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MINERALOGIC CONTROLS ON THE COMPOSITION OF NATURAL WATERS DOMINATED BY SILICATE HYDROLYSIS

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ABSTRACT. A detailed mineral-solute mass-balance spreadsheet model has been developed to improve understanding of mineralogic controls on water composition in surface waters and groundwater systems dominated by silicate lithologies. The spreadsheet-based approach is used to investigate mass-balance solutions over a range of mineral compositions for predominant, multi-element phases such as plagioclase, biotite, chlorite, amphibole, and dioctahedral smectite. The mass-balance technique has been applied to a variety of hydrogeologic environments including calibrated watersheds, springs and groundwater systems. Lithologic settings include plutonic, metamorphic, minor volcanic, and sedimentary (alluvial and glacial deposits) materials. Sites investigated, most of which allowed comparison with earlier work, include ephemeral and perennial springs of the central Sierra Nevada Mountains, California; the Loch Vale, Colorado high-altitude watershed; four catchments in the Inyo Mountains, California and Nevada; watersheds in the Catoctin Mountain, Maryland area; and ground-water flow systems in Vekol Valley, Arizona and in the Trout Lake area, Wisconsin.

Analytical mass balances were derived with a novel approach that permits graphic analysis of the functional dependency of mineral mass-transfer coefficients on variations in major silicate composition. A 10 x 10 matrix of mineral-solute reaction equations was used to solve for the best mass balances. Alternative methods were developed to investigate cases where the number of mineral phases exceeds the number of solute constraints (10) that are commonly found in clastic, silicate-dominated systems with diverse sources and/or phase mixtures of variable chemistry (such as an assortment of plagioclase compositions). Techniques were also developed to allow for important structurally controlled compositional variation in clay minerals. Final mass-balance choices were tempered by thermodynamic stability calculations for various minerals under near-surface weathering conditions. Mineral mass-transfer *ratios* were also found to be useful in restricting mass balances. Additional constraints were provided by establishing consistent sets of similar mineral assemblages and mineral compositions for a series of wells along a ground-water flow path, or through comparison of multiple nearby watersheds subject to similar climatic and vegetative conditions.

Whereas unique analytical solutions from spreadsheet mass balances were not always possible, a surprisingly limited range was obtained for mineral assemblages and compositions satisfying observed mineral occurrences and thermodynamic stability conditions. Our results demonstrate the importance of having well-characterized mineral compositions for both reactant and product phases. The mass-balance results are particularly sensitive to the compositions of plagioclase, dioctahedral smectite, and a few primary mafic mineral groups (trioctahedral mica, amphibole, and pyroxene).

In addition to mineral controls, the specific examples studied demonstrate effects of dolomite and calcite overprints on silicate weathering, biomass fluctuations, road salt contamination, and on buried evaporite salts. A comparison of the mass-balance results from surface- and groundwater systems indicates strong similarities, suggesting that similar processes dominate the mineral controls in both settings, and that, under soil weathering conditions ion exchange might have been overemphasized, except under conditions where pre-existing waters are displaced by solutions of significantly different composition.

INTRODUCTION, BACKGROUND, AND PREVIOUS WORK

The hydrolysis of rock-forming silicate minerals is an important process that controls the chemical composition of most natural waters, and has long been the focus

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of many geologic and geochemical investigations. Such controls have direct implications for the global geochemical cycling of elements and their response to natural and human-induced climate change, controls on the chemistry of groundwater, soil water, rivers and streams, and the fundamental chemical and physical mechanisms involved in silicate mineral dissolution and their rate under natural conditions.

The classic studies of Goldich (1938) and Reiche (1950) provide an early basis for much of the field-based studies today. Their work focused largely on the weathering of silicate mineral phases and corresponding changes in bulk-rock chemistry, and to a lesser extent on the waters derived from weathering. Goldich's work was one of the first to recognize the use of natural water chemistry to better understand the mechanisms and rates of weathering; however, this approach was little exploited until many years later.

In subsequent work by Sillen, Garrels, Holland, and others, these implications were more clearly realized (Bricker and Garrels, 1966; Garrels, 1967; Garrels and Mackenzie, 1967; Holland, 1978, 1984; and Sillen, 1967). Garrels, (1967), summarized publications before the 1960's that gave credit to the qualitative ideas of earlier workers back to those of F.W. Clarke (1924).

As early as 1967, several concepts that are summarized below were generally accepted for silicate terrains.

1. The solute content of soil and groundwater reflects mineral interaction with soil waters having CO_2 concentrations much higher (1-2 orders of magnitude) than waters in direct contact with the atmosphere.
2. Plagioclase and mafic minerals (amphibole and pyroxene) have substantially higher dissolution rates than K-feldspar and quartz.
3. Plagioclase is the principal source of calcium in most crystalline or silicate-dominated clastic terrains.
4. Dissolved silica is derived almost entirely from plagioclase and mafic minerals with relatively little contribution from K-feldspar and virtually no contribution from quartz.
5. Potassium and magnesium in soil water derive chiefly from the dissolution of biotite and hornblende.
6. Under conditions of relatively continuous flushing with dilute waters, the dominant product formed is kaolinite. Smectite or oxyhydroxides of aluminum and iron may be produced as a result of dry or very wet leaching regions, respectively, and by either unreactive or very reactive parent rock lithology.

Qualitatively, our understanding of these observations has changed surprisingly little since 1967. Quantitatively, these concepts have been explored in detail since then over a broader range of spatial and temporal scales.

The work of Garrels and colleagues stands out as milestones in the study of mineralogic controls of natural waters. In their classic paper, Garrels and Mackenzie (1967) calculated mass balances derived from spring-water data in the Sierra Nevada Mountains, California, based on the extensive analyses of spring waters by Feth, Roberson, and Polzer (1964). This single paper stimulated much work on the contribution of silicate weathering to water composition, especially using mass balance approaches, and provided a more quantitative approach to the qualitative studies of earlier workers. More recently, Drever (1997c); Plummer, Prestemon, and Parkhurst (1991); and Appelo and Postma, (1996) have commented on their work, and made some important interpretative modifications. Review and re-evaluation of this material provides the starting point for the mass-balance analyses described later in this paper.

Two important points emerging from the previous work that have driven much of the subsequent research are: 1) the fundamental influence of mineralogy on the major ion chemistry of natural waters; and 2) the importance of mineral dissolution mechanisms and kinetics. Subsequent work has followed up on the implications of Garrels'

conclusions, and has explored mineral reaction rates and their influences across a variety of settings and scales.

The two major lines of research that have evolved from these earlier studies include: 1) laboratory and theoretical studies of single mineral dissolution rates and their controls; and 2) field-based, watershed investigations largely driven by concerns for effects of acid rain, forest clear-cutting, and global change on effluent water compositions. The field studies represent a polymineralogic environment, and have largely emphasized the resulting fluid composition and control by the parent rock mineralogy, with less emphasis on the weathering products.

By the mid 1980's, it was recognized that mineral dissolution rates deduced from lab and field approaches were in fundamental disagreement, and that the rates determined by the two approaches differed by orders of magnitude (Paces, 1983; Drever, 1997b; Colman and Dethier, 1986; Velbel, 1985a; and Lerman, 1988). This problem has a direct bearing on the interpretation of comparative mass-transfer coefficients in the spreadsheet mass balances, which are strongly influenced by differential mineral dissolution and/or precipitation rates. Considerable effort has subsequently gone into resolution of this disparity (Blum, 1994; White, 1995; White and Blum, 1995; White and Brantley, 1995; Drever, 1997c; Blum and White, 1998; Sverdrup and Warfvinge, 1995; and White and others, 2001).

Blum and Stillings, (1995), summarized the wide range of dissolution rates for feldspars derived from field and laboratory studies, and listed important factors contributing to differences between rates measured in the field and laboratory studies. These and other published explanations include:

- Problems with experimental conditions, such as unrealistically high acidities (Casey and others, 1993);
- Brief duration of experimental studies compared to natural rates over thousands of years (Swoboda-Coberg and Drever, 1993)
- Experimental artifacts from short-term studies (Blum, 1994)
- Hydrologic complexity, such as the heterogeneity of soils (Blum and Stillings, 1995; Neal, Robson, and Christophersen, 1997)
- The difficulties of evaluation of the surface area of minerals in natural settings (Brantley and Stillings, 1996; Brantley and others, 1999; Clow and Drever, 1996; Drever, 1997c; White and Blum, 1995; White and others, 1996):
- Crystal defects (Inskeep, Clayton, and Mogk, 1993; Inskeep and others, 1991);
- Complexities with unsaturated zone hydrology (Neal, 1996);
- Soil-solution chemistry (local pH and saturation state), (Neal, 1997);
- Surface coatings (Velbel, 1993b);
- Biological effects (Velbel, 1995);
- Wetting and drying cycles (Eberl, Srodon, and Northrop, 1986); and
- Temperature (White and others, 1999a; and Velbel, 1990)

From a catchment perspective, Clow and Drever (1996) discounted the preeminence of defects and surface coatings (as did Velbel, 1993b, 1996); they placed more emphasis on the degree of saturation ("affinity") and effective surface area. Field-lab differences might also be reduced by appropriate experimental consideration of surface area (especially roughness) and time (Suarez and Wood, 1998), or partial wetting and weathering product inhibition (Sverdrup and Warfvinge, 1995). Significant progress in understanding the explicit controls on rates and mechanisms of silicate weathering has been made in recent years (White and Brantley, 1995; White, and others, 2001).

From a crystallographic point of view, it is not surprising that experimental dissolution results are as diverse as they are (Blum and Stillings, 1995). The plagioclase series is a complex mineral group, having not only a wide range of chemical composition, but also a diversity of structural states. Typical plagioclases are characterized by

chemical zonation and sub-microscopic unmixing phenomena. Experimental dissolution studies generally ignore these complexities, and treat the mineral grains as homogeneous and of one structural state (Smith, 1983).

