balance equations (n , each for a different species, c) equals the number of unknowns (ϕ , the number of phases j whose transformations account for changes of mass of c within the system), eq 1 can be solved for mineral weathering rates (α_j) by conventional techniques of linear algebra. The "balance sheet" method of Garrels and Mackenzie (1967), which has also been employed by numerous other workers (see Taylor and Velbel, 1991) to calculate individual mineral weathering rates, is merely a long-hand, pencil-and-paper solution to the system of mass balance eqs (1). The relationship between this use of mass balance eqs (1) and that of Plummer and Back (1980) is discussed by Velbel (1986a).

Plagioclase weathering at Coweeta is described by the reaction (Velbel, 1985a; Taylor and Velbel, 1991):



(where x is the mole fraction anorthite in the plagioclase [$0 < x < 1$], and y is the fraction of Al released by feldspar weathering which goes into gibbsite [$0 < y < 1$]). As noted above, the plagioclase feldspars of the Carroll Knob Complex at Coweeta have compositions of $\text{An}_{30 \pm 4}$ (oligoclase/andesine; $x = 0.30$).

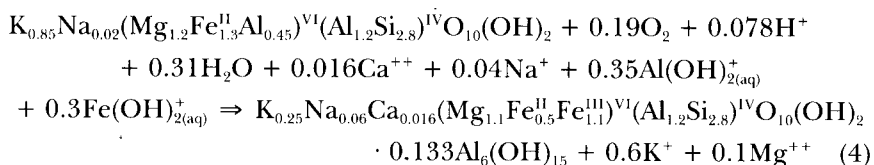
A stoichiometric expression for hornblende weathering at Coweeta (Velbel, 1989) is:



where some indeterminate amount (z) of kaolinite is formed. (z) must fall within the range 0 (all Al to gibbsite) to 1.35 (all Al to kaolinite) and could

be determined if the Si content of the gibbsite + kaolinite + goethite microboxwork assemblage were known (Velbel, 1989).

Biotite occurs in rocks of the Carroll Knob Complex in Coweeta W3; the weathering reaction for biotite to vermiculite in the schists and gneisses of the surrounding Tallulah Falls Formation (Velbel, 1985a) is:



Given the sodic character of the Carroll Knob plagioclase, calcite is almost certainly required to account for the exceptionally high Ca concentration and Ca/Na ratio of W3 streamwater (table 1; Swank and Douglass, 1977; Swank and Waide, 1988; Swank, 1988). Carroll Knob rocks contain minor amounts of calcite (Walter, ms), and agricultural lime was applied to W3 in the 1940s (Swank and Douglass, 1977; Swank, 1988).

Stoichiometric coefficients from these mineral weathering reactions in Coweeta Watershed 3 are summarized in table 2A.

Weathering rates are calculated as moles of mineral weathered per hectare per yr, using Na, Ca, Mg, and K concentration data for Coweeta W3 (Swank, 1988, table 25.3) (silica was also analyzed and is briefly discussed below) and an estimated discharge of 100cm per year (see above). The resulting fluxes are corrected for atmospheric input (which was not measured for W3) by subtracting an amount equal to the average atmospheric influx of each element for the two nearest control water-

TABLE 2

Geochemical mass balance of mineral weathering, Carroll Knob Complex, watershed 3, Coweeta Hydrologic Laboratory

A. Matrix of stoichiometric coefficients				
	Na	Mg	K	Ca
Plagioclase	+0.70	0	0	+0.30
Hornblende	+0.5	+2.6	0	+2.0
Biotite Mica	-0.04	+0.1	+0.6	-0.016
Calcite	0	0	0	+1.0
B. Net fluxes (moles/ha/yr)				
	Na	Mg	K	Ca
	300	160	61	1500
C. Weathering rates (moles of mineral per hectare per yr)				
Plagioclase	393			
Hornblende	115			
Biotite Mica	407			
Calcite	1270			

Units: For minerals – moles of element released to (+) or consumed from (–) solution per mole of reaction as written (see equations in text). Mineral weathering rates are positive when net effluxes are positive.

sheds (2 and 34) from the budgets of Swank and Waide (1988, table 4.11). The net fluxes used in this study are summarized in table 2B.

