Rates and time scales of clay-mineral formation by weathering in saprolitic regoliths of the southern Appalachians from geochemical mass balance

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ABSTRACT

Rates of clay formation in three watersheds located at the Coweeta Hydrologic Laboratory, western North Carolina, have been determined from solute flux-based mass balance methods. A system of mass balance equations with enough equations and unknowns to allow calculation of secondary-mineral formation rates as well as the more commonly determined primary-mineral dissolution rates was achieved by including rare earth elements (REE) in the mass balance.

Rates of clay-mineral formation determined by mass balance methods have been used to calculate the time needed for a 5% (50 g kg^{-1}) change in relative clay abundance in the saprolite at Coweeta; this corresponds to the "response time" of the clay mineral to, for example, a change in climate. The 5% change in relative clay abundance is the smallest change that can generally be detected using X-ray diffraction (XRD). Response times range from tens of thousands to hundreds of thousands of years. Extrapolating the Coweeta clay formation rates to other southern Appalachian regoliths, the time required to form measured clay abundances ("production times") in eastern Blue Ridge and Inner Piedmont regolith have been calculated. The production times of clay-mineral assemblages range from 2 k.y. to 2 m.y., with mean values ranging from 50 k.y. to 1 m.y. The results of this study are consistent with the arguments of Thiry (2000) that the best resolution of the paleoclimatic record in marine clay-rich sediments and mudrocks is ~1 or 2 m.y.

Keywords: clays, rates, mass balance, Appalachians, regolith.

INTRODUCTION

Continental weathering processes generate unconsolidated material available for erosion; these unconsolidated materials ultimately contribute clastic materials to sedimentary basins. Thus, the physical record of erosion and [chemical] weathering is found in clastic sedimentary deposits (e.g., Derry and France-Lanord, 1997). As the weathering of silicate rocks is typically incongruent, clays form, which may then accumulate in sedimentary basins and serve as direct evidence of continental silicate weathering. Secondary minerals or their associations may be diagnostic for certain types of climatic environments (e.g., Griffin, 1962; Biscaye 1965; Menking, 1997; Chamley, 1997; Yuretich et al., 1999; Price et al., 2000; Tabor et al., 2002; Migoń and Lidmar-Bergström, 2002; John et al., 2003). However, Thiry (2000) states that terrigenous material in sedimentary deposits reflects climate only if the source area landscape is covered with a substantial blanket of mature soils in equilibrium with the environment. Time scales of secondary-mineral formation during rock weathering and landscape evolution are difficult to determine (Schroeder et al., 2001). Based on geochemical calculations and the geomorphic occurrences of soils and paleosols, Thiry (2000) argues that a time span of at least 1–2 m.y. is necessary to form a landscape blanketed with a thick kaolinitic regolith. In contrast, Schroeder et al. (2001) determined a formation time scale of thousands of years for the gibbsite portion of predominantly kaolinitic saprolitic regolith in the southeastern United States.

Using flux-based watershed mass balance methods, this study has calculated the rates of clay (hydrous aluminosilicates and hydroxides) formation in a modern weathering profile at the Coweeta Hydrologic Laboratory in western North Carolina. These clay formation rates are used to calculate the response times of clay minerals to changes in climate; that is, to test Thiry's (2000) hypothesis that 1–2 m.y. are required to form appreciable kaolinitic regolith. In addition, the clay formation rates determined from mass balance have also been utilized to calculate the time needed to produce measured abundances of given clay minerals in regolith of the southern Appalachians.

BACKGROUND

Study Area

The study area incorporates three watersheds (Table 1) of the U.S. Forest Service Coweeta Hydrologic Laboratory located in the southeastern Blue Ridge Province of western North Carolina (Figs. 1 and 2). The southern Blue Ridge Province includes low- to high-grade metamorphic rocks that have been thrust northwestward over the unmetamorphosed sedimentary rocks of the Valley and Ridge Province (O'Hara et al., 1995; Mossa, 1998; Miller et al., 2000; Fig. 1). The eastern Blue Ridge is generally similar lithologically to the adjacent Inner Piedmont, and together these two belts comprise the Piedmont Terrane (Williams and Hatcher, 1982, 1983; Miller et al., 2000; Fig. 1).

The Coweeta Basin is quite rugged (average slope of ~45%/23°) and is underlain by the metasediments of the Coweeta Group (mid-Ordovician; Miller et al., 2000) and the Otto Formation (Upper Precambrian; Hatcher, 1980, 1988). The Coweeta Group may be subdivided into three lithostratigraphic units. The basal Persimmon Creek Gneiss is dominantly a massive quartz diorite orthogneiss (Hatcher, 1980). The overlying Coleman River Formation is characterized by metasandstone and quartz-feldspar gneiss. The Coleman River Formation is overlain by the Ridgepole Mountain Formation, which consists of coarse mica-garnet schists and quartzites (Hatcher, 1980). In contrast to the maturity of the Coweeta Group protolith sediments (e.g., arkoses and quartz arenites), the Otto Formation is derived from sedimentary protoliths of low compositional maturity (e.g., graywackes) and

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GSA Bulletin; May/June 2005; v. 117; no. 5/6; p. 783–794; doi: 10.1130/B25547.1; 2 figures; 7 tables; Data Repository item 2005083.

TABLE 1. WATERSHED DATA FOR USE IN THIS STUDY

Watershed	Bedrock	Area (ha)	Midslope elevation (m)	Land slope (%)	Mean annual precipitation (cm)	Mean annual runoff (cm)	Mean annual temperature (°C)	Aspect
2	Otto Formation	12.26	857	60	177.17	85.39	11.7	South-southeast
34	Otto Formation	32.70	1025	52	200.94	117.47	10.6	South-southeast
27	Coweeta Group (Persimmon Creek Gneiss, Coleman River Formation, Ridgepole Mountain Formation)	39.05	1257	55	245.08	173.74	9.1	North-northeast

Note: Data from Swank and Crossley (1988); Swift et al. (1988); Swank and Waide (1988).

is predominantly biotite paragneiss and biotite schist (Hatcher, 1980, 1988). Amphibolite facies regional metamorphism is associated with the Ordovician Taconic Orogeny when the Piedmont Terrane was probably accreted (or reattached) to Laurentia (Hatcher, 1988; Miller et al., 2000). Coweeta Group and Otto Formation rocks are juxtaposed as a result of thrusting of the pre-metamorphic Shope Fork Fault (Hatcher, 1988; Fig. 2). The eastern Blue Ridge Province has, however, been affected by all the major tectonic events that shaped the southern Appalachian orogen (Miller et al., 2000). There is evidence of Early Cretaceous through Holocene compressive intraplate tectonism in the southern Appalachians with greatest uplifts in the Blue Ridge Mountains (Prowell and Christopher, 1993, 2000).

Saprolite mantles the landscape at Coweeta, although bedrock crops out locally, especially near ridge crests. Saprolite is an isovolumetric residuum of chemical weathering in which the altered mineralogy, petrography, and structural fabric of the saprolite reflect the original crystalline rock types (Mills et al., 1987; Velbel, 1990). The average weathering profile (saprolite and soil) is ~6 m thick (Berry, personal commun., 1976; Yeakley et al., 1998). The saprolite is not an ancient, relict, deep weathering profile, as evidenced by its great thickness (up to 18 m; Berry, personal commun., 1976; Ciampone, 1995) despite residing on very steep slopes (Velbel, 1984a, 1985). The soil, mostly Ultisols and Inceptisols, comprises the uppermost 30 cm of the profile (Velbel, 1984a, 1985, 1988).