Model Studies

In papers cited above and elsewhere, models are described which consider local to regional effects of weathering over a broad range of geologic and climatic settings, and which have attempted to integrate a variety of environmental and edaphic variables. Model approaches can be classified into two general categories, watershed simulations and geochemical models. The former tend to stress hydrologic, climatic, pedologic and mixing factors, primarily with reference to flow pathways and fluid composition, whereas the latter emphasize mineralogic reactions and lithologic variation/controls. As a consequence, watershed models focus on relatively rapid reactions, such as sorption and exchange, in contrast to a more purely geochemical emphasis on mineral dissolution reactions and the composition of reaction products. Geochemical models, in turn, can be subdivided into mass transfer (forward), or mass balance (inverse) types. A number of catchment studies have attempted a variable degree of integration of all these approaches, and this will be discussed later.

Mass Transfer Models

Mass transfer or reaction/transport models based on considerations of chemical equilibrium have been used to describe the geochemical evolution of closed basin waters, hydrothermal systems, and deep basin groundwaters, employing thermodynamic speciation and mineral saturation calculations. Though successfully applied to systems dominated by carbonate and evaporite mineral geochemistry, the application of these models to natural settings dominated by silicate hydrolysis has been severely hampered by the lack of reliable, internally consistent, thermodynamic data for common silicate minerals (Nordstrom and others, 1990; Melchior and Bassett 1990), and the general difficulty of finding unique, analytical solutions to these problems (for example, Kenoyer and Bowser, 1992a, 1992b).

Despite limitations, the forward modeling approach can be useful to define the saturation state of minerals whose thermodynamic constants are reasonably well known, or to determine whether or not some silicate phases are close to equilibrium. Burch, Nagy, and Lasaga (1993) and Taylor and others (2000), have shown that dissolution rates of silicates decrease significantly at near-equilibrium, and that such effects can be important, especially with regard to the feldspars.

Mass Balance Models

Ever since the work of Garrels and Mackenzie (1967) in the Sierra Nevada of California and Bricker, Godfrey, and Cleaves (1968) in the Maryland Piedmont, the majority of the watershed modeling studies described in the literature from bare rock catchments in the western United States or the forested experimental watersheds in Europe and the eastern United States have utilized mineral mass balance in some form (Bassett, 1997).

The method is based on principles of mass conservation during mineral-water reaction, and is fundamentally unconstrained by thermodynamic considerations. The technique was adapted for general hydrochemical computation by Plummer, Parkhurst, and Thorstenson (1983). Subsequently, the implementation of the mass balance approach has been extended considerably (Plummer, Prestemon, and Parkhurst, 1991; Bowser and Jones, 1990; Parkhurst, 1995). Drever (1997a) has given an important review of key concepts and papers in the development of the method.

Since thermodynamic criteria for mineral saturation are not required for mass-balance, model solutions must be tempered with knowledge of the saturation state of waters with respect to the reactive minerals. Nevertheless, our focus on the extensive

influence of silicate mineral reaction on water chemistry favors mass balance emphasizing mineral composition, dissolution, and product formation, and not thermodynamic properties.

Clearly, there are other fundamental restrictions to the application of mass balance models across the range of environments covered here. Inasmuch as mass balance approaches are the main thrust of this paper, full discussion is found in the methods section to follow.

Integrated Studies

A number of catchment studies have attempted to integrate field, laboratory, and model results, particularly in an effort to resolve the disparity of field and laboratory dissolution rates (Blum, Schulz, and White, 1998; Sverdrup, 1990; Swoboda-Coberg and Drever, 1993). White and Brantley (1995) brought together perhaps the broadest spectrum of mineral dissolution rate studies to date, but the included articles generally reflect the breadth of approaches, rather than an integrative understanding of mineral dissolution controls under both field and laboratory conditions. The recent effort of White, and others (2001) has provided an effective synthesis of detailed data on physical and chemical properties in granite regolith to model differential rates of feldspar weathering.

In recent years, considerable attention has been paid to the consequences of rock weathering to the dynamics and total ion concentration of natural waters. Some level of mineralogical control on the chemistry of natural waters seems obvious, yet the literature ranges in the degree to which mineral knowledge is incorporated into watershed studies, even those utilizing mineral mass balances (Drever, 1997a). Driven by acid precipitation research on impacted catchments, attention has frequently focused on hydrogen/base-cation ion exchange, and has not distinguished between true ion exchange and irreversible acid hydrolysis of silicate minerals (Likens and others, 1998; Hyman and others, 1998).

Yet the fact remains that the general problem of controls on natural water chemistry is fundamentally a mineralogic one, and that transfer of specific study results to other areas or sites requires a better understanding of mineral weathering controls in natural, mixed soil-rock environments. Although solute composition can be strongly modified by surficial or secondary non-mineralogic processes, the overall mineral assemblage and mineral chemistry of the underlying material ultimately determine it. Mineralogy is more than important; it's essential to our knowledge of compositional controls on natural waters.

SCOPE AND OBJECTIVES

It is our purpose to illustrate through detailed consideration of specific examples the general applicability of mineral mass balances to evaluation of the controls on the chemistry of natural waters. Further, we will illustrate the importance of mineral-phase characterization in the study of reactants and products of weathering, and to highlight some of the unresolved problems in the application of mass-balance analysis to natural waters.

We have analyzed published chemical data on waters from six regions of the United States that provide an assortment of common rock-forming silicate-mineral assemblages, and that reflect a range of geochemical environments and processes. Questions about the role of ion exchange, calcite precipitation and dissolution, atmospheric inputs (for example, acidic precipitation), surface-water contamination from road salt, and the nature of weathering products (esp. clay minerals) have been raised from analysis of this data set. The study sites were chosen to illustrate a wide range of problems and processes, and are drawn partly from the published literature and partly from ongoing work at the Long-Term Ecological Research site in northern Wisconsin (Magnuson and Bowser, 1990). Four of the examples presented here are

Fig. 1. Locations of case studies employed in mass balance analyses.

based on watershed studies using knowledge of stream chemistry and bedrock lithology, and two are drawn from ground-water systems in clastic sediment. Locations of case studies are shown in figure 1. Lithologic and hydrologic characteristics of the sites for the six case studies are shown in table 1.

TABLE 1

Lithologic and hydrologic characteristics of the sites for the six case studies

SITE	LITHOLOGIC CHARACTERISTICS	HYDROLOGIC CHARACTERISTICS
SIERRAN SPRINGS, CA	Granodiorite	Shallow, intermediate spring waters
LOCH VALE, CO	Granodiorite	Calibrated watershed
INYO MTS, CA-NV	Adamellite – Granodiorite, dolmite, limestone	Adjacent watersheds
CATOCTIN MT, MD.	Metamorphic greenstones	Calibrated watershed
VEKOL VALLEY, AZ	Granitic and volcanic clastic alluvial sediment	Ground waters along flow path
TROUT LAKE, WI	Cabonate-free, clastic glacial sediment from Canadian Shield	Ground waters along flow path

The studies discussed herein are based partly on data available from sites with which we have worked personally, and partly on the basis of data from colleagues whose studies were familiar and readily accessible to us. We made no attempt to provide a balanced collection of locations that represent the diversity of common weathering environments; to do so would have expanded the number of case studies well beyond what was reasonable. The preponderance of sites from semiarid western and mountain environments serves partly to broaden the range of study sites subject to mass-balance analysis, and to eliminate or reduce the effect of some of the variables that are more influential in humid and mesic environments (for example, vegetation, amorphous residuals, and anthropogenic influences, such as cultivation, clear-cutting, or atmospheric contamination). Our goal is to demonstrate the applicability of the approach, using well-constrained mineralogic data and quality aqueous chemistry, to a broad range of environments, not to be comprehensive in scope of all weathering environments.

The case studies for our analysis are from predominately silicate terranes, and are presented roughly in order of increasing complexity. Beginning with a review of the classic study of Sierran springs and associated rocks by Garrels and Mackenzie (1967), a lithologically similar watershed (Loch Vale) in Colorado with more mineralogic and hydrologic detail (Mast and others, 1990) is re-examined. Thereafter, some adjacent small catchments in crystalline and largely plutonic terrane in the semiarid Inyo Mountains, in part with significant carbonate overprint, illustrate what can be done with a few low-flow analyses and consideration of solid solution in products as well as reactants. The Catoctin watersheds (Katz, 1989; Katz, Bricker, and Kennedy, 1985; O'Brien and others, 1997) add contributions to unique silicate mineralogy from acid rain, road salt (and resulting "reverse" exchange), and biomass degradation. Review of the Vekol Valley mass-balance results of Robertson (Robertson, 1991) points out the assemblage constraints posed by intermediate locations along the flow path, and a system closed to CO_2 down dip in crystalline, alluvial groundwater. Finally, the analyses of Trout Lake groundwater raise the issues of flow-path refinement, mixed-phase mineralogy of glacial deposits, and specific hydrologically significant lithologic changes along the groundwater flow path.

All cases considered use paired water analyses, either spring/creek and precipitation, or ground-water compositions along a groundwater flow path. All water analyses used in the final mass balances are presented in table 2.

CURRENT STUDY

The Spreadsheet Approach to Mass Balance

Mass-balance programs are currently available in a number of forms, perhaps the most comprehensive being NETPATH (Plummer, Prestomen, and Parkhurst, 1991) and PHREEQC (Parkhurst and Appelo, 1999). These programs are largely batch oriented, and the output is in tabulated, numeric form. The latest version of PHREEQC (version 2.1) includes an inverse-modeling option with the added capability of specifying uncertainties of analytical solute species. Charlton, Macklin, and Parkhurst, (1997) have added an interface that allows interactive modification of the input files, but to date there is no graphic output.

In contrast, the general availability of commercial software capable of mass-balance computations underscores the need for a widely available tool that can be used for a range of mass-balance situations, and that can be readily adapted for graphic presentation, which aids convergence on the most plausible models. As part of this work, we have developed a spreadsheet-based mass-balance calculation for modeling simultaneous multiple mineral-water reactions. An important feature of this spreadsheet program is the ability to evaluate output as a function of one or more mineral solid-solution compositions, and to view the results in graphical form. The advantages

of this approach will be demonstrated in the examples chosen for discussion below. A more abbreviated description of the technique was given in Bowser and Jones (1990). Work presented herein derives solely from use of this spreadsheet program.[1]

Methods

The mass-balance approach used herein is focused on weathering of common rock-forming silicates, other minor reactive phases, and the evolution in composition of a single water type. The cases discussed here exclude those that involve mixing of waters, isotopic constraints, carbon speciation, and redox processes, although there is no general restriction from doing so with appropriate modifications of the existing spreadsheet technique.