The presence of four reactive minerals (plagioclase, hornblende, biotite, and calcite) makes it impossible to calculate botanical uptake as one of the unknowns in the system of simultaneous mass-balance equations (Velbel, 1985a, 1986a; Taylor and Velbel, 1991), because it would constitute a fifth unknown in a system of only four mass balance equations. However, W3 contains an aggrading forest, still recovering from clearcutting in the 1940s, in contrast with the more mature, less-recently disturbed forest stands on the schist and gneiss watersheds studied by Velbel (1985a) and Taylor and Velbel (1991), all of which are control watersheds. The following approximation was therefore introduced to facilitate calculation of the four mineral weathering rates: Taylor and Velbel (1991) show that botanical uptake of K into the forest biomass increases weathering rates of K-bearing silicates (biotite) up to 3.5 times over the value calculated directly from stream effluxes, and that Ca-Mg-bearing silicates show a similar, albeit smaller ($1.5\times$), effect, even in control watersheds. Biotite is the only K-bearing silicate in W3; the Ca-Mg silicate is hornblende. To account for the likely role of botanical uptake of K, Ca, and Mg into the forest biomass of W3, I assume, following Taylor and Velbel (1991), that the actual weathering rates of biotite and hornblende are, respectively, 4 and 2 times greater than the values calculated from stream fluxes. Use of these high values is justified by the aggrading nature of the W3 biomass (still in advanced stages of recovery from the logging and farming of the 1940s), in contrast to biomass in the control watersheds (which is at least several decades older). The actual botanical uptake for a recovering forest stand may be even somewhat larger than the values used here, but, as shown below, the values used result in excellent agreement with weathering rates of plagioclase and biotite in the surrounding watersheds, for which the rates were calculated by directly including botanical uptake terms (Velbel, 1985a; Taylor and Velbel, 1991).

RESULTS

Table 2C shows the results of the mass balance. Weathering of hornblende (115 moles/ha/yr), biotite (407 moles/ha/yr), plagioclase (393 moles/ha/yr), and calcite (agricultural lime or naturally occurring calcite; 1270 moles/ha/yr) can account quantitatively for all alkali and alkaline earth cations in streamwater. The calculated rates are not particularly sensitive to the subtle differences between the amphibole stoichiometry of Helms and others (1987) and Velbel's (1989) slightly idealized version based on Helms and others' (1987) data; plagioclase and hornblende weathering rates calculated using the two stoichiometries differ by less than 4 percent, and the ratio of the two rates is nearly identical using either stoichiometry.

Silica flux data are available, but neither the plagioclase nor the hornblende weathering reactions (reactions 2 and 3) uniquely predict the

amount of silica released by mineral weathering, because the relative proportions of gibbsite and kaolinite formed (determined by y in the plagioclase weathering reaction and z in the hornblende reaction) are not known. However, limiting conditions can be calculated.

The formation of the aluminous interlayers in the products of biotite weathering consumes 142 moles of Al per hectare per yr (407 moles/ha/yr times 0.35; reaction 4). If all the Al released by plagioclase and hornblende weathering goes into gibbsite or aluminous interlayers or is exported in dissolved form and none goes into kaolinite, all the silica released by the weathering of plagioclase and hornblende is leached from Watershed 3, resulting in a flux of 1800 moles of silica per hectare per yr. At the other extreme, if all Al in excess of the amount required to form aluminous interlayers in vermiculite goes into kaolinite, much of the silica released by plagioclase and hornblende weathering is taken up in the formation of kaolinite, leaving only 834 moles/ha/yr of silica to be exported by streams. The measured silica concentration in streams leaving Coweeta W3 corresponds to a silica flux of 1540 moles/ha/yr, which falls as it should between the limiting values. This indicates that Al released by plagioclase and hornblende weathering (besides that consumed as hydroxy-interlayers in products of biotite weathering) is precipitated both directly as gibbsite and by combining with Si to form kaolinite, consistent with the observed mineralogy of weathering products in Coweeta W3 (Velbel, 1989).