The Coweeta Basin experiences appreciable climate variability from west to east. Mean annual precipitation varies from 250 cm on the upper slopes along its western boundary to 170 cm at the lower elevations to the east (Swank and Douglass, 1977). Stream specific discharge from the areas of high precipitation is more than double that from areas of low precipitation (Grantham and Velbel, 1988). Precipitation is distributed fairly evenly throughout the year with only a minor amount falling as snow (Swank and Douglass, 1977; Swift et al., 1988). Overland flow on a well-forested watershed is essentially nonexistent (Swank and Douglass, 1977), as rain almost always soaks into the forest floor as fast as it falls (Helvey and Patric, 1988). Velbel (1984a, 1985) demonstrated that the

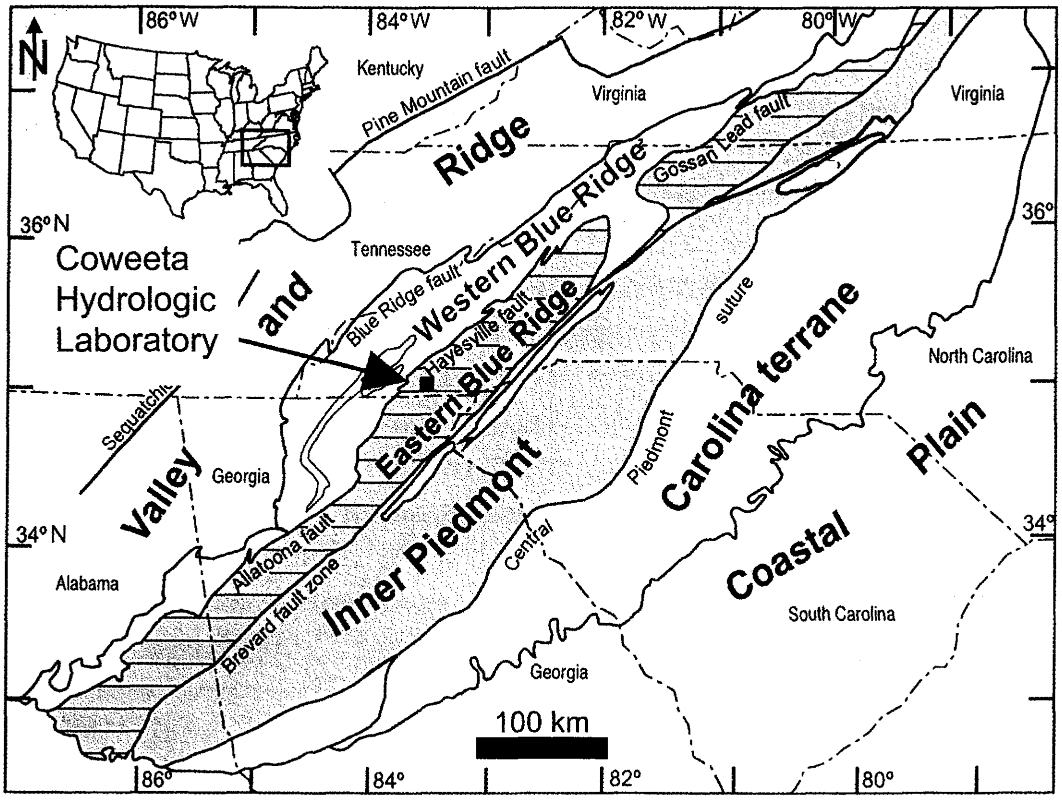

Figure 1. Generalized geologic map of the southern Appalachian orogen showing the Valley and Ridge Province, eastern Blue Ridge, Brevard Fault Zone, Inner Piedmont, and Coweeta Hydrologic Laboratory. The eastern Blue Ridge and Inner Piedmont together form the Piedmont Terrane (shaded) (Williams and Hatcher, 1982, 1983; Miller et al., 2000). Modified from Merschat and Kalbas (2002, their Fig. 1A).

streams at Coweeta are samples of subsurface water that have undergone no significant change after leaving the saprolite to enter the streams, except re-equilibration with atmospheric gases that affect pH. Coweeta has a temperate climate with a mean annual temperature of 12.6 °C (Swift et al., 1988). There is no evidence for alpine glaciation during the Pleistocene in or near Coweeta (Michalek, 1969; Velbel, 1984a; Mills et al., 1987).

An extensive groundwater aquifer has not been shown to exist at Coweeta (Hewlett, 1961). Instead, nearly all stream water passes through the soil and saprolite mantle, with continuous base flow to perennial streams resulting from water draining from pore space in the unsaturated zone (Hewlett, 1961; Hewlett and Hibbert, 1963; Velbel, 1984a, 1985, and references therein).

Geomorphic Considerations

Source areas for terrigenous clay sediment may be classified along a continuum between two end members (Stallard and Edmond, 1983; Johnsson, 1992): "Weathering-limited" source areas are characterized by steep slopes where transport processes are more rapid than the weathering processes generating the clay, whereas "transport-limited" landscapes have gentle slopes where the maximum weathering rate exceeds the ability of transport processes to remove sediment. Both end members pose concerns for paleoclimatologists trying to use clay mineral assemblages from clay-rich sediments to interpret source-area climate changes through geologic time. These concerns arise because clay detritus eroded from a transport-limited landscape may originate from paleosols and may not reflect the climatic conditions during erosion and transport of the clay to the depositional basin (Thiry, 2000; Migoń and Lidmar-Bergström, 2002). A transport-limited environment may require several million years to develop a deep mature profile, and under such circumstances only long-term (1 or 2 m.y.) paleoclimatic changes may be recorded in the clay mineral assemblages of marine sedimentary deposits (Thiry, 2000). Weathering-limited landscapes also present problems for paleoclimatic interpretations because the regolith may not be retained for adequate duration to permit equilibration of clay mineral assemblages with climate. The Coweeta landscape may be interpreted to be intermediate between weathering- and transport-limited landscapes; it has deep clay-rich saprolite as in transport-limited landscapes, but primary minerals remain in abundance sufficient to impart distinct bedrock character to the surface waters leaving the regolith (Velbel, 1992) as in weathering-limited landscapes.

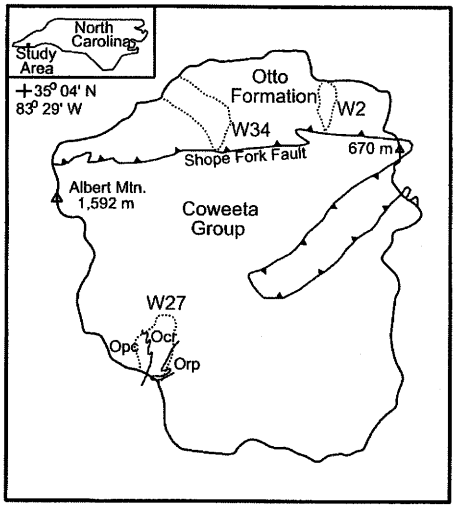

Figure 2. Map of Coweeta Hydrologic Laboratory showing watershed locations, bedrock geology. Bedrock units for W27: Opc—Persimmon Creek Gneiss; Ocr—Coleman River Formation; Orp—Ridgepole Mountain Formation.