The simplified mass-balance expression is modified from Parkhurst and others (1982) and Plummer and others, (1983).

$$\sum_{j=1}^{j} MTC_p \alpha_p^i = \Delta m_i = m_{i(final)} - m_{i(initial)}, \qquad (1)$$

Where:

j = the number of phases
p = the plausible reactant and product phases used for the mass-balance model.
MTC = the mass-transfer coefficient for any phase (p) in moles.
α = the stoichiometric coefficient of element, i, in phase p.
m = total moles of element, i, the initial and final solutions (or Δm, the net change in the number of moles)
i = chemical element used in the mass balance.

Other restrictions apply to the mass-balance method: (1) the number of plausible phases included in the model must be equal to the total number of analyzed solute species in the water; (2) the solute species considered are restricted to those elements whose stoichiometric coefficients in the minerals are well-known or definable from direct mineralogical or mineral-chemical analysis (that is, not as trace elements such as Mn, Zn, Co, Ni, Cu, et cetera); (3) precise mineral-chemical definition is not always possible, especially in mechanically mixed, clastic aquifers and sedimentary rock-dominated terrains; (4) analytic solutions to mass-balance analyses do not always provide unique results; (5) mineral dissolution is controlled by its inherent rate, effective surface area, reaction temperature, and closeness to equilibrium, not simply the modal abundance.

Of course, field estimates of mineral mass transfers are inherently measures of kinetic processes at conditions *generally* far removed from mineral equilibrium. As such resulting mass-transfer coefficients are dependent on mineral surface area, mineral modal abundance, inherent mineral-dissolution rates, and degree of mineral undersaturation ("affinity effect"). Comparison of field-based rates with comparable laboratory rates is accordingly difficult except under conditions where the relative grain size (surface area) of different mineral species is virtually identical. Despite these obvious restrictions, comparisons of field and laboratory rates have been attempted with some degree of success (Swoboda-Coberg and Drever, 1993; Velbel, 1993a; Sverdrup and Warfvinge, 1995).

[1] An elaborate spreadsheet has evolved over the years with convenient formatting and input. Currently it is designed to run a 10 by 10 mineral/solution matrix. The current Excel spreadsheet is available without charge through the internet (http://water.usgs.gov/software). Users are expected to credit the program appropriately. Suggestions for improvement are welcomed.

TABLE 2

Hydrochemical data used for mass balance models. Values shown are for the differences between paired water analyses; where not specified, atmospheric precipitation is taken as the initial water. Ten-year data for Hauver Branch, Catoctin Mtns., MD, from O'Brien (1997) not shown

	CHANGE IN WATER COMPOSITION						
	SIERRAN SPRINGS, CA	SIERRAN SPRINGS, CA	LOCH VALE CO	INYO MTS. CA	INYO MTS. CA	INYO MTS. CA	INYO MTS. CA
	Ephemeral	Ephemeral to Perennial		Cottonwood Ck.	Sage Hen Ck.	Crooked Ck.	Wyman Ck.
Elements	μmol/Kg	μmol/Kg	μmol/Kg	μmol/Kg	μmol/Kg	μmol/Kg	μmol/Kg
Al	0.0	0.0	0.0	1.2	0.7	0.0	0.0
C	310.0	567.0	206.0	2561.6	906.3	2698.1	4074.0
Ca	68.0	182.0	120.0	639.7	340.3	1105.5	1630.6
Cl	0.0	16.0	0.0	2.8	2.8	92.1	50.4
Fe	0.0	0.0	0.0	0.3	0.5	0.0	0.0
K	20.0	12.0	17.0	16.4	22.8	91.0	102.0
Mg	22.0	42.0	33.0	617.0	28.0	198.8	556.6
Na	110.0	125.0	63.0	49.6	271.4	576.7	418.3
Si	270.0	137.0	154.0	75.7	282.1	398.6	343.9
SO_4	0.0	15.0	1.0	27.9	90.4	204.5	404.3

TABLE 2

(continued)

	CATOCTIN MT. MD	CATOCTIN MT. MD	VEKOL VALLEY AZ	VEKOL VALLEY AZ	VEKOL VALLEY AZ	TROUT L. WI	TROUT L. WI	TROUT L. WI
	Hauver Br. 1983	Hunting Ck. 1983	V0->V1	V1->V2	V2->V3	K87->K70	K70->K71	K71->K5
Elements	μmol	μmol	μmol	μmol	μmol	μmol	μmol	μmol
Al	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C	1680.0	2250.0	-1250.0	-1477.0	-166.0	89.1	335.9	141.3
Ca	846.0	1167.5	-1200.0	-423.0	-1.0	0.0	0.0	0.0
Cl	528.0	1670.0	250.0	1326.0	282.0	-0.8	-0.3	-1.5
Fe	0.0	0.0	0.0	0.0	0.0	-7.7	-1.5	3.9
K	21.0	94.8	-90.0	36.0	89.0	0.2	0.5	-1.5
Mg	634.0	695.6	-140.0	-510.0	25.0	20.7	70.9	25.7
Na	576.0	1550.0	1466.0	2784.0	435.0	25.3	15.2	-1.0
Si	1420.0	1890.0	79.0	-100.0	33.0	106.6	70.2	82.1
SO_4	324.0	250.0	55.0	479.0	238.0	-0.7	1.3	-4.1

Our peculiar use of the term "phase" herein requires some elaboration. With apologies to J. Willard Gibbs (Gibbs, 1961), the term "phase" is used somewhat loosely here, and only in the context of mass-balance analysis. It is used to indicate a compositional species, and not a mineral in the strictest sense. Where sulfate and calcium are added in equimolar proportions, the "phase" has been called "gypsum" although it only implies a 1:1 ratio of calcium to sulfate, and not the actual mineral, or any structural state of $CaSO_4$. Thus, gypsum and anhydrite are considered the same "phase" in that they both contribute calcium and sulfate to water on dissolution, and the mineral structure or mineral water content has nothing to do with mass balance considerations. Similarly, quartz, amorphous silica, tridymite, or other structural states of naturally occurring silicon dioxide are treated as the same "phase" here.

We define a *mean reactive* composition in the case of clastic mixtures of minerals of the same species, but each differing in composition (for example, a mechanical mixture of plagioclase grains). This is simply the single composition of the mineral species (for example, plagioclase) that on dissolution would yield the same solute composition as a variable composition mixture of individual grains. This concept will be elaborated on in the section on Trout Lake, where its use is critical to help solve the mass-balance models.

A similar problem exists with complex mixtures of compositionally variable mafic minerals (for example, biotite, chlorite, pyroxene, and amphibole[2]). Mixtures of minerals can be treated as one "phase" if their dissolution or precipitation rates are always in the same proportion to one another. For example, a defined mixture of biotite and chlorite, each of a fixed composition and always weathering in the same ratio, could be considered as a "phase" in mass-balance calculations. We refer to such arbitrary and fixed mineral mixtures as *fictive phases*, representing a weighted-average composition of two or more separate, but structurally similar minerals. The ratio of the mineral mixture can be used as an input variable in the calculations. The choice of end-member phase chemistry for specific minerals can also be taken as what we would define as a *mean reactive composition*. For example, a mixed biotite/chlorite "phase" was used in the Loch Vale and Trout Lake case studies. Similarly, we have used a fictive phase representation for pyroxene/amphibole mixtures and for road salt. The phase "*road salt*" is defined here as a constant ratio mixture of NaCl, KCl, and $CaCl_2$ (see discussion of the Catoctin Mountain watershed). Finally, we employed the phase "*acid rain*" here merely as a means of adding sulfate via rain independent of balancing cations (principally Ca), as is typically done for normal rainwater. Essentially, we chose to ignore hydrogen mass balance in our models.

Although perhaps it may seem somewhat artificial, this approach has the important advantage of lumping several mafic minerals together under one solid, albeit complex, "phase" composition. This allows reduction of the number of "phases" to equal the number of solute constraints. Inasmuch as the appropriate mass-balance solutions are strongly determined by the coupled ratios of Si/Al, Fe/Mg, and Ca/Mg, it seems more appropriate to use these fictive "phase" compositions as mixtures of real, analyzed ferromagnesian silicates rather than to arbitrarily and independently vary each element to satisfy the mass balance. The results are very sensitive to the choice of appropriate mineral compositions; therefore, considerable mineralogic experience and judgment is required to apply these approaches. The success of the resultant models gives confidence in our method.

These modifications only demand that the stoichiometry of each of these "phases" be explicitly defined. They become useful tools in the investigation of cases where the number of phases exceeds the number of solute species, or where specific phases have

[2] A similar approach was used for the evaluation of the $CaCl_2$ and KCl percentages in "road salt" in the Catoctin Mt. study.

a broad range of chemical compositions and, therefore, do not have explicitly defined stoichiometric coefficients.

Solution to mass-balance equations requires the solution of a set of simultaneous equations where the number of solute constraints equals the number of phases considered in the weathering reaction. Model solutions to these sets of equations can be handled with matrix methods. The matrix mass-balance solution:

$$\begin{bmatrix} \alpha_{p1,1} & \alpha_{p1,2} & \cdots & \alpha_{p1,i} \\ \alpha_{p2,1} & \alpha_{p2,2} & \cdots & \alpha_{p2,i} \\ \cdots & \cdots & \cdots & \cdots \\ \alpha_{pj,1} & \alpha_{pj,2} & \cdots & \alpha_{pj,i} \end{bmatrix}^{-1} \begin{bmatrix} m_{i1} \\ m_{i2} \\ \cdots \\ m_{ii} \end{bmatrix} = \begin{bmatrix} MTC_{p1} \\ MTC_{p2} \\ \cdots \\ MTC_{pj} \end{bmatrix} \tag{2}$$

can be represented in simplified form:

$$[P]^{-1}[\Delta W] = [MTC], \tag{3}$$

Where:

$[P]^{-1}$ is the inverse matrix of mineral phase, stoichiometric coefficients
$[\Delta W]$ is the vector of solution composition changes
$[MTC]$ is the resultant vector of mass-transfer coefficients for each of the plausible mineral phases involved in the solute evolution of the water[3]. Depending on the chemical units chosen, output is either in molar concentrations (μmoles/kg, herein) or, in mass per unit area, for calibrated watersheds.