DISCUSSION

Plagioclase weathering rates.—The sodic (An_{30} oligoclase-andesine) plagioclase of the Carroll Knob Complex weathers at essentially the same rate (393 moles/ha/yr) as sodic (An_{25-32} oligoclase-andesine) plagioclases of the surrounding Tallulah Falls Formation and Coweeta Group gneisses (230–662 moles/ha/yr; Velbel, 1985a; Taylor and Velbel, 1991). This may be due in part to the similarity in plagioclase composition between the two units. However, the rates are similar *in spite of* likely differences in modal abundance between the two rock types. Modal proportions of plagioclase in the Carroll Knob Complex are “complementary to those of hornblende” (20–70 percent; Walter, ms, p. 20–21); as noted above, modal hornblende in the local study area is at the low end of Walter’s (ms) range, suggesting that the modal plagioclase abundance in W3 is considerably greater than the modal plagioclase abundance in one of the nearby schist-gneiss units (Coweeta Group; approx 8.3 volume percent; Velbel, 1985a, table 2). Modal abundances are not available for the Tallulah Falls Formation; plagioclase is likely to be somewhat more abundant in the Tallulah Falls Formation than in the Coweeta Group, because of the lesser compositional maturity of the sedimentary protoliths of the Tallulah Falls Formation relative to the Coweeta Group (Velbel, 1985a,b and references therein), but plagioclase abundances comparable to those of the Carroll Knob Complex are not likely. This suggests that, despite the similarity in composition between the Carroll

Knob and Tallulah Falls plagioclases, the Carroll Knob plagioclase weathers somewhat less readily per unit abundance. Factors other than composition apparently influence the relative weathering rates of plagioclase in the two rock types. Some of these depend more on rock texture than rock composition. For example, if plagioclase crystals are coarser in the Carroll Knob Complex than in the Tallulah Falls Formation, the smaller surface-area-to-volume-ratio of the coarser crystals in the former unit could render their total surface area available for weathering smaller than the surface area of less-abundant but finer-grained crystals in the latter. Any textural or physical property that reduces the reactive surface-area per unit modal-abundance of the Carroll Knob Complex (relative to the Tallulah Falls Formation) would be adequate to explain the apparently lower reactivity of more-abundant plagioclase in the Carroll Knob Complex relative to plagioclase in the Tallulah Falls Formation.

Biotite weathering rates.—The biotite weathering rate in W3 (407 moles/ha/yr) is near the high end of the range of biotite weathering rates in the surrounding schists and gneisses (85–432 moles/ha/year; Taylor and Velbel, 1991). This is in part a consequence of the assumptions regarding high botanical demand for potassium due to the aggrading state of forest stand on W3 (discussed in methods section above). Assuming that the biotite in the Carroll Knob Complex is compositionally identical with the biotite in the Coweeta Group and the Tallulah Falls Formation, the higher weathering rates of the Carroll Knob biotite could also be due to higher modal abundance of biotite in the Carroll Knob Complex, but there are no data to evaluate this possibility.

Dissolution of calcite.—The high Ca content and the high Ca/Na ratio (table 1) of streams draining Coweeta W3 (Swank and Douglass, 1977; Swank, 1988) are due to weathering of calcite, which occurs either as trace calcite within the Carroll Knob Complex (Walter, ms) or as residual agricultural lime applied in the 1940s (Swank and Douglass, 1977; Swank, 1988). In crystalline-bedrock landscapes of North Carolina, groundwaters in mafic rocks have significantly higher Ca/alkali ratios than groundwaters in felsic rocks even in the absence of anthropogenically applied lime (LeGrand, 1958). In principle, this might be due to weathering of Ca-rich silicates. However, weathering of even trace quantities of calcite, occurring as “hidden” veins (Katz, Bricker, and Kennedy, 1985; Bricker, 1986; Drever and Hurcomb, 1986; Dethier, 1988; Katz, 1989), as grain boundary calcite (Mast, Drever, and Baron, 1990), as exotic limestone introduced by glacial transport (not important at Coweeta, but important elsewhere; April, Newton, and Coles, 1986), or as carbonate dust introduced by eolian processes (Litaor, 1987) can produce streamwater Ca/Na ratios higher than bedrock-plagioclase values (Mast, Drever, and Baron, 1990; Stauffer, 1990a).