Coweeta Hydrologic Laboratory provides a unique opportunity to evaluate the temporal resolution of clay mineral assemblages in paleoclimatic reconstructions, as the site is characterized by appreciable climatic variability, a thick (6 m) modern weathering profile (Berry, personal commun., 1976; Velbel, 1984a, 1985; Yeakley et al., 1998), and extensive hydrochemical data for use in mass balance determinations of clay formation rates (Velbel, 1985). The long-term average major element solute-flux data for Coweeta watersheds are based on weekly measurements and constitute one of the longest running catchment flux records in North America (the published period of record is 20 yr; Swank and Waide, 1988; Velbel, 1993a).

Clay Formation Rates

Barshad (1955, 1957) is likely the earliest researcher to provide an estimate of total clay formation rates in soils. Based on bulk chemical analyses of the whole soil and the amount of clay in the soil, Barshad (1957) found that total clay formation in soils was enhanced by poor drainage (influenced by topography), grass-type vegetation (as opposed to tree type), and finer grained and more basic bedrock. Barshad (1957) reported total clay formation rates ranging from 0.001 to 0.2 g kg^{-1} yr^{-1}. Using soil sequences ranging in age from less than 100 yr to ~5.5 k.y. in the Hudson Bay area, Canada, Protz et al. (1984, 1988; data summarized by Righi and Meunier, 1995) found that the clay mineralogy of C horizons in all soils was nearly identical but changed with time in the A horizons. Chlorite and mica contents decrease with increasing age, and vermiculite content increases, becoming (after 4.5 k.y.) the dominant clay mineral present, along with a small amount of smectite (Protz et al., 1984). Their XRD data for the Hudson Bay coastal area suggest a formation rate of vermiculite in the clay size fraction of soil of ~0.06 g kg^{-1} yr^{-1}. In a similar study of a soil chronosequence (developed on nearly identical parent material as the Hudson Bay study) from the southern James Bay area, Canada, Protz et al. (1988) found that vermiculite formed at a rate twice as fast as that of the cooler and drier Hudson Bay area. They also found that both chlorite and mica weathered rapidly to vermiculite and ultimately to smectite.

Lowe (1986) presents an excellent literature review and results on weathered New Zealand tephras and summarizes the factors that control rates of clay genesis during weathering of airfall tephras. He found that temperature and duration of weathering were subordinate factors to mineralogical and chemical composition of the parent rock and macro- and microenvironmental factors in governing clay genesis and weathering rates. Environmental factors that are most important are those that affect the concentration of SiO_2 in solution and the movement and availability of Al; specifically, pH and drainage (a function of precipitation/climate). Total clay formation rates for the tephras of New Zealand when calculated using percent clay and age of weathering profile range from ~0.001–0.1 g kg^{-1} yr^{-1}.

Recently, Schroeder et al. (2001) have determined time scales for gibbsite formation in a predominantly kaolinitic saprolitic Piedmont regolith at Panola Mountain, Georgia, by radiocarbon dating of carbon incorporated into gibbsite. Gibbsite from soil C-horizon samples gave model ages of ca. 8 ka; gibbsite from deeper (unsampled) portions of the regolith was inferred to be very young on the assumption that most active secondary-mineral formation takes place at the weathering front; and gibbsite from soil A- and B-horizons gave model ages of ca. 2–4 ka. Recrystallization of gibbsite during regolith evolution accounts for up-profile younging of gibbsite between the various soil horizons (Schroeder et al., 2001).

METHODS

Field Work

Watersheds sampled at Coweeta for this study were W2, W34, and W27 (Fig. 2, Table 1). Only the control watersheds (undisturbed since 1927) were sampled in order to minimize the influence of biomass state on the stream mineral nutrient budgets, although the biomass component of the mass balance has been included in calculations. All watersheds used in this study are covered with mixed mature hardwoods characterized in greater detail by Swank and Douglass (1977) and Swank and Crossley (1988).

Stream waters were sampled for REE analyses at the weir and filtered in the field using 0.45 µm pore-size Millipore™ filters. The filtered stream water was collected in acid-cleaned polypropylene (Nalgene) bottles. The ~60 ml of filtered stream water was acidified with 200 µl of HNO_3. The field sampling kits were provided by the aqueous geochemistry research group at Michigan State University. The ultra clean sampling protocols used to sample the Coweeta streams were established by this same group and follow methods outlined by Nriagu et al. (1993, 1996), Benoit (1994), Benoit et al. (1997), Horowitz et al. (1994, 1996), and Hurley et al. (1996).

Petrography

Thin sections of bedrock, soil, and saprolite were prepared by standard methods. Additional bedrock samples were obtained by Berry (personal commun., 1976) during a regolith coring investigation at Coweeta. All samples collected as part of this study were prepared commercially by Petrographic International (Choiceland, Saskatchewan, Canada). Due to the friable nature of the saprolite and soil, clear epoxy was used to vacuum impregnate the samples collected in chrome tubes. Grain mounts were also prepared for soil samples collected by the Coweeta staff.

X-ray Diffraction

X-ray diffraction (XRD) was used to characterize the clay minerals present in the Coweeta regolith. Separation of the clay size fraction (<0.2 µm) from regolith samples collected at all levels in the weathering profile (including bedrock) was performed by gravity settling, with the clay-size fraction being separated with a pipette, and the aliquots being filtered onto a 0.45 µm Millipore™ filter following rapid-suction mounting techniques (production of oriented mounts, also termed the Millipore™ Filter Transfer Method of Drever [1973] and described by Moore and Reynolds [1997]). Four oriented XRD mounts of each sample were prepared at room temperature; air dried (naturally occurring exchange ions), potassium saturated, magnesium saturated, and magnesium saturated/ethylene glycolated. After the initial XRD analyses the potassium-saturated samples were heated to 575 °C and rescanned. The Rigaku Geigerflex XRD (Department of Geological Sciences at Michigan State University) uses CuKα radiation and is equipped with a nickel foil filter. XRD analyses were conducted using divergence, receiving, and anti-scatter slits of 1/2°, 0.3 mm, and 2°, respectively, a step size of 0.02° 2θ, and count times of 20 seconds. Identification of diffractogram peaks followed Brown and Brindley (1984), Wilson (1987), Eslinger and Pevear (1988), and Moore and Reynolds (1997).

Scanning Electron Microscopy (SEM): Secondary and Backscattered Electron Imaging (BSE)

Polished thin sections and stubs of Coweeta bedrock and regolith were either carbon- or gold-coated for examination by SEM and analyzed by energy dispersive X-ray spectroscopy (EDS) for element composition. Imaging and analyses were performed at Michigan State University's Center for Advanced Microscopy (CAM) using a JEOL® JSM-35CF SEM with EDS and BSE capabilities.

Electron Microprobe Phase Analyses (EMPA)

Electron microprobe analyses of Coweeta bedrock and regolith minerals in thin section were completed at the University of Michigan's Electron Microbeam Analysis Laboratory (EMAL) using a wavelength dispersive Cameca SX 100 electron microprobe analyzer. Accelerating voltage and beam current were 15 keV and 10 nA, respectively, and a beam diameter of 2 µm was used. Calibration standards for Na, Si, Al, Mg, Fe, Mn, Ti, Ca, and K were respectively albite (natural Tiburon), tanzanite (natural), andalusite (natural), enstatite (synthetic), ferrosilite (synthetic), rhodonite (natural Broken Hill), geikielite (natural), tanzanite (natural), and adularia (natural St. Gothard).