Watershed data can be converted to molar concentrations provided data are available for the annual water mass flow.

The solution of the set of simultaneous equations is readily handled by matrix operations offered on several commercially available spreadsheets. This approach has been developed for the work presented here. A matrix of stoichiometric coefficients for the host minerals is set up for each of the elements involved in the mass balance analysis. The vector of water compositions (difference between two related waters) is used to solve for the mass-transfer coefficients of the "plausible phases" of the matrix. By use of spreadsheet lookup tables, this approach allows rapid modification of a wide range of water compositions, and investigation of various combinations of geologically reasonable mineral phases associated with these waters. Matrices of various dimensions can be readily set up to explore different combinations of phases and solute species. The compositional variations of minerals or waters can be easily modified. Through use of table-generating functions in the spreadsheet, the results can be viewed in both graphical and numeric form immediately after the changes are made. This provides a powerful means of sorting out allowable ranges of mineral composition that satisfy the mass-balance models.

Critical use of geologic and mineralogic evidence for the composition of the reactant and product phases is essential to proper interpretation of the results. Wherever possible, evidence for each mineral phase present and its chemical composition should be used. If suitable data are lacking from any study site, it is possible to use reasonable phase compositions from similar geologic environments, but only where good mineral composition data are unavailable. Clearly, there is no real substitute for

[3] Note that the model mass balance coefficients are dependent on the convention for specific formulations of the mineral stoichiometry chosen. For example, kaolinite is typically written as $Al_2Si_2O_5(OH)_4$, with two silica and aluminum atoms per formula unit, not one. Similarly gibbsite and goethite are written with one aluminum and iron per unit cell, respectively, not two, as is sometimes written. The resulting mass-transfer coefficients may thus differ by a factor or two for these minerals, depending on the specific formula convention used. For comparative purposes, we have chosen formulas based on those used by the original authors for each case study. Mineral formulae used are shown in the text associated with each specific case study.

careful definition of mineral chemistry in samples for which the approach is being used, and mass balance results can be significantly improved by having such data available. In examples to follow, the importance of carefully analyzed mineral samples will be illustrated.

An example utilizing the spreadsheet technique is shown using data from Sierran spring waters (Garrels, 1967). The data for average ephemeral waters are shown in table 3 along with the matrix of stoichiometric coefficients for the proposed mineral phases in the weathering reactions and the resulting mass-balance solution.[4] Further discussions of the results from this example follow later, but are brought up here only to illustrate the model outputs, and restrictions on their interpretation.

Particular attention is paid to the point at which certain mineral *mass-transfer coefficients* (MTC's) become zero, or change from negative to positive[5] (termed here the phase "*crossover point*"). MTC's for primary igneous and metamorphic silicates that are not formed under weathering conditions are restricted to positive values (that is, as reactants). Conversely, products of weathering are restricted to negative values. This approach emphasizes the fact that mass-balance solutions commonly allow a continuous range of possible mineral mass transfers depending on the range of phase compositions chosen. Furthermore, the lack of a unique mass-balance solution does not preclude upper or lower compositional bounds on the mineral compositions; thus, limits can be placed on mineral compositions defined by critical crossover points (mineral MTC=0), a point that is especially well-illustrated in the discussion of the Inyo Mountain watersheds that follows below.

The mass-transfer coefficients (MTC's; positive sign for reactants and negative sign for products) can be viewed graphically as a function either of the anorthite/albite ratio or by the An-number of the plagioclase as used here.

$$An - number \equiv \frac{CaAl_2Si_2O_8}{NaAlSi_3O_8 + CaAl_2Si_2O_8} = \frac{Ca}{Na + Ca} \tag{4}$$

In principle, both albite and anorthite could be used as separate "phases" (An-0 = albite; An-100 = anorthite) or, as we chose here, combined as a single phase of appropriate composition. The former approach is admissible using the loose definition of phase herein, and simply increases the dimension of the stoichiometric coefficient matrix by one. We have chosen the more realistic approach, and recognize plagioclase as a single phase. The table of MTC's is calculated and plotted as a function of the plagioclase composition (An-number). Example results are shown graphically in figure 2. It is important to appreciate the coupled effect of the An-number on the Si/Al ratio of plagioclase, and consequently on the mass-balance results obtained. Modeled MTC's from plagioclase and other Si-Al-bearing phases are critically dependent on the Si/Al ratios of the participating phases. Consequently, proper definition of the phase compositions is critical to appropriate model solutions.

Careful attention is paid to the range of possible mass-balance model solutions demanded by the thermodynamic constraints of mineral stability. Thus, plagioclase

[4] The results are shown for illustrative purposes here. We use similar phase assemblages and compositions as the original results from Garrels and Mackenzie (1967). Improved assemblages and mineral compositions are shown later in the discussion of the Sierran Spring case.

[5] EXCEL has a particularly useful function to help solve for the plagioclase (or other phase) composition at the point of crossover for any other phase in question. The "goal seek" function can be used to set the mineral MTC in the output to zero by pointing to the cell that contains the compositional variable to be changed (An-number, clay interlayer-K, montmorillonite/beidellite ratio, et cetera). Typically this is the compositional boundary above or below which the mass-balance models are impossible, based on the sign of the mineral MTC, and whether it should be thermodynamically stable or unstable under weathering conditions.

TABLE 3

Input and output data for Sierran ephemeral springs. Shown are the original water data for average snow and ephemeral spring waters, the mineral stoichiometric coefficient matrix, and the model mineral mass transfer coefficients (MTCs) for phases used. Results from (Garrels and Mackenzie, 1967) shown for comparison

WATER COMPOSITIONS (Units: μmol/L)

	Al	C	Ca	Cl	Fe	K	Mg	Na	Si	SO_4
Sierran Snow	0.0	18.0	10.0	14.0	0.0	8.0	7.0	24.0	3.0	10.0
Ephemeral Springs	0.0	328.0	78.0	14.0	0.0	28.0	29.0	134.0	273.0	10.0
Difference	0.0	310.0	68.0	0.0	0.0	20.0	22.0	110.0	270.0	0.0

MINERAL STOICHIOMETRIC COEFFICIENT MATRIX

Minerals (10)	Al	C	Ca	Cl	Fe	K	Mg	Na	Si	SO_4
Plagioclase	1.38	---	0.38	---	---	---	---	0.62	2.62	---
Kfeldspar	1.00	---	---	---	---	1.00	---	---	3.00	---
Biotite	1.00	---	---	---	---	1.00	3.00	---	3.00	---
Kaolinite	2.00	---	---	---	---	---	---	---	2.00	---
Smectite_ss	2.50	---	0.25	---	---	---	---	---	3.50	---
CO2-gas	---	1.00	---	---	---	---	---	---	---	---
Calcite	---	1.00	1.00	---	---	---	---	---	---	---
Goethite	---	---	---	---	1.00	---	---	---	---	---
Halite	---	---	---	1.00	---	---	---	1.00	---	---
Gypsum	---	---	1.00	---	---	---	---	---	---	1.00

MINERAL MASS TRANSFERS AND COMPOSITIONAL VARIABLES USED

(Units: μmol/L)	MTC (this study)	MTC *
Plagioclase	178.00	177.0
Kfeldspar	12.67	13.0
Biotite	7.33	7.3
Kaolinite	-128.00	-166.0
Smectite	-10.00	0.0
CO2-gas	310.00	328.0
Calcite	0.00	0.0
Goethite	0.00	0.0
Halite	0.00	0.0
Gypsum	0.00	0.0
Interlayer Charge	0.50	
% Montmorillonite	0.00	
Interlayer-K	0.000	
Plagioclase An-no.	38.2	
Plag./K-feldspar =	14.050	
K-feldspar/Biotite =	1.730	
Fe/Mg =	0.000	

* (Garrels and Mackenzie,1967)

compositions yielding primary (reactant) mineral MTC results with negative values (that is, precipitated) are considered outside the expected range of mass-balance solutions.

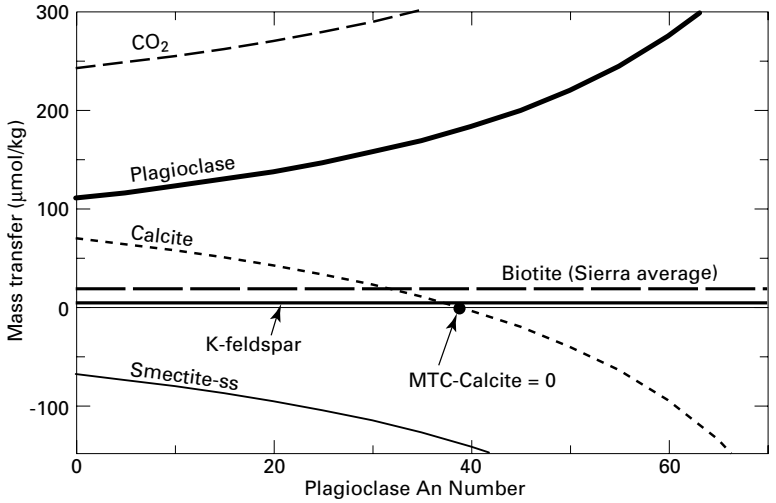

Fig. 2. Plot of mass transfer coefficients (MTC) vs. plagioclase composition for ephemeral spring waters of the Sierra Nevada Mts., CA (Garrels and Mackenzie, 1967). Positive values are for mineral dissolution, and negative for precipitation. The average plagioclase composition (An38) for Sierran granodiorites is near the point where the MTC for calcite changes from positive to negative values.

Calcite is especially important in the interpretation of results from silicate terrains where it is either present in small quantities or absent. The plagioclase An-number corresponding to the calcite cross-over point is emphasized in several of the examples that follow, and is a key feature in the interpretation of mineral control on waters derived from weathering of silicate terrains. In the Sierran water example shown (fig. 2), the plagioclase An-number where the calcite MTC becomes zero (the cross-over point for calcite) is at An-38, the composition chosen by Garrels and Mackenzie (1967) for their model solutions, and geologically reasonable for the granodioritic rocks described from the area (Feth and others, 1964). Thus, calcite is not required to produce the ephemeral spring water compositions observed, a conclusion in accordance with the earlier results.