Amphibole weathering rates.—The average modal abundance of hornblende in the Carroll Knob Complex in and near Coweeta W3 is 19.2 percent. The hornblende weathering rate (115 moles/ha/yr) is only about 29 percent of the oligoclase-andesine weathering rate (393 moles/

ha/yr; table 2). If the modal abundance of plagioclase is "complementary" to that of hornblende (ranging up to approx 70 percent; Walter, ms, p. 20–21), then the hornblende/plagioclase modal-abundance ratio is approx $19.2/70 = 0.27$. The molar weathering rates (0.29 mole of hornblende weathered for every mole of plagioclase; table 2) are almost exactly proportional to modal abundance (0.27 modal percent hornblende for each modal percent plagioclase). This suggests that hornblende and plagioclase weather at almost exactly the same rate per unit modal abundance. This is consistent with Goldich's (1938) empirical weathering series in which hornblende weathers somewhat more readily than biotite and equals oligoclase-andesine plagioclase feldspars in vulnerability to weathering (Goldich, 1938).

Methodological inconsistencies prevent direct comparison of calculated rates among the different mass-balance studies of amphibole weathering rates. Many published studies report amphibole weathering rates only in moles per liter (without reporting water yield in liters per hectare, for conversion to fluxes, which enables calculation of weathering rates) or as ratios of weathering rates relative to some other mineral. Most mass balances assume that weathering is the only intrawatershed process that affects solute fluxes, thereby omitting other processes. Although such assumptions are sometimes justified (biomass uptake is probably trivial in alpine watersheds [Reynolds and Johnson, 1972; Drever and Hurcomb, 1986; Giovanoli and others, 1988; Frogner, 1990; Turner and others, 1990; Stauffer, 1990a], and there are watersheds in which depletion of the soil cation exchange pool is demonstrably negligible [Clayton, 1988; Stauffer, 1990b]), more often they are an inadvertent omission (Taylor and Velbel, 1991). No previously published amphibole weathering rate was calculated from geochemical mass balance including botanical terms, even in forested watersheds, where neglecting biomass uptake may introduce errors of several hundred percent (Taylor and Velbel, 1991).

Solute mass balances in naturally or artificially acidified watersheds in Scandinavia and northeastern North America are influenced by depletion of Ca and Mg from the soil cation-exchange complex ("present day" rates of April, Newton, and Coles, 1986; Sverdrup and Warfvinge, 1988; Frogner, 1990; Kirkwood and Nesbitt, 1991). In such watersheds, amphibole weathering rates estimated from Ca and Mg fluxes may be erroneously high. Other studies ("long term" rates of April, Newton, and Coles, 1986; Kirkwood and Nesbitt, 1991) report rates in moles/ha/yr but are based on time-integrated rates estimated from changes in bulk soil chemistry since deglaciation of the parent material, not on present-day solute fluxes. Rates calculated in such studies are considerably slower than rates from solute mass balance; some possible reasons for the difference include accelerated rates of mineral weathering and/or depletion of the soil cation-exchange complex due to recent environmental acidification and the abundance of fine-grained material in glacially comminuted parent materials (April, Newton, and Coles, 1986; Sverdrup and Warfvinge, 1988; Kirkwood and Nesbitt, 1991).

Even for the few solute mass-balance studies that do report weathering rates in moles/ha/yr or convertible units, insufficient data exist on amphibole composition, grain size, grain geometry, modal abundance, and regolith thickness to evaluate the influence of these parameters on rates or to permit estimation of the reactive mineral surface area contributing to the observed flux (Velbel, 1986a). Consequently, it is impossible to renormalize most weathering rates determined by solute mass-balance to mineral-surface area for direct comparison of absolute rates in the field with rates in the laboratory (Pačes, 1983; Velbel, 1985a). Therefore, the following discussion is based largely on rate ratios (with field rates normalized to modal abundance) instead of absolute rates.