Allanite and epidote formulae calculated from the EMPA data are stoichiometric and not structural. Structural formulae of allanite can only be calculated for nonmetamict samples (Ercit, 2002), and structural formulae for any mineral can only be calculated when the EMPA data contain both ferrous and ferric iron. By analogy with allanite and epidote compositions reported by Deer et al. (1986), the calculated formulae for Coweeta allanite likely contain ferrous and ferric iron in approximately equal stoichiometries, and the Coweeta epidote has been assigned all ferric iron (Price et al., 2005). The structural formula of vermiculite was calculated using a method that assumes that the aluminosilicate layers have not been modified during the transformation of biotite to vermiculite (Velbel, 1984a, 1985; Newman, 1987).

Rare Earth Element Analyses by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Rare earth element analyses of both stream waters and mineral phases in thin section were performed on a Micromass Platform Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at Michigan State University. The REE included in this study are lanthanum (La), cerium (Ce), neodymium (Nd), gadolinium (Gd), dysprosium (Dy), and ytterbium (Yb). These six REE were selected based on their relatively high abundance (above background) in a preliminary scan of Coweeta stream waters. All six of these have been included in the mineral structural/stoichiometric formulae; however, only stream flux data for La, Nd, and Dy have been utilized in the mass balance calculations. Stream solutions were analyzed by the ICP-MS using a concentric nebulizer, and indium (In) was used as an internal standard. The concentrations (in $\mu g\ ml^{-1}$) were calculated using regression lines with standard solutions.

Laser ablation ICP-MS (LA-ICP-MS) analyses were performed using a Cetac LSX 200^+ laser ablation system on sample thin sections. LA-ICP-MS provides high resolution sampling capabilities and multielement high sensitivity (Fryer et al., 1995; Neal et al., 1995). For all minerals analyzed (biotite, vermiculite, plagioclase, garnet, epidote, and allanite), the beam size was 25 µm (using a UV, 266 nm beam), and the pulse rate was 20 Hz, with the exception of the phyllosilicates for which a pulse rate of 10 Hz was used. A reduced pulse rate for the phyllosilicates was necessary as the structural water and perfect basal cleavage resulted in a mineral that was susceptible to extensive damage at higher pulse rates. LA-ICP-MS and EMPA analyses spots were adjacent to one another, and Ca was used as the internal standard for all laser ablation analyses (Fryer et al., 1995; Longerich et al., 1996). NIST 612 glass was used as a calibration standard and results were obtained in $\mu g\ g^{-1}$ following methods outlined by Norman et al. (1996).

Watershed Mass Balance Methods

Watershed geochemical mass balance methods are considered the most accurate means of quantifying weathering reactions in nature and elemental transfers at the Earth's surface (Clayton, 1979). Mass balance methods follow those of Plummer and Back (1980), Velbel (1985, 1986a; Taylor and Velbel, 1991), and Drever (1997a), with rates of clay mineral genesis determined following methods outlined by Cleaves et al. (1970), Finley and Drever (1997), and recently by Bowser and Jones (2002, and references therein). For mass balance modeling of watersheds, input fluxes include precipitation, biomass if degrading, and mineral weathering reactions, while output fluxes include evapotranspiration, biomass if aggrading, clay genesis, and stream discharge. Analytical techniques outlined above have permitted determination of clay composition and provide the stoichiometries of clay genesis. These data have been combined with published hydrological and hydrogeochemical data (i.e., Swift et al., 1988; Swank and Waide, 1988). Nutrient data for Coweeta biomass is from Day and Monk (1977) and Boring et al. (1981). Chloride is approximately in balance in all watersheds (Swank and Douglass, 1977), and hence groundwater storage or leakage is not of concern.

Following matrix algebraic methods, to perform solute-based mass balance calculations the number of unknowns (i.e., the weathering rates or mass transfer coefficients) must equal the number of solute mass balance equations (i.e., the number of elements for which stream solute fluxes are available). Therefore, the mass balance calculations were represented as a grand matrix of simultaneous equations (Velbel, 1986a). Each column in the matrix represents the stoichiometry of a mineral involved in weathering, and each row represents an element for which net solute efflux data (output minus input) has been obtained. The grand matrix multiplied by the mineral weathering/formation rates (the unknowns in a column vector) is then equal to the column vector containing the net solute flux data. For any element included in the solute flux, every phase undergoing weathering that contains that element must be included in the mass balance matrix. In order to obtain equal numbers of unknowns and equations, REE have been included in the calculations of this study (specifically La, Nd, and Dy). The algebraic calculations of this study were performed using MATLAB® software. This investigation is the first time that trace elements have been included in mass balance methods. The REE are an ideal choice to include in the mass balance model, as allanite is an important weathering phase at Coweeta (Price et al., 2005) and is also a substantial REE host (Meintzer, 1981; Braun and Pagel, 1994; Braun et al., 1993, 1998; Harlavan and Erel, 2002; Ercit, 2002). Further details on the mass balance methods are beyond the scope of this paper.

RESULTS

Mineral Compositions

The primary minerals weathering at Coweeta are plagioclase, biotite, garnet, and allanite. Secondary minerals present at Coweeta are vermiculite, kaolinite, and gibbsite. Primary-mineral alteration textures and reactant-product textural relations observed by optical petrography and SEM are similar to those previously reported for plagioclase (Velbel, 1983, 1986b), biotite (Velbel, 1984a, 1985), and garnet (Velbel, 1984b, 1993b) from Coweeta; new results for allanite are reported elsewhere (Price et al., 2005). Major and rare earth element analyses for all minerals used in mass balance calculations of this study are provided in Tables DR1 and DR2[1], with structural and stoichiometric formulae provided in Table DR3. For kaolinite and gibbsite, standard formulae are reported, as these minerals have negligible substitution and do not appreciably host structural REE (e.g., Nesbitt, 1979; Duddy, 1980; Burt, 1989; Braun et al., 1993; Finley and Drever, 1997). The mineral compositions of the Coleman River Formation were chosen for the mass balance because it is the dominant lithostratigraphic unit in W27, especially at the warmer lower elevations where weathering is most intense in the watershed (Fig. 2). The matrices of stoichiometric coefficients are provided in Tables DR4 and DR5. Table DR6 contains the major and rare element analyses and fluxes of stream waters from W2, W34, and W27.

Watershed Mass Balance and Rare Earth Elements

Rare earth elements are included because they are relatively mobile during weathering as they are not contained in secondary minerals (with the exception of vermiculite discussed below) that remain stable during progressive weathering (e.g., Nesbitt, 1979; Cramer and Nesbitt, 1983; Banfield and Eggleton, 1989; Braun et al., 1990, 1993, 1998 and references therein; Marker and De Oliveira, 1990; Braun and Pagel, 1994; van der Weijden and van der Weijden, 1995; Koppi et al., 1996; Nesbitt and Markovics, 1997). The only exception is Ce^{3+}, which oxidizes to Ce^{4+} in the weathering environment and precipitates as cerianite (CeO_2).