In the example above, rocks with average plagioclase compositions that are well below An-38 would demand calcite or another calcium-bearing mineral phase as a reactant to explain the water composition observed, or conversely, for a rock with a significantly higher plagioclase An-number, calcite would have to be a weathering product to adequately explain the water composition. Similar types of plots can be generated for any phase of variable composition (amphiboles, smectites, et cetera) or for ratios of two related phases (for example, biotite/chlorite).

Consideration of mass-balance results for two or more phases of variable composition (reactants and/or products) requires a higher "dimensionality" to express the results, but all essentially involve finding a range of mineral compositions that limits specific phases to positive or negative MTC's consistent with their presumed stability under weathering conditions. Thus, rather than finding unique combinations of specific mineral compositions to explain the observed changes in water composition, we have limited our interpretations to the compositions of key mineral phases that put effective boundaries or limits on mineral compositions. For example, a case where there is geologic, mineralogic, or pedologic evidence exist that calcite is a weathering product derived from primary rock-forming minerals would put upper or lower limits on the range of possible plagioclase compositions. In some cases, the range of possible mineral compositions that would yield satisfactory mass-balance solutions is surpris-

ingly narrow (compare Vekol Valley case below), providing a "window" of appropriate mineral compositions. Satisfactory mass-balance solutions generally are not unique, but they do provide critical compositional limits for minerals and waters.

The size of the matrix used for mass-balance analysis obviously depends on the water chemistry and mineralogical data available. For previous studies, matrices range from 9×9 to as few as 4×4 (Katz and others, 1985; Plummer and others, 1991). The size of the matrix is largely limited by the compositional data available for most mineral phases, and by the number of aqueous ions analyzed. Larger matrices would presumably provide additional constraints, but typically data are lacking to justify their use. A 10×10 array is employed for the examples that follow. Aqueous species used for the discussions include: Ca, Mg, Na, K, SO_4, Cl, total inorganic carbon, Si, Al, and Fe. Isotopic constraints may provide additional dimensions to the matrices (Plummer and others, 1991) as in NETPATH, but, with the exception of strontium (Blum and others, 1993; Bullen and others, 1996), isotopic data and fractionation constants are generally only available for carbonate mineral systems, and are of relatively little use in the silicate-dominated systems emphasized here.

An alternate approach suggested by Michael Velbel (written communication) would be to solve for a smaller 9×9 matrix, use the resulting equations to calculate the value of solute concentration left out by using a smaller dimension matrix, and to compare the calculated and observed values, as he did in his Coweeta Mountain studies (Velbel, 1985a; 1992). We chose instead to use the approach that would allow us to include an additional mineral phase, and increase the model constraints by using the larger matrix.

Although aqueous concentrations of aluminum and iron are usually negligible in natural waters, they are used here as virtual dummy variables to allow inclusion of added restrictions in the mineral composition matrices. Iron and aluminum are very low in concentration in typical weathering fluids, and effectively transfer to other Fe- or Al-bearing solid phases on weathering (for example, goethite, hematite, kaolinite, gibbsite, clays). Varying the concentration of these elements in solution has little effect on the solute balance, but changes in the Si/Al or Fe/Mg ratio of mineral phases can significantly alter the mass-balance results. Prior published work typically assumed or used idealized end-member mineral compositions, which is useful in the absence of more definitive data, but the results are thus more equivocal (Finley and Drever, 1997).

Analysis of watersheds typically involves the comparison of an outlet stream composition with precipitation and/or soil-water chemistry (corrected or uncorrected for atmospheric solutes, such as Cl and SO_4). Analysis of ground-water systems involves comparison of two or more samples from wells along a flow path. As will be shown later in the Vekol Valley, Arizona, and Trout Lake, Wisconsin, examples, use of multiple ground-water sample analyses from a common flow path with comparable aquifer mineralogy can add considerable confidence to the mass-balance results, underscoring the importance of flow-path delineation.

Correction of input water analyses for solutes from precipitation typically assumes that chloride and sulfate ions are balanced by sodium and calcium, respectively, (shown as "halite" and "gypsum" in the mass-balance results), but situations arise where such assumptions do not apply. Acidic precipitation typically involves addition of sulfate ion not linked to calcium, and is corrected by treating the balancing cation as a hydrogen ion. The "acid rain" phase used in the Catoctin Mountain and Trout Lake examples illustrates this approach. Another example of chloride input not linked to precipitation is that supplied to a watershed through anthropogenic activities, most commonly due to treating highways to remove winter snow and ice. The effect of concentrated solutes added in this way is not only in terms of salt-loading of streams or shallow ground water, but also in changing the cation mix in solution through "reverse" exchange, whereby abundant sodium is exchanged for alkaline-earth nor-

mally preferred on silicate mineral surface sites. Shanley (1994) has offered effective criteria and calculations for correcting these input water compositions, which are explained and utilized later in the Catoctin Mountain case study.

Fundamental Mineral Assemblages

In all the silicate-dominated terrains considered herein, a consistent set of minerals is taken as the minimal or fundamental reactant assemblage whose weathering and dissolution provides the basic source of major ions in the associated natural waters. This assemblage includes at least plagioclase and alkali feldspar, and some ferromagnesian (mafic) silicate(s), which react with natural carbonic acid derived from aqueous uptake of carbon dioxide (augmented by organic activity) to form solutes and product minerals, including clays, oxides, and perhaps carbonate minerals (especially calcite). In accordance with prior studies, quartz, which is abundant but sparingly soluble, is considered virtually inert, although this is not true of other forms of silica. For non-clastic calibrated watersheds the number of silicate reactant and product phases to be considered in such a typical mass balance is almost invariably less than ten and typically is half that. In the six watershed examples examined here, a total of eighteen phases were considered. Plagioclase, K-feldspar, clay, goethite, CO_2 gas, and salt were included in all the mass balances. Some compositional variation within principal silicates was also addressed in all the examples.

The compositional range in primary silicates and clay minerals is significant in the majority of field occurrences, and readily exceeds the analytical error for solutes determined in most of natural solution compositions. Thus, it is probably insufficient to consider the range of possible analytical solutions only due to the variance in solute concentrations and not to the variance in mineral compositions. Variation in major cation ratios (Ca/Mg, Na/K, Si/Al, et cetera) in the waters of interest is indicative of multiple mineral sources, as the solutions seldom have cation ratios corresponding to those even in the most abundant reactant phases. Obtaining a reasonable mass-balance result in silicate systems thus requires a specific evaluation of mineral composition range at least for the most abundant mineral phases (for example, plagioclase and clay).

In the absence of direct and precise determination of solid-phase compositions, estimates of reasonable compositional variations for silicate solid solutions can be made from mass transfers of the simpler, chemically homogeneous phases, such as iron oxide, silica, or calcite. The relative proportions of these simple reaction products that are required to obtain a mass balance can be definitive indicators of the stoichiometry of the reactant minerals.

Based on hydrochemical mass balance with minimum soil or biomass over several annual cycles in the high altitude, crystalline catchment of West Glacier Lake, Wyoming, Finley and Drever (1997) questioned the numerical evaluation of weathering reactions by mass-balance techniques, chiefly because the number of mineral phases exceeds that of solute constraints in so many watersheds. However, alternative approaches, such as the mean reactive and/or fictive phase concepts utilized in our spreadsheet, allow reducing the phase number and can produce mass-balance solutions that are narrowly limited in mineral-composition space. This is especially evident in the results from Loch Vale and Trout Lake, discussed later in the text. Our case studies generally confirm Finley and Drever's (1997) final conclusion that even semi-quantitative mass-balance arguments can at least significantly constrain rates of mineral alteration.

In most silicate-dominated watersheds, the most influential *reactant phase* is plagioclase feldspar (Drever, 1997a). Typically, it is the most important source of

solute calcium and essentially the only significant source of solute sodium.[6] Alternative Ca-silicate sources include amphibole, epidote-zoisite, and more rarely, pyroxenes (in igneous settings). Substitution of calcium for sodium in plagioclase (increasing An number) is coupled to an equivalent substitution of aluminum for silicon. With the exception of carbonate minerals in the Inyo Mountain watersheds and amphibole in the silt layer in the aquifer at Trout Lake, plagioclase mass transfers dominate the balances in our examples.

Similarly, the most common *products* of weathering are kaolinite and other clays. Dioctahedral smectite can be considered representative of the more compositionally complex 2:1 (tetrahedral:octahedral) phyllosilicates. This is more important because phyllosilicates are subject to coupled Mg plus Si substitution for Al plus ferric iron in the principal layers. In terms of specific end-member clay-mineral species, this can be considered a beidellite-montmorillonite solid solution. The effect of a high Al content in reactant or product minerals is to reduce the proportions of cations derived from dissolution because of low aluminum solubility (and thus solute flux) in normal (near-neutral pH) waters. In this regard, vermiculite can be considered a high-interlayer-charge smectite resulting from Al substituting for Si, and for this reason, vermiculite is not specifically used as a "phase" name in the text. Similarly, mixed layering is not specifically identified, because the average composition of the layers considered as a single 2:1 clay phase is chemically sufficient for the mass-balance calculations.

On the other hand, the metal ion content of the smectite interlayers can have small but important effects on cation ratios and solution mass balances. Exchangeable K or Ca from the interlayer is particularly important, and as such, we use interlayer K and interlayer charge as important variables to evaluate in our mass balances. All of these factors figure prominently in the case studies presented herein, but particularly for those watersheds (Sierra Nevada, Loch Vale, Inyo Mountains) dominated by weathering of plutonic rocks. Without the capability to allow for complex compositional interdependency, it is unlikely that satisfactory mass-balance solutions for any silicate-dominated watershed could be achieved.

The nature and composition of weathering ferromagnesian minerals play a key role in controlling the cation ratios of weathering solutions. Though iron oxyhydroxide minerals are virtually insoluble in near-neutral oxidized waters, increased Fe/Mg ratios in *reactant* mafic silicate solids not only decrease Mg relative to other cations within the reactant phase itself, but also with respect to solutes derived from other sources (such as Ca and K). Though compositionally diverse, the typical mafic minerals weathering under most geologic conditions are also the most common (for example, biotite, hornblende, augite-pyroxene, and chlorite).