Absolute rates of silicate-mineral weathering determined in the laboratory are typically as much as one to three orders of magnitude slower than rates for the same minerals in natural systems as estimated by geochemical mass balance and other methods (Pačes, 1983; Velbel, 1985a, 1986b; Drever and Swoboda-Colberg, 1989; Drever and others, 1989; Sverdrup and Warfvinge, 1988; Frogner, 1990; Turner and others, 1990; Sverdrup, 1990), yet relative rates (rate ratios) are in excellent accord. If mineral weathering rate ratios calculated for multiple minerals ($r_{\text{garnet}}/r_{\text{albite}}, r_{\text{hornblende}}/r_{\text{albite}}$) from internally consistent mass balance studies are compared with similar ratios from laboratory data sets in which all minerals were pretreated, dissolved, and analyzed identically, the rate ratios generally agree very well. For example, equal bulk rates of feldspar and olivine weathering in the Filson Creek (Minnesota) study area, despite a feldspar:olivine ratio in the parent material of 25:1, imply that olivine weathers 25 times faster than the same amount of plagioclase (Siegel and Pfannkuch, 1984a), in excellent accord with the 25-fold difference in rates determined for release of divalent cations from the same two minerals by Siegel and Pfannkuch (1984b). Similarly, the garnet weathering rate is normalized to mineral surface area 4.2 times faster than the feldspar weathering rate in Coweeta Watershed 27 (Velbel, 1985a), in excellent agreement with a rate-ratio of 3.6 determined experimentally by Nickel (1973).

Table 3 shows that the correspondence between the amphibole/feldspar rate ratio calculated here for Coweeta W3 (approximately equal rates, giving a ratio of 1) and amphibole/feldspar rate ratios determined in internally consistent laboratory experiments is reasonably good. The dissolution rate of tremolite (table 3A; Schott, Berner, and Sjöberg, 1981) is 3.5 times faster than the dissolution rate of albite at pH 6 (Holdren and Berner, 1979) and 2.0 times faster than that of alkali feldspar at pH 5 (Holdren and Speyer, 1985). Given that more calcic plagioclase (oligoclase-andesine) should weather somewhat more quickly than albite (Goldich, 1938; Holdren and Speyer, 1987; Casey, Westrich, and Holdren, 1991), the ratio of tremolite/oligoclase-andesine weathering should be lower than the values calculated here (<3.5 , <2.0). The results of Mast and Drever (1987) are consistent with this inference (table 3B). Dissolution

TABLE 3

Amphibole plagioclase weathering rates from laboratory studies

Mineral	Dissolution rate (moles/cm ² /sec)	Reference
A.		
Tremolite	1.45×10^{-15}	Schott, Berner, and Sjöberg (1981)*
Albite	4.2×10^{-16}	Holdren and Berner (1979)**
Alkali feldspar	7.33×10^{-16}	Holdren and Speyer (1985)***
B.		
Tremolite	2.0×10^{-16}	Mast and Drever (1987)
Oligoclase	$\pm 1 \times 10^{-16}$	Mast and Drever (1987)
C.		
Hornblende	1.82×10^{-16}	Nickel (1973) [†]
Albite	1.05×10^{-16}	Nickel (1973) [†]
D.		
Hornblende	$4.2\text{--}8.3 \times 10^{-16}$	Sverdrup (1990) [§]
Albite	1.6×10^{-16}	Sverdrup (1990) ^{§§}

* Calculated from linear portion of the pH 6 silica release curve of Schott, Berner, and Sjöberg (1981, fig. 13), assuming stoichiometric dissolution.

** pH 6; calculated from Velbel's (1986b) tabulation of silica release rates from plagioclase feldspars, assuming 3 moles of silica released per mole of alkali feldspar.

*** pH 5; calculated from Velbel's (1986b) tabulation of silica release rates from plagioclase feldspars, assuming 3 moles of silica released per mole of alkali feldspar.

[†] Calculated from the silica release rate at pH 5.6, from Nickel (1973, fig. 18), assuming stoichiometric dissolution and a hornblende stoichiometry calculated from Nickel's reported composition.

[§] Calculated from the silica release rate at pH 5.6, from Nickel (1973, fig. 5), assuming stoichiometric dissolution and endmember albite stoichiometry.

[§] Calculated from the total cation release rate (Sverdrup, 1990, table 3.16), assuming twelve cation equivalents per mole of hornblende.

^{§§} Calculated from the total cation release rate (Sverdrup, 1990, table 3.5), assuming one cation equivalent per mole of albite.

rates near pH 5 for tremolite and oligoclase give a tremolite/oligoclase weathering rate ratio of 2 (Mast and Drever, 1987).