Atmospheric Inputs of Rare Earth Elements

At Coweeta, atmospheric major element inputs have been measured and subtracted from the stream solute flux data, yielding a net stream flux value that reflects only the mineralogic contributions of major elements to surface water (Swank and Waide, 1988, their table 4.11). However, REE concentrations in precipitation at Coweeta or anywhere in the southern Appalachians have never been measured. Nevertheless, the atmospheric contribution of REE to Coweeta stream waters is believed to be negligible. In thick (greater than several meters), unpolluted weathering profiles, the dissolved REE distribution in stream waters will be controlled by bedrock weathering, and atmospheric REE contributions will not be detectable (Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Braun et al., 1998; Tricca et al., 1999; Probst et al., 2000; Aubert et al., 2001, 2002). Because Coweeta contains a thick regolith (on average 6 m, but up to 18 m; Berry, personal commun., 1976; Ciampone, 1995; Yeakley et al., 1998), the REE input to natural soil and surface waters from mineral weathering should overwhelm atmospheric inputs.

Mineralogic Sources and Sinks of Rare Earth Elements

Allanite is the only accessory mineral at Coweeta that contains REE, is weathering, and is present in significant quantities in unweathered bedrock (Price et al., 2005). The abundance and ubiquity of allanite have been observed petrographically. The case for high weatherability of allanite is widespread in the literature, as it may be completely dissolved below the weathering front (e.g., Goldich, 1938; Meintzer, 1981; Banfield and Eggleton, 1989; Braun et al., 1993; Braun and Pagel, 1994; Harlavan and Erel, 2002; Price et al., 2005). Apatite is routinely invoked as being the source of REE found in interstitial regolith waters, groundwaters, and surface waters (e.g., Banfield and Eggleton, 1989; Marker and De Oliveira, 1990; Braun and Pagel, 1994; van der Weijden and van der Weijden, 1995; Braun et al., 1993, 1998; Tricca et al., 1999; Aubert et al., 2001, 2002; Harlavan and Erel, 2002). At Coweeta, however, apatite is so scarce that none was encountered during the point counting of bedrock thin sections.

In Coweeta soil, vermiculite is the only secondary mineral containing appreciable amounts of REE. The REE concentration in vermiculite has been quantified by ICP-MS and is included in the mass balance calculations (Tables DR4 and DR5). Exclusion of the REE abundances in vermiculite yields geochemically unreasonable mass balance results. Previous studies have demonstrated that kaolinite (Nesbitt, 1979; Duddy, 1980; Braun et al., 1993), gibbsite, and goethite (Braun et al., 1993) do not host appreciable abundances of structural REE, but probably participate in cation exchange in relatively small ways (e.g., Coppin et al., 2002).

Aluminum and Rare Earth Element Stream Fluxes

Like major elements, REEs show seasonal and temporal variations in stream waters (Ingri

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[1] GSA Data Repository item 2005083, Tables DR1–6, is available on the Web at http://www.geosociety.org/pubs/ft2005.htm. Requests may also be sent to editing@geosociety.org.

et al., 2000). In order to average out this variability, a minimum seven year period of record of weekly stream water sampling and analysis is needed (Likens and Bormann, 1995). The Coweeta major element long-term average solute-flux data used in this study is based on a 20 yr period of record (Swank and Waide, 1988; Velbel, 1993a). However, the Al and REE stream water chemistry used is a one-time sample, collected on May 22, 2002. In order to calculate an approximate long-term average Al and REE solute-flux from the single sample episode, SiO_2 was included with the Al and REE analyses. The ratio of the long-term SiO_2 flux (Swank and Waide, 1988) to the one-time May 2002 SiO_2 flux was then used to convert the one-time Al and REE stream solute concentrations to approximate long-term averages (Table DR6). Silica was used because it is negligibly influenced by biomass, and, despite relatively small abundances being incorporated into kaolinite, it represents the element with the greatest loss from the weathering profile (e.g., Bowser and Jones, 2002).

Primary Mineral Weathering Rates and Secondary Mineral Formation Rates

The results of the mass balance calculations are presented in Table 2. Watersheds 2 and 34 differ only by climate and are nearly identical with respect to bedrock, aspect, vegetation, weathering history, and being undisturbed control watersheds (Velbel, 1993a). Watershed 27 is significantly cooler, with higher precipitation (Table 1) than either W2 or W34. For purposes of comparison, mass balance calculations using REE have also been performed on W27; a watershed underlain by three lithostratigraphic units (Fig. 2), all of which are less reactive than the rocks of the Otto Formation (Velbel, 1984a).

Nine solutes (Table DR6) are available for mass balance calculations, although the watersheds only have eight unknowns; i.e., the seven mineral weathering/dissolution/formation rates plus the botanical uptake/degradation rate. The solutes used in the mass balance calculations are the six major elements, as well as Dy and La for W2 and W34 (Table DR4) and La and Nd for W27 (Table DR5). Lanthanum was chosen for all watersheds because it has the highest concentrations in stream waters. Dysprosium was included in W2 and W34 calculations because it occurs in both allanite and garnet. By leaving all element stoichiometries positive in Tables DR4 and DR5 and using positive stream flux values, the calculated rates of minerals being destroyed will be positive, and rates of minerals forming will be negative (Table 2). If no REE content for garnet was included in the W2 and W34 mass balance calculations, geochemically unreasonable results were obtained (e.g., a negative garnet weathering rate). Geochemically unreasonable results were also obtained if Dy was included in the W27 calculations. Again, a negative garnet weathering rate was obtained.

The significant figures of the rates in Table 2 are important. The REE stream flux data have been limited to one significant figure because the ICP-MS calibration lines were dominated by standards with concentrations higher than that of the solutes. The only mineral that has a rate calculated exclusively from REE solute fluxes is allanite, and appropriately the allanite weathering rate is reported to one significant figure. Garnet too has a weathering rate influenced by Dy, and appropriately the garnet rate will be reported to one significant figure. All of the other minerals, however, have weathering or formation rates calculated from major element fluxes; the biotite and vermiculite rates are calculated from K, plagioclase is calculated from Na, and kaolinite and gibbsite are calculated from Si and Al. Therefore, three (or two for rates in tens of mol ha^{-1} yr^{-1}) significant figures are reported for the weathering/formation rates of these minerals.

The differences in mineral weathering/formation rates between W2 and W34 reflect the difference in climate as these two watersheds are identical in bedrock and aspect. Watershed 2 receives relatively less rainfall and experiences warmer temperatures than does W34 (Table 1). The mineral weathering/formation rates of W27, however, reflect less chemically reactive bedrock and a wetter and cooler climate relative to the bedrock and climatic conditions of either W2 or W34 (Table 1).

DISCUSSION

Response Times for Watersheds at Coweeta Hydrologic Laboratory

The ultimate goal of obtaining the clay mineral kinetic data above is to permit calculation of clay mineral response times. That is, at the current clay formation rates for a given watershed, how much time is required to achieve a 5% (or 50 g kg^{-1}) relative change in regolith clay mineral abundance. The choice of 5% reflects the minimum changes in relative clay abundance that can be detected by changes in XRD peak intensities (e.g., Brown and Brindley, 1984; Moore and Reynolds, 1997).