Non-silicate minerals in crystalline rock weathering reactions (for example, carbonates, oxides, and sulfides) can be involved as either reactant or product phases. Calcite is especially important, and its role as a reactant or product phase has to be judged in terms of its thermodynamic stability under specific weathering conditions, as well as the physical (textural) evidence for its involvement.

A commonly encountered example of the use of mineralogic "common sense" is in consideration of the products of silicate weathering in the mass balances. This involves assessing the compatibility of phases even when they cannot be rigorously defined mineralogically. For instance, aluminum sesquioxides (for example, gibbsite) are typically product phases in some weathering conditions (low ionic-strength waters, temperate to tropic weathering). Natural mineral assemblages of kaolinite/gibbsite or kaolinite/smectite are well known (Kittrick, 1969, 1977), but gibbsite/smectite or gibbsite/kaolinite/smectite are incompatible as equilibrium assemblages. Such associa-

[6] Excluded, of course, are halides and carbonates and other non-silicate phases that are not significant sources of calcium and sodium in typical silicate weathering-dominated settings.

tions in natural weathering environments are evidence of one or more relict phases, and/or formation under slightly different but adjacent conditions.

Similarly, the aluminous-phase gibbsite is not expected to coexist with an amorphous silica phase, but instead to eventually react and form an aluminosilicate clay. In as much as aluminum hydroxide solubility is at least three orders of magnitude less than silica in near-neutral pH natural waters, a decrease in the Si/Al ratio of a product phase assemblage can be used as a qualitative estimate of the degree of weathering. Si/Fe can be similarly indicative. The importance of these expected phase relations is demonstrated in those situations where the actual products of weathering reactions are difficult to define by normal mineralogic techniques (for example, Miller and Drever, 1977), and/or the phases are inseparable (Finley and Drever, 1997). Such considerations aid in deciphering the clay product assemblages in crystalline rock terrane, and suggest the relation to climate conditions seen in decadal-scale mineral mass-balance variations, as in the Catoctin Mountain watersheds.

Our case studies offer a number of illustrations of the advantage of using the interactive spreadsheet in considering both regular solid solutions, such as plagioclase and smectite, and highly mixed mineral assemblages characteristic of immature siliciclastic sediments. The mineral mass balances for waters associated with multiple-sourced clastics of the Vekol Valley, the glacial deposits of the Trout Lake area, or the intrusive-metamorphic terrain of the Inyo Mountains all require calculations testing uncertainties in the chemical composition of both the major reactant and product mineral phases. Although the spreadsheet approach permits the selection of mass balances that might not otherwise be considered, informed mineralogic judgment is key to improvement of the modeling process. *Critical consideration of the weathering phases, their solid products, and the fluid are all important in the evaluation of mineralogic controls on weathering solutions, and we have chosen examples here that illustrate how important it is to consider all three elements of the weathering equation.*

The ready adaptability of mineral-solution mass balances to matrix (spreadsheet) manipulation allows for immediate testing of model sensitivity. This includes not only variations and analytical uncertainty in the net solute fluxes between any two points in a hydrologic system, but also the testing of different mineral phases and/or their compositions. This permits rapid comparison of the effects of generic versus specific (for example, analytically determined) mineral compositions, solid solution or interlayer complex variations, and phase compatibility. Further, the limitations of the mineral solute constraints (number of equations = number of constraints) can be mineralogically alleviated by the use of *fictive phases* (for example, linear mixtures of pure mineral compositions for structurally compatible phases, such as biotite and chlorite). This approach is especially important where the bedrock contains multiple and abundant mafic phases, such as at Loch Vale, Colorado and in the Catoctin Mountain, Maryland watersheds. For clastic mixtures of silicate minerals with variable composition, such as in Vekol Valley, Arizona, or at Trout Lake, Wisconsin, further constraints are added through use of *mean reactive compositions* of mineral solid solutions, such as plagioclase.

SURFACE WATER AND SPRING WATER STUDIES

Results from work on Sierran Spring waters (Garrels, 1967) and more recently on catchment waters from Loch Vale (Mast and others, 1990) are complementary and provide key insights into the other case studies that follow. Each case is discussed separately yet the similarity of results from the two sites and to an extent the ensuing section on the Inyo Mountain watersheds clearly associates these sites.

Sierran Springs, California, and Loch Vale, Colorado

Sierra Nevada Springs.—A classic paper by Garrels and Mackenzie (1967) provided the pioneering work on mass-balance analysis of silicate-dominated hydrologic systems.

The study calculated a mass balance for two average spring-water analyses from the Sierra Nevada Mountains taken from Feth, and others (1964). Working backward from the final spring water average compositions and with knowledge of the mineralogy of rocks through which the waters flowed, and correcting for input of atmospheric solutes, they calculated the MTC's for presumed or known reactant and product mineral phases.[7] Results were obtained for relatively immature waters (ephemeral springs), and deeper, more evolved spring waters (perennial springs). The most abundant reactant minerals in the granodioritic rocks were plagioclase (An 26-41), potash feldspar, and biotite, with quartz present, but considered essentially inert. The weathering product of silicate hydrolysis by CO_2-charged ephemeral waters was mainly kaolinite, but included lesser amounts of smectite and/or silica, and goethite, especially for the perennial spring waters.

Garrels & Mackenzie (1967) suggested that calcite dissolution was required to explain the composition of perennial spring waters, although this was not proven mineralogically. This suggestion was driven by the fact that the Ca/Na ratio of ephemeral spring waters was much higher than that predicted by dissolution of An-38 plagioclase, the composition used as representative of the local Sierran rocks. It could be argued that they were the first to recognize the so-called "calcium problem" (Bowser and Jones, 1993), although not the first to explicitly use the term.

With relatively minor but critical differences, our mass-balance results corroborate the findings of Garrels and Mackenzie (1967). Unique to our study is the evaluation of the mass-balances for the waters as a function of the composition of one or more key variable-composition phases, especially plagioclase. The plot of the MTC for each phase as a function of the plagioclase composition was discussed earlier for *ephemeral spring waters*, and illustrates the dominant role that the plagioclase plays in controlling the sodium/calcium content of waters (fig. 2). As can be seen, the MTC for calcite is positive at low An-numbers and negative at higher values. Solving the mass balance equations for the point where MTC-Calcite equals zero (the cross-over point) produces a plagioclase composition of An-38, the same values used by Garrels and Mackenzie (1967) for Sierran granites in the area of the springs.

Our mass balance does suggest a small difference in the details of the silicate assemblage (table 3). If smectite is included as a phase in the mineral matrix, dissolution (rather than precipitation) achieves a balance by supplying sufficient silica in excess of alumina to make kaolinite the only clay product. However, smectite is more likely to be a product than a reactant in the surficial weathering environment of the ephemeral springs. If gibbsite formation results from alumina unbalanced by silica, as can be expected on continued leaching of kaolinite, mass balance is achieved by producing gibbsite in amounts equivalent to the smectite dissolved in the earlier model.

Comparable results were obtained for the evolution of the *perennial* spring waters, but slight differences highlight several problems that were not addressed in the original study. Using a phase/solute matrix of smaller dimension, Garrels and Mackenzie (1967) ignored the potassium in their calculation, and based the amount of biotite dissolved solely on the change in magnesium concentration (Plummer and others, 1991; Charlton and others, 1997; Parkhurst and Appelo, 1999; Parkhurst and others, 1990). If Mg and K are only derived from biotite, the only Mg- and K-bearing phases in the assemblage, then the Mg/K ratio in the water should be the same as the

[7] Although apparently dissimilar in approach to the matrix methods used here and in other versions of mass balance studies (Parkhurst and others, 1982; Parkhurst and others, 1990; and Plummer and others, 1991) the approaches are essentially identical to those used by Garrels and Mackenzie (1967), only different in that they used techniques for direct solution of the simultaneous equations rather than matrix methods. The fact that our analytical results are identical to theirs when we use the same mineral compositions and solution chemistry indicates that the two methods are essentially the same.

stoichiometry in biotite. If K-feldspar is included in their mass balance, it becomes a weathering product rather than a reactant, an unlikely case based on both thermodynamic and kinetic considerations.

Following the lead of Mast and others (1990) at Loch Vale, if provision is made for potassium uptake in smectite interlayer positions, K-feldspar then becomes a reactant phase in the mass balance. Using a beidellitic smectite with 0.25 percent interlayer K, the ratio of plagioclase to K-feldspar MTC's becomes the same as calculated for the ephemeral waters, typically ranging from 5:1 to 20:1. In our experience, the MTC ratio of these two phases is a useful reference, and in other cases studied, model results that produce ratios well outside the range 5 to 20 are considered less likely.

An important speculation from the Garrels and Mackenzie (1967) study is that additional calcium is contributed by calcite dissolution, explaining the fact that the Ca/Na ratios of the spring waters are much higher than could be explained by plagioclase (An-38) weathering alone. As seen from figure 3, the cross-over point for calcite (MTC=0) occurs at An-44. If calcium were derived solely from weathering of plagioclase, the model would require a plagioclase composition considerably more calcic than expected from the local granodioritic source rocks. This problem of excess calcium has been recognized by a number of other investigators (Nesbitt, 1984; Velbel, 1985a, 1992, 1995; Paces, 1986; Drever and Hurcombe, 1986) and we have referred to it as the "calcium problem" (Bowser and Jones, 1993).