Laboratory rates of hornblende dissolution (table 3C and D) are similar to those of tremolite. Nickel's (1973) experimentally determined albite and hornblende dissolution rates give a hornblende/albite weathering rate ratio of 1.7:1 (table 3C). Sverdrup (1990, table 3.16 and 3.5) shows that the flux of alkali and alkaline-earth metals (in cation equivalents) per unit time and surface area is 31 to 62.5 times higher from hornblende than from albite near pH 6. Approximately twelve cation equivalents are released per mole of hornblende weathered, compared with one eq per mole of albite; thus, amphibole weathers 2.6 to 5.2 times faster than albite on a molar basis (table 3D) (Sverdrup, 1990). Once again, both these ratios are upper limits, because albite does not weather as quickly as oligoclase-andesine.

Comparing hornblende weathering-rate ratios normalized to plagioclase weathering rates assumes equal weathering rates for a unit abundance (or unit surface area) of sodic plagioclase in all studies. Rates of sodic feldspar weathering determined in laboratory studies vary an order of magnitude or more among laboratory studies, suggesting that composition alone does not control the rates of plagioclase weathering (Helgeson, Murphy, and Aagaard, 1984; Velbel, 1986b; Holdren and Speyer, 1985, 1987). Other factors besides bulk abundance (for example, differences in the ratio of effective surface area to total surface area) influence the dissolution rates of individual feldspars, even for different feldspars of the same composition (Helgeson, Murphy, and Aagaard, 1984; Velbel, 1986b; Holdren and Speyer, 1985, 1987). Nevertheless, the hornblende and plagioclase weathering rates determined for the Carroll Knob Complex in Coweeta Watershed 3 resemble most experimentally determined rates, in that most rate determinations indicate that amphibole and oligoclase-andesine weathering rates are approximately equal to within a factor of four. These rates are consistent with the relative persistence of amphiboles and sodic plagioclase in the Goldich (1938) weathering series. Data on amphibole weathering rates are not sufficiently abundant to determine whether compositional variability among different amphiboles is responsible for all or part of the variation in rates and rate-ratios.

The hornblende molar weathering rate is only 29 percent of the plagioclase weathering rate. However, if aluminum is conserved in products of plagioclase weathering, hornblende weathering consumes 67 percent of the total acidity consumed by all silicate-mineral hydrolysis reactions; oligoclase-andesine hydrolysis consumes almost all the rest (31 percent). The magnitude of acid-neutralization by hornblende weathering (relative to other silicate minerals) determined here is comparable to that determined in other mass-balance studies (Katz, Bricker, and Kennedy, 1985; April, Newton, and Coles, 1986; Bricker, 1986; Drever and Hurcomb, 1986; Rochette, Drever, and Sanders, 1988; Katz, 1989).

SUMMARY AND CONCLUSIONS

Feldspar and biotite weathering rates in amphibolite of the Carroll Knob Complex in Coweeta Watershed 3 are similar to previously calculated rates for compositionally similar minerals in the surrounding gneissic/schistose watersheds (Velbel, 1985a; Taylor and Velbel, 1991). Similarity of mineral compositions between amphibolite and metasedimentary schists and gneisses is likely due to significant compositional modification of the small amphibolite body in W3 by elemental exchange with the surrounding metasediments during metamorphism. Consequently, the results of this study are not representative of the weathering of compositionally unmodified amphibolites, which contain among other things much more calcic plagioclase than that of the amphibolite in W3. The similarity of feldspar weathering rates despite significant differences in modal abundance (Velbel, 1985a; Walter, ms) suggests that feldspar in

the Carroll Knob Complex is somewhat less reactive per unit modal abundance than is plagioclase in the surrounding rocks; simple textural (crystal-size) and/or other similar factors may account for this apparent difference in reactivity.

Hornblende and plagioclase weathering rates are equal in the Carroll Knob Complex of Coweeta Watershed 3 (when normalized for differences in modal abundance of the two minerals). This is consistent with experimentally determined rates (Nickel, 1973; Schott, Berner, and Sjöberg, 1981; Mast and Drever, 1987; Sverdrup and Warfvinge, 1988; Sverdrup, 1990) and empirical weathering series (Goldich, 1938).

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