TABLE 2. RESULTS OF THE MASS BALANCE CALCULATIONS

Phase	Weathering/Formation Rate (mol ha^{-1} yr^{-1})		
	Watershed 2	Watershed 34	Watershed 27
Allanite	30	7	10
Plagioclase	485	435	243
Garnet	40	40	100
Biotite	433	142	112
Vermiculite	–308	–38	–69
Kaolinite	–304	–150	–4
Gibbsite	–288	–513	–546

Note: A positive rate indicates weathering of a mineral; a higher rate indicates more rapid destruction. A negative rate indicates formation of a mineral; the more negative the rate the faster the formation.

TABLE 3. TIME REQUIRED FOR A 5% (50 G KG^{-1}) CHANGE IN REGOLITH CLAY ABUNDANCE

Watershed	Kaolinite (years)	Gibbsite (years)	Vermiculite (years)
2	81,000	280,000	47,000
34	160,000	160,000	380,000
27		150,000	210,000

Note: Response times based on calculated rates in Coweeta watersheds.

The time required to achieve a change of 50 g kg^{-1} in clay abundance in the Coweeta watersheds investigated is reported in Table 3 and is based on the rates calculated using mass balance methods. Table 3 shows that it would take 81,000 yr to increase the kaolinite abundance in W2 by 5% at the current kaolinite formation rates. The same increase in W34 would take longer (160,000 yr). The same relationship exists for vermiculite in W2 and W34, but a gibbsite increase of 50 g kg^{-1} is more rapid in W34 (160,000 yr) than W2 (280,000 yr). The relatively low kaolinite formation rate of W27 (Table 2) has not been used to calculate clay response times. Although the kaolinite formation rate for W27 is believed to be a robust value, it is not believed to be typical of most southern Appalachian weathering profiles. The W27 gibbsite and vermiculite response times are comparable to those of W34. The response times (Table 3) are clearly too long to permit Coweeta clay mineral assemblages to reequilibrate with climate during the Holocene (since 12.5 ka for the southeastern United States; Delcourt and Delcourt, 1985).

Clay Formation Rates in the Southern Appalachians

In order to calculate the time needed to form measured regolith clay abundances, additional weathering profile information is needed. Conversion of fluxed-based watershed clay genesis/dissolution rates in mol ha^{-1} yr^{-1} to g kg^{-1} yr^{-1} is easily accomplished, with the rate in g kg^{-1} yr^{-1} then being used to calculate the time needed to produce the measured clay abundance. However, clay abundances in the literature are

TABLE 4. DATA FOR THE CALCULATED REPRESENTATIVE COWEETA REGOLITH

Horizon	W2 Horizon thickness (cm)†‡	Bulk density (g cm^{-3})†	Calculated weighted profile bulk density (g cm^{-3})
A	11	1.30	
B	46	1.54	2.11
C	543	2.17	

†Berry (1976, personal commun.).
‡Yeakley et al. (1998).

routinely reported by soil horizon, with each horizon having different physical properties (i.e., bulk density) and constituting different fractions of the overall regolith. Because the clay genesis/dissolution rate from mass balance calculations reflects the mineral-water interactions for the entire profile, an average clay abundance is needed that is weighted to reflect the bulk density and clay mineralogic differences of each horizon. Furthermore, the weighted average regolith should also be representative of the entire landscape, as the weathering profiles of ridges, slopes, and drainages typically vary significantly in both overall thickness and the relative thicknesses of the individual soil horizons.

Yeakley et al. (1998) measured soil horizon thicknesses along an 85 m transect perpendicular to the stream of W2, which began at the streambank and ended on the watershed divide (ridge). In total, soil horizon thicknesses were measured at 14 stations along the transect (Yeakley et al., 1998). These soil horizon thicknesses were then combined with additional measurements that included bulk density, performed by Berry (personal commun., 1976). These data permitted calculation of a representative weathering profile that accounted for variations in soil horizon thickness, soil horizon bulk density, and regolith thickness, all of which may be influenced by geomorphic position (Table 4). The calculated representative weathering profile (Table 4) is very comparable to Coweeta regolith data reported by Berry (personal commun., 1976) and Knoepp and Swank (1994).

With clay formation rates calculated (Table 2) and a representative weathering profile developed (Table 4), the time required to form measured clay abundances (herein termed production times) in Piedmont Terrane (the eastern Blue Ridge and Inner Piedmont together form the Piedmont Terrane; Fig. 1) regolith may be determined. In other words, clay formation rates and average regolith physical characteristics, both for Coweeta, will be applied to measured clay abundances in weathering profiles found elsewhere and reported in the literature (Table 5). The application of Coweeta-derived clay formation rates will be limited to physically comparable regolith. Therefore, only clay abundances from Piedmont Terrane regolith have been included. Many of the studies reported in Table 5 provide clay abundances for the entire regolith; however others only provide clay abundances for the silt- and clay-size fractions. Both types of studies will be included in the calculations herein, with the assumption that quantities of clay in the sand-sized fraction of the weathering profiles are negligible relative to the quantities in the silt- and clay-size fractions. For southern Appalachian regoliths developed on crystalline rock, the times needed to generate the abundances of clay reported in Table 5 are contained in Table 6.

The application of mineral weathering/formation rates for calculating regional clay production times assumes that the Coweeta rates are representative of the Piedmont Terrane. Plagioclase dissolution is the most important weathering reaction in silicate-dominated natural hydrologic systems (Bowser and Jones, 1993, 2002; Drever 1997b; Jacobson et al., 2003), especially with respect to Si and Al, which constitute the neoformed clays. Plagioclase dissolution rates are also constrained by Na flux, which is minimally influenced by biomass (Taylor and Velbel, 1991; Velbel, 1993a,

TABLE 5. CLAY ABUNDANCES IN PIEDMONT TERRANE (FIG. 1) REGOLITH AS REPORTED IN THE LITERATURE

Reference			Stolt and Baker (2000)	Norfleet et al. (1993)	Norfleet et al. (1993)	Norfleet et al. (1993)	Coleman et al. (1949)	Coleman et al. (1949)	Stolt and Baker (2000)	Coleman et al. (1949)	Calvert et al. (1980)
Physiographic Province			Blue Ridge	Blue Ridge	Blue Ridge	Blue Ridge	Blue Ridge	Blue Ridge	Piedmont	Piedmont	Piedmont
State			Virginia	NW South Carolina	NW South Carolina	NW South Carolina	North Carolina	North Carolina	Virginia	North Carolina	North Carolina
Sample Name			Pilot	ED-1	ED-2	ED-3	Rabun Soil	Fannin Soil	Lovingston	Cecil Soil	–
Bedrock			Granites, gneisses, and schists	Mica-rich gneisses or schists	Mica-rich gneisses or schists	Mica-rich gneisses or schists	Basic crystalline rock	Mica schist	Granites, gneisses, and schists	Granite and granite gneiss	Granite gneiss
A Horizon	Vermiculite (%)	Silt	55	5	3	5	1	2	44	0	
		Clay					2	2		2	
	Kaolinite (%)	Silt	20	2	7	3	2	0	28	0	14
		Clay					15	3		11	
	Gibbsite (%)	Silt	0	6	1	5	1	2	4	0	
		Clay					12	6		3	
B Horizon	Vermiculite (%)	Silt	36	12	15	15	0	0	22	0	
		Clay					5	3		2	
	Kaolinite (%)	Silt	42	1	37	13	1	0	54	1	37
		Clay					38	13		34	
	Gibbsite (%)	Silt	1	12	8	14	2	1	2	1	
		Clay					31	16		14	
C Horizon	Vermiculite (%)	Silt	6	3	3	2	0	0	10	0	
		Clay					4	3		0	
	Kaolinite (%)	Silt	32	1	11	4	2	0	55	9	25
		Clay					64	8		39	
	Gibbsite (%)	Silt	2	11	3	4	1	1	0	3	
		Clay					41	21		14	

1995). Therefore, plagioclase dissolution rates may be used to assess the regional representativeness of Coweeta clay formation rates. Table 7 contains plagioclase dissolution rates calculated as part of this study, as well as from other central and southern Appalachian watersheds as reported in the literature. From Table 7 it is evident that the Coweeta plagioclase dissolution rates fall near the mean of southern and central Appalachian plagioclase dissolution rates. This observation supports the regional representativeness of the Coweeta mass balance calculations and their use in calculating clay production times for the Piedmont Terrane.