The fact that the Ca/Na ratio of the shallow, *ephemeral* spring waters was virtually identical to that predicted by a representative An-number for the plagioclase is especially significant. First, it indicates that the granodiorite plagioclase, which is the only significant source of aqueous sodium, dissolves congruently with respect to calcium and sodium. Further, hornblende or other Ca-bearing phases (such as zoisite, apatite, or sphene), which could be still present in the regolith, might be expected to produce higher Ca/Na ratios if they were a significant contributor of Ca to the ephemeral spring waters. These results suggest that calcite was depleted from the shallow saprolite, but not from the deeper bedrock that contributed most to the perennial spring composition. White and others (1999a) have indicated that even in

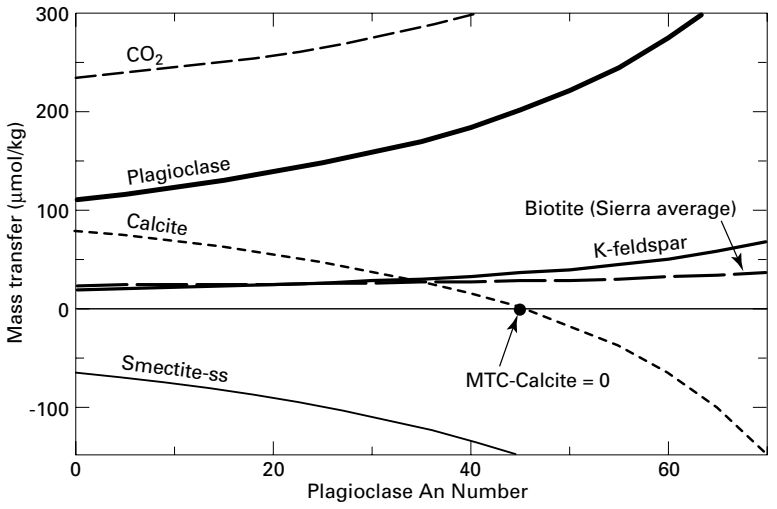

Fig. 3. Plot of mass transfer coefficients (MTC) versus plagioclase composition for perennial spring waters of the Sierra Nevada Mts., CA. Note the point where the MTC for calcite goes to zero (MTC-Calcite arrow) is well above An-38, indicating that calcite is needed as a supplemental reactant with average plagioclases (An-38).

well-drained tropical regolith, the hydraulic conductivity in saprolitic rock ("saprock") can be low enough to retard the leaching of small amounts of calcite. Earlier, Fritz (1975) had demonstrated by mass-transfer modeling that calcite could be expected as a product of normal plagioclase weathering in a closed system.

This problem of the excess calcium encountered in several comparable hydrologic environments arises from the fact that there are few abundant primary silicates other than plagioclase that contain appreciable calcium, or especially sodium.

Of course, an alternative to the problem of "excess calcium" might be the recognition of a significant sodium sink (for example, any sodium-bearing weathering product). However, in a study of weathering and solute release in the granitic terrane of the Tesuque watershed of northern New Mexico, Graustein (ms, 1981) noted ". . . sodium, and in some cases silica, are the only major rock-forming elements whose concentration in solution is controlled entirely by the dissolution of primary minerals." The only exception to this is in cases where evaporative concentration of waters leads to precipitation of saline residues (evaporites), well outside the range of conditions considered in the cases here. Resolution of the calcium problem is controversial, but recently White and others (1999b), evaluating the role of calcite in plutonic rocks around the world, have concluded that its role is largely underestimated. Especially in weathered, mountainous terrains with significant physical erosion, fresh surfaces of minerals with microcrystalline calcite are common and can influence the weathering solutions significantly. However, in clastic terrains or static saprolitic landscapes, the effect seems to be minimal, because the production of fresh, unweathered mineral surfaces is minor to nonexistent.

The primary mineral assemblages of the Sierran plutonic rocks illustrate the ability of the spreadsheet approach to rapidly and quantitatively consider variable composition of both reactant and product phases. Other mineral phases of variable composition (besides plagioclase) are the reactant ferromagnesian minerals (biotite, chlorite, and calcic amphibole) and the weathering product smectite. Garrels and Mackenzie (1967) used an idealized, end-member biotite (phlogopite) with only Mg and K as the octahedral and interlayer cations. More realistically, biotite contains significant octahedral Fe, a critical factor in determining the K/Mg ratio of the weathering mica.

Models using a higher interlayer-K for the beidellitic smectite would require that kaolinite be a reactant phase when the plagioclase composition is An-38, an undesirable solution. The sign and magnitude of the silica MTC is critically dependent on the smectite solid-solution composition (beidellite-montmorillonite). By solving mass balances using smectite with approximately 11 percent montmorillonite in solid solution, the silica MTC goes to zero, and becomes positive (a reactant) at higher montmorillonite solid-solution percentages.[8] By using appropriate phase compositions, the mass-balance results are significantly improved, highlighting the importance of direct measurement of composition for the reacting phases. The work on the Loch Vale watershed in the Rocky Mountains by Mast and others (1990) described later in this paper further highlights this point.

In addition, the relative mass transfers of K-feldspar and biotite are critically dependent on the Fe/Mg ratio of the biotite chosen. Because silicate weathering under oxygenated conditions produces nearly insoluble iron oxyhydroxide (goethite in our mass balances), the omission of iron might not seem significant. Yet, it should be evident that the Mg/K ratio of solutions derived from the dissolution of biotite is

[8] The optimum combination of percent montmorillonite and interlayer-K was calculated iteratively using the "goal seek" function of the Microsoft Excel spreadsheet. By adjusting the percent montmorillonite to produce a MTC-silica of zero, then adjusting the interlayer-K to set the MTC-ratio of plagioclase to K-feldspar to 20, and iteratively optimizing these two conditions, the final values were calculated.

TABLE 4

Comparison of MTCs using ideal, pure phlogopite (Garrels and Mackenzie, 1967) versus Sierran average biotite (Dodge and others, 1969) for perennial spring waters. Arrows indicate mineral mass transfers most significantly affected by using analyzed biotites. Mineral composition data and mineral mass transfer coefficient ratios are also shown

SIERRAN PERENNIAL SPRING WATERS			
BIOTITE COMP. →	Phlogopite MTC	Sierran Avg. MTC	(μmol/L)
Plagioclase	175.8	175.8	
Kfeldspar	8.7	8.2	
Biotite	16.1	42.3	
CO2-gas	445.2	450.6	←
Silica	0.0	0.0	
Calcite	121.8	116.4	
Smectite_ss	-111.9	-130.8	
Goethite	0.0	-54.6	←
Halite	16.0	16.0	
Gypsum	15.0	15.0	
	Mineral Composition		
Plagioclase An-No	38.0	38.0	
Pct. Montmorillonite	11.120	12.527	
Interlayer-K	0.114	0.252	
Interlayer Charge	0.500	0.500	
	Ratios		
Plag./K-feldspar =	20.1	21.5	
K-feldspar/Biotite =	0.543	0.193	
Fe/Mg (Biotite)	0.000	1.088	

determined by its Fe/Mg ratio, and that determines how much potassium is derived from the biotite and K-feldspar. Although Garrels and Mackenzie (1967) used a pure phlogopitic biotite with no iron, a more realistic model can be derived using biotites from the Sierras (Dodge and others, 1969) with Fe/Mg ratios of nearly one. Table 4 illustrates the differences in mass-balance models using pure phlogopite and average Sierran biotites. Notably, the MTC-biotite and MTC-K-feldspar are changed, but the other phases are little affected, except for the increase in product smectite. Because the iron is essentially insoluble in the fluid phase, the increased MTC-goethite reflects iron derived from the biotite.

Final mass transfers for both the ephemeral and perennial spring cases are summarized along with best-fit models for all other cases in (table 6). Reported mass-transfer coefficients incorporate adjusted interlayer-K and percent montmorillonite, and thus differ in detail from the results of Garrels and Mackenzie (1967). Using a more realistic biotite composition from analyzed material (Dodge and others, 1969) gave significantly different biotite and K-feldspar MTC's. Both ephemeral and perennial spring models gave satisfactory results with average biotite reactant and both kaolinite and smectites as clay mineral products. Note that the smectite composition utilized in the perennial spring mass balance can also encompass what, based on physical properties, might be readily termed a vermiculite.

Lock Vale, Colorado.—A similar mineral-water interaction approach to that of Garrels and Mackenzie (1967) has been used to elucidate the source of solutes in the alpine-subalpine watershed of Loch Vale in the Front Range of Colorado (Mast and others, 1990), a geologic and climatic setting comparable to that of the spring waters of the Sierra Nevada Mountains, but differing in that the latter was a surface-water catchment study, whereas the former was focused on spring waters. Additionally, (Mast and others, 1990) documented the mineralogy by x-ray diffraction and mineral compositions by electron microprobe analysis, which allowed them to improve on the approach used by Garrels and Mackenzie (1967).

The approach differs from the Sierran spring-water case in that it is a product of an integrated watershed study. Water compositions for mass-balance calculations were based on average annual budgets, effectively eliminating seasonal fluctuations of ion ratios caused by biogeochemical and other short-term processes. The mass balances assumed that the biomass was at a steady state and the release of cations from soil exchange was small compared to the net cation flux from primary mineral weathering. Of unknown significance is that the water-sampling site was downstream from a small, productive lake. Therefore, *in-lake* loss of major constituents (especially silica) must be assumed as small compared to the net watershed flux.

Granite, biotite-sillimanite schist, and granite gneiss containing quartz, An-27 plagioclase, microcline, and biotite underlie the Loch Vale watershed. Alteration along fractures and joints has replaced plagioclase with sericite plus epidote, and biotite with chlorite. Over 80 percent of the watershed consists of bare rock and active talus slopes. Soils found in forested areas, are typically acidic and less than 50 centimeters deep, and are developed on glacial till and bedrock. The soil and sediments derived from the bedrock contain kaolinite and a 2:1 layer silicate referred to as mixed-layer illite-smectite, with lesser amounts of vermiculite, gibbsite, and cryptocrystalline iron-aluminum oxides. Representative compositions for the principal silicate phases were obtained from electron microprobe and bulk chemical analysis. The Fe/Mg ratio is 1.3 and 1.5 in reactant biotite and chlorite, respectively, and 0.64 in the product smectite. The smectite contains 30 percent illite layers (effectively incorporating potassium in the interlayer sites as fixed and non-exchangeable).[9] Calcite was identified with the alteration products, as well as along grain boundaries and microfractures in the granite. This was an important observation, considering the calcite hypothesized to explain the high Ca/Na ratios of Sierran spring waters (Garrels and Mackenzie, 1967).

Mast and others (1990) used sodium as a limiting factor because plagioclase is the only significant source of this element in the watershed, and, like many other weathering environments with low ionic-strength waters, no demonstrated sodium sink

[9] The choice of either an interlayer-potassium clay, or a mixed-layer smectite-illite is immaterial for the mass-balance calculations presented here. Only the bulk chemical composition of the potassium-bearing clay needs to be considered. For purposes of mass-balance calculations it doesn't matter whether the phases are vermiculite, mixed-layer smectite, or mixtures of these phases, only the stoichiometry.

existed (Graustein, ms, 1981). This results in a weathering model indicating that plagioclase is not the sole source of solute calcium, a result consistent with the perennial spring observations of Garrels and Mackenzie (1967). Mast and others (1990) argue that nearly 40 percent of the total calcium derived within the Loch Vale watershed is contributed by the dissolution of calcite.