The clay production times reported in Table 6 are based on a representative weathering profile and reflect clay formation rates calculated for present-day conditions at Coweeta. The production times of clay mineral assemblages range from 2 k.y. to 2 m.y. with mean values ranging from 50 k.y. to 1 m.y. Based on the present-day weathering rates of primary minerals, Velbel (1984a, 1985) reports a Coweeta saprolite residence time of ~100 k.y. This residence time falls within the range of mean clay production times for regolith of the Piedmont Terrane.

Schroeder et al. (2001) determined time scales for gibbsite formation in a predominantly kaolinitic saprolitic Appalachian Piedmont regolith at Panola Mountain, Georgia, by radiocarbon dating of carbon incorporated into gibbsite. Kaolinite, the dominant clay mineral, cannot be dated by the same methods (Schroeder and Melear, 1999). Gibbsite model ages among different horizons in this Piedmont soil range from 2 to 8 ka (Schroeder et al., 2001). Cosmogenic nuclide systematics of quartz in the Panola Mountain soil suggest a residence time of ca. 90 to125 ka for the upper 2 m of this Piedmont ridgecrest regolith (Schroeder et al., 2001). This regolith residence time compares well with the regolith residence time (ca. 140–160 ka) estimated for Coweeta saprolite from solute mass balance by Velbel (1985). Time scales for overall development of saprolitic regolith appear broadly similar (order of 100 ka) at both Coweeta and Panola Mountain despite methodological differences in determining the time scales. Coweeta (e.g., Table 2) and Panola Mountain (Schroeder et al., 2001) results are also similar in that both imply rapid formation of gibbsite during the Holocene. The overall gibbsite inventory appears to have formed on shorter time scales at Panola Mountain than at Coweeta (Table 3), other Blue Ridge regoliths (Table 6), or most other Appalachian Piedmont regoliths

TABLE 6. TIME NECESSARY TO FORM THE REPORTED CLAY ABUNDANCE IN A GIVEN PIEDMONT TERRANE (FIG. 1) REGOLITH USING THE CLAY FORMATION RATES CALCULATED FROM THIS STUDY AND ASSUMING A PHYSICALLY COMPARABLE WEATHERING PROFILE TO THAT OF COWEETA

	Reference	Stolt and Baker (2000)	Norfleet et al. (1993)	Norfleet et al. (1993)	Norfleet et al. (1993)	Coleman et al. (1949)	Coleman et al. (1949)	Stolt and Baker (2000)	Coleman et al. (1949)	Calvert et al. (1980)			
	Physiographic Province	Blue Ridge	Blue Ridge	Blue Ridge	Blue Ridge	Blue Ridge	Blue Ridge	Piedmont	Piedmont	Piedmont			
	State	Virginia	NW South Carolina	NW South Carolina	NW South Carolina	North Carolina	North Carolina	Virginia	North Carolina	North Carolina			
	Sample Name	Pilot	ED-1	ED-2	ED-3	Rabun Soil	Fannin Soil	Lovingston	Cecil Soil	—			
	Bedrock	Granites, gneisses, and schists	Gneisses and schists	Mica-rich gneisses or schists	Mica-rich gneisses or schists	Basic crystalline rock	Mica schist	Granites, gneisses, and schists	Granite and gneiss	Granite gneiss	Minimum	Maximum	Mean
Watershed 2 Rates	Kaolinite	500 k.y.	20 k.y.	200 k.y.	80 k.y.	1 m.y.	100 k.y.	900 k.y.	700 k.y.	400 k.y.	20 k.y.	1 m.y.	400 k.y.
	Gibbsite	100 k.y.	600 k.y.	200 k.y.	300 k.y.	2 m.y.	1 m.y.	10 k.y.	900 k.y.		10 k.y.	2 m.y.	600 k.y.
	Vermiculite	90 k.y.	40 k.y.	40 k.y.	30 k.y.	40 k.y.	30 k.y.	100 k.y.	2 k.y.		2 k.y.	100 k.y.	50 k.y.
Watershed 34 Rates	Kaolinite	1 m.y.	30 k.y.	400 k.y.	200 k.y.	2 m.y.	300 k.y.	2 m.y.	2 m.y.	800 k.y.	30 k.y.	2 m.y.	1 m.y.
	Gibbsite	60 k.y.	300 k.y.	100 k.y.	200 k.y.	1 m.y.	700 k.y.	7 k.y.	500 k.y.		7 k.y.	1 m.y.	400 k.y.
	Vermiculite	700 k.y.	300 k.y.	300 k.y.	200 k.y.	300 k.y.	200 k.y.	900 k.y.	10 k.y.		10 k.y.	900 k.y.	400 k.y.
Watershed 27 Rates	Gibbsite	60 k.y.	300 k.y.	100 k.y.	100 k.y.	1 m.y.	600 k.y.	7 k.y.	500 k.y.		7 k.y.	1 m.y.	300 k.y.
	Vermiculite	400 k.y.	200 k.y.	200 k.y.	100 k.y.	200 k.y.	100 k.y.	500 k.y.	8 k.y.		8 k.y.	500 k.y.	200 k.y.

Note: Clay abundances are reported in Table 5.

TABLE 7. COMPARISON OF COWEETA PLAGIOCLASE DISSOLUTION RATES WITH SOUTHERN AND CENTRAL APPALACHIAN PLAGIOCLASE DISSOLUTION RATES REPORTED IN THE LITERATURE

Reference	Location	Physiographic Province	Bedrock	Reported composition	Rate (mol ha^{-1} yr^{-1})
O'Brien et al. (1997)	South Fork Brokenback Run, Virginia	Blue Ridge	Old Rag Granite	An_{22}	666
O'Brien et al. (1997)	Hauver Branch, Maryland	Blue Ridge	Catoctin Formation Metabasalt	An_{53}	514
O'Brien et al. (1997)	Fishing Creek Tributary, Maryland	Blue Ridge	Catoctin Formation Metabasalt	An_{0}	299
Furman et al. (1998)	Shaver Hollow, Virginia	Blue Ridge	Pedlar Granodiorite with Catoctin Basalt Dikes	An_{30}	639
Furman et al. (1998)	White Oak Run, Virginia	Blue Ridge	Chilhowee Metasedimentary Sequence	An_{30}	157
Furman et al. (1998)	Deep Run, Virginia	Blue Ridge	Chilhowee Metasedimentary Sequence	An_{30}	128
White et al. (2002)	Panola Mountain, Georgia	Piedmont	Panola Granite	An_{23}	341
Cleaves et al. (1970)	Pond Branch, Maryland	Piedmont	Lower Schist Member of the Wissahickon Formation	An_{22}	146
O'Brien et al. (1997)	Mill Run, Virginia	Valley and Ridge	Massanutten Sandstone	An_{5}	158
O'Brien et al. (1997)	Shelter Run, Virginia	Valley and Ridge	Massanutten Sandstone	An_{5}	243
This study	W2	Blue Ridge	Otto Formation	An_{28}	485
	W34		Otto Formation	An_{28}	435
	W27		Coweeta Group	An_{30}	243
Mean					343
Minimum					128
Maximum					666

Note: The Coweeta rates are near the mean for southern and central Appalachian plagioclase dissolution rates.

(Table 6). However, Holocene time scales for gibbsite formation (similar to those of Schroeder et al., 2001) are inferred from our mass balance approach for the Lovingston soil on Virginia Piedmont granites, schists, and gneisses (Stolt and Baker, 2000). Additional work on dating, mass balance, and landscape evolution at a number of sites would provide a stronger basis for further comparisons.

The influence of periglacial climates on the chemical weathering of Appalachian crystalline bedrock has been discussed by Cleaves (1993). Using an isovolumetric weathering model, he argues that reduced soil CO_2 and decreased groundwater moving past the weathering front during periglacial times would result in an average rate of saprolitization over the last million years being as little as 24% of that of the present. If Cleaves (1993) is correct, then estimates for the mean age or residence time of the saprolite at Coweeta, clay-mineral response times clay mineral at Coweeta, and clay-mineral production times for saprolitic regolith in the Piedmont Terrane (all estimated here using short-term Coweeta weathering and clay-genesis rates) are all as much as a factor of four longer than the values presented here.

Since the Middle Pleistocene, episodes of cold climates have been interspersed with interglacial paleoclimates that were warmer than the present (Emiliani, 1972; Bowen, 1979; Clark, 1993; Winograd et al., 1997; Bradley, 1999). Post-Middle Pliocene glacial-interglacial oscillations occurred on time scales of ~100 k.y. (Winograd et al., 1997, and references therein). Based on the clay production times (Table 6), the present-day mineral abundances in any Coweeta weathering profile reflect the "average" climate that has occurred over the last ~500 k.y.

Even under present-day (interglacial) conditions favorable for chemical weathering and clay-mineral formation in the southern Appalachians, the time scales for forming clay minerals by weathering are long relative to the time scales of known glacial-interglacial climatic variation. If rates of weathering and clay formation in the southern Appalachians during northern hemisphere glacial episodes were slower than at present, then the time scales for clay-mineral formation are even longer. In most saprolitic regoliths of the southern Appalachians, clay minerals do not form by weathering sufficiently rapidly for regolith clay-mineral assemblages to be closely adjusted to climatic fluctuations with time scales shorter than hundreds of thousands of years. To the extent that saprolitic regolith in the southern Appalachians resembles the deep weathering profiles that dominate much of Earth's continental surface (e.g., Nahon, 1991), similar considerations of time scale may apply elsewhere as well.

Clay-mineral assemblages in saprolitic regoliths time-average (or integrate over time) clay accumulation over time scales that include wide variations in climate. Eroded sediments derived from such regoliths sample this time-integrated clay-mineral assemblage. The sedimentary record of paleoenvironmental change as preserved in detrital clay minerals cannot have a finer temporal resolution than the source regolith. Modern-day weathering and clay formation rates in the southern Appalachians, the abundances of clay in southern Appalachian saprolitic regoliths, and the time scales of northern hemisphere glacial-interglacial climate fluctuations, all combine to support Thiry's (2000) assessment that the best temporal resolution attainable from the marine sedimentary record of terrigenous detrital clay minerals is on the order of 1–2 m.y.

CONCLUSIONS

Clay mineral formation rates have been calculated using watershed mass balance methods at the Coweeta Hydrologic Laboratory located in western North Carolina. The mass balance calculations included rare earth elements (REE), which is fundamentally different from previous studies performed at Coweeta or elsewhere. The primary advantage of using additional elements such as the rare earths is that a larger number of equations can be constructed, allowing determination of a larger number of unknowns. This situation does not always exist in mass balance calculations.

Coweeta is an ideal locality to perform such a study, because it is an intermediate landscape between weathering-limited and transportedlimited end members. The rates have been calculated for three watersheds, two of which only vary by climate (W2 and W34), and a third (W27) that varies from the other two by both climate and lithology. By calculating present-day mineral weathering/formation rates, the rates could be directly correlated with the modern climate.

Based on the present-day clay formation rates determined by mass balance methods for Coweeta, detectable changes in relative clay mineral abundance (i.e., 50 g kg^{-1} using XRD detection limit) occur on time scales of tens of thousands to hundreds of thousands of years. Such time scales are comparable to the duration of glacial-interglacial oscillations (~100 k.y.). As a result, clay mineral assemblages in the sedimentary record at best reflect long-term (tens of thousands to hundreds of thousands of years) average climate changes.

Clay production times in Piedmont Terrane regolith have been calculated using clay formation rates for present-day conditions at Coweeta and are based on a representative Coweeta weathering profile. The production times of clay mineral assemblages range from 2 k.y. to 2 m.y., with mean values ranging from 50 k.y. to 1 m.y. Certainly, the clay mineral assemblages present in the Coweeta regolith today have not equilibrated with the modern Holocene interglacial climate. Therefore, the present-day clay mineral abundances and assemblages in any Piedmont Terrane weathering profile reflect an "average" climate that has occurred over the last ~2 k.y. to 2 m.y.

Marine sediments derived from saprolitic regoliths cannot have a finer temporal resolution of paleoenvironmental change than the source regolith. The present-day detectable changes in relative clay mineral abundance calculated for the southern Appalachians and the time scales of northern hemisphere glacial-interglacial climate fluctuations both combine to support Thiry's (2000) assessment that the best temporal resolution attainable from the marine detrital clay sedimentary record is on the order of 1–2 m.y.

ACKNOWLEDGMENTS

The authors wish to thank Associate Editor Christian France-Lanord and reviewers Arthur White and Anne-Marie Karpoff for their comments and suggestions, which greatly enhanced the quality of this manuscript. Thanks, too, to the Coweeta Hydrological Laboratory staff, especially Wayne Swank and Jennifer Knoepp, who provided assistance during field activities. David Szymanski and Meredith Lindeman also deserve thanks for their help with stream water sampling and analyses. Brian Teppen and Randy Schaetzl provided helpful and insightful comments during manuscript preparation. Funding for this project was partially provided by a Grant-in-Aid of Research from Sigma Xi, The Scientific Research Society, Michigan Space Grant Consortium Graduate Fellowship, and Clay Minerals Society Student Grant.

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MANUSCRIPT RECEIVED BY THE SOCIETY 17 DECEMBER 2003
REVISED MANUSCRIPT RECEIVED 17 AUGUST 2004
MANUSCRIPT ACCEPTED 7 SEPTEMBER 2004

Printed in the USA