We have used the five-year average input-output data of Mast and others (1990) in an attempt to reexamine the mass balances obtained for the Loch Vale watershed. The results of eight models are shown in table 5 in terms of mineral-phase assemblages and mass-transfer coefficients. The models are shown here to demonstrate the effect on the final MTC's of choosing various product and reactant-phase combinations.

Successful mass-balance solutions were obtained using the same primary silicate phases and chemical compositions employed by Mast and others (1990), but in somewhat different combinations (model # 1). Significant amounts of calcite were required in the models considered. They used secondary chlorite in addition to biotite to account for the variation in the K/Mg ratio, whereas K-feldspar, cited to be one of the major primary silicates present, was omitted from the mass balance. By including K-feldspar with biotite and chlorite, the only weathering products are kaolinite and goethite. Though the ratio of plagioclase to K-feldspar MTC's was reasonable (9.5) in the model, the MTC for chlorite exceeded that for biotite, a result that is inconsistent with experience from mass-balance studies from other localities.

A second mass balance was obtained with biotite only (no chlorite), but the model required the addition of considerably more reactant silica as feldspar (model #2), which was again a questionable result. Beidellitic smectite (with the same interlayer-K and layer charge, 0.5) employed by Mast and others (1990) was obtained as a principal weathering product in this model, but the mass-balance solution allowed no iron or magnesium in the clay mineral composition. An interlayer K content was chosen in accordance with their reported values. As with the Sierran springs, the mass transfers of biotite, K-feldspar, and chlorite are strongly influenced by the Mg/Fe ratio of the mafic phases. More Fe in the biotite or chlorite requires greater mass transfer of these phases to supply sufficient solute Mg, or conversely, needs more K-spar dissolution to provide the required solute potassium.

Using the analyzed chlorite of Mast and others (1990) instead of biotite in the model (#3), a mass-balance solution was obtained with a decrease in the required silica, but the necessary K-feldspar mass transfer was nearly half of that for plagioclase, which is unacceptably high based on our experience and that of others with field-based MTC ratios (Velbel, 1993a). A balance could also be achieved without biotite by considering sericitic mica as a reactant, an alternate K source, but the MTC for mica is reduced to zero as the biotite proportion of the total phyllosilicate fraction reaches 37 percent.

Consideration of amphibole as a reactant (in combination with biotite or chlorite) (models 4 and 5) produces reasonable balances, with a plagioclase to K-feldspar MTC ratio ranging from 6.2:1 to 1.97:1. However, direct examination of the watershed by one of the authors provided no evidence for any significant amounts of amphibole minerals in source rocks, and suggested that biotite (± chlorite) was indeed the predominant mafic silicate contributing to the weathering. However, a comparison of models 2 and 3 with models 4 and 5 indicates that the inclusion of a small amount of amphibole in the balance eliminates the need to call on a separate source of silica reactant (although a small amount of quartz dissolution is certainly possible). The small amphibole MTC compared to the biotite MTC or the chlorite MTC in both these models is consistent with the very minor influence of amphibole on the final solutions, and suggests that plagioclase and calcite are the dominant sources of calcium in the watershed. Velbel (oral communication) has explored the specific question of the role of amphiboles in the Loch Vale area. Careful examination of glacial boulders derived from the watershed and subsequent thin-section analysis failed to turn up any amphi-

TABLE 5

Summary of mineral mass balance models considered for Loch Vale watershed using varying phase combinations. Note: Models #1 and #8 are essentially identical (e.g. sum of biotite + chlorite from model #1 is same as MTC For the fictive phase "biotite/chlorite" in model #8). The latter permits consideration of smectite, which remains near 0 MTC. Combination of the two models allow a mass balance solution for 11 phases with two 10 × 10 matrices

COMPARISON OF MODELS FOR LOCH VALE WATERSHED

	MODEL							
PHASES	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Plagioclase	86.30	86.30	86.30	81.50	84.25	86.30	86.30	86.30
Kfeldspar	9.02	7.43	43.52	13.15	42.69	9.02	9.02	8.63
Biotite	8.14	33.00		26.00				
Chlorite	13.73		18.23		16.58			
Amphibole				7.00	3.00	0.00	0.00	
Biotite/Chlorite						21.88	21.88	21.96
Zoisite							47.85	
Calcite	95.70	101.56	102.53	88.56	96.88	95.70		95.63
Smectite		-68.99	-80.36	-65.53	-77.85			0.61
Kaolinite	-84.14					-84.14	-155.92	-84.77
Silica		50.13	18.59					
Goethite	-48.18	-43.89	-49.59	-62.59	-57.07	-48.18	-48.18	-48.15
Halite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gypsum	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
CO2-gas	110.30	104.44	103.47	117.44	109.12	110.30	206.00	110.37
MINERAL CHEMISTRY SETTINGS								
Plagioclase An-No.	27.00	27.00	27.00	27.00	27.00	27.00	27.00	27.00
Interlayer-K (mol %)		0.33	0.33	0.33	0.33			0.33
Interlayer charge		0.50	0.50	0.50	0.50			0.50
Biotite/Chlorite fraction [0..1] ->	0.593	---	---	---	---	0.592	0.592	
RESULTANT VALUES								
Plag/K-feldspar ratio ->	9.566	11.622	1.983	6.198	1.974	9.567	9.566	10.000
K-feldspar/Σmafic ratio ->	0.412	0.225	2.387	0.398	2.181	0.412	0.412	0.393

(1) Kaolinite reactant model. Similar to that used by Mast and others (1990), (2) Biotite only model with kaolinite/silica, (3) Chlorite only model with smectite/silica, (4) Biotite amphibole model, (5) Chlorite amphibole model, (6) Amphibole chlorite/biotite model (identical to model one), (7) Zoisite model to contrast with model (6), (8) Smectite/kaolinite model (virutally same as model one).

bole, which suggests that it is either absent, or that a much more intensive investigation of the watershed is warranted.

Two models (#6 and #7) were calculated using the fictive phase "biotite/chlorite" to consider amphibole, biotite, and chlorite together. Interestingly, the results were identical to model #1, with the MTC for biotite/chlorite the same as the sum of biotite and chlorite from model #1. The MTC was zero for amphibole, further supporting the argument that amphibole has little influence on the composition of the waters from the area. These two models further differ in that zoisite was substituted for calcite in model #7. Zoisite is essentially equivalent to calcite and has little effect on the final MTC's, except for a near-doubling of the kaolinite produced. Models using both zoisite and calcite together produced unacceptably large MTC's for both minerals (considerably larger than all other reactant and product phases), with zoisite as a reactant and calcite as a product.

In model #8, a reasonable mass balance could be obtained using the fictive phase biotite/chlorite. This produces a model with essentially only smectite as a product and a reasonable ratio of 10:1 of the plagioclase/K-feldspar MTC's. No mass balance could be obtained using the gibbsite product suggested by Mast and others (1990), undoubtedly because the total primary (reactant) mineral assemblage has a Si/Al ratio equal to or greater than one, the kaolinite value. Thus, the achievable mass balances contain either kaolinite or smectite as products. All of the mass-balance models presented in table 5 give comparable MTC's for plagioclase, calcite, CO_2, and goethite. Of the eight models we have presented, models #1 and #8 are almost identical and are the most reasonable.

A more recent study of a small alpine sub-basin in the Loch Vale watershed (Clow and Drever, 1996) derived mineral weathering rates from mass-balance calculations using solute fluxes from the soil measured over five summers. The weathering reactions used were those set forth by Mast and others (1990), except that this time K-feldspar was added to the phase assemblage. The values presented for the weathering rates of the primary reactant silicates and calcite for climatically similar years are nearly identical, and quite close to the MTC's obtained in our models #1 and #8. Mast and others (1990) recognized at higher flow that solute silica exceeded what could be ascribed to the weathering of feldspars to kaolinite, which is addressed in our models (models 2 & 4) by inclusion of dissolving silica, amphibole, and/or more biotite with smectite as the principal clay product. Their calculations for subsequent years indicated that calcite and biotite-weathering rates exhibited the greatest increase in response to increases in mean seasonal discharge, with a similar but more irregular trend for feldspar. They attributed the rate increases to increased flushing of micropores, that is, the effects of continuous versus discontinuous transport. In silicate mineral mass-balance terms, this is expressed by extent of reaction, as illustrated by comparing results for ephemeral and perennial springs in the Sierra Nevada (Garrels and Mackenzie, 1967). The greater extent of reaction in the more highly weathered horizons of the ephemeral springs is illustrated by kaolinite as the only clay product in the balance, whereas smectite is the clay phase providing a suitable balance for the perennial spring case.

A comparison of our spreadsheet results with the published mass balances for the Sierran Springs studied by Garrels and Mackenzie (1967) and for the Loch Vale watershed investigated by Mast and others (1990), and Clow and Drever (1996) is presented in table 6. This reveals some important similarities and differences attributable not only to details of the method, but also to the mineral-water interaction in felsic plutonic rocks. The MTC's for both feldspars, calcite, and total clay are similar within each pair of balances, although the Loch Vale watershed values for silicate are less than half those for the Sierran Springs, and the plagioclase-An number is notably lower. At the same time, the variation in mafic minerals (biotite + chlorite) and iron oxyhyrox-

TABLE 6

Comparison of spreadsheet mineral mass balances with published data from Garrels and Mackenzie (1967), Mast and others (1990) and Clow and Drever (1996)

COMPARISON OF SIERRA SPRING AND LOCH VALE RESULTS							
	SIERRAN SPRINGS, CA				LOCH VALE, CO		
	μmol/Kg/yr 1	μmol/Kg/yr 2	μmol/Kg/yr 3	μmol/Kg/yr 4	moles/ha/yr 5	moles/ha/yr 6	moles/ha/yr 7
	This paper	G&M	This paper	G&M	This paper	Mast, et. Al.	Clow/Drever
PHASES	EPHEMERAL SPRINGS		PERENNIAL SPRINGS		Model 1, 8	Loch Vale	1990
Plagioclase	178.0	177.0	175.8	175.0	86.3	86.0	83
K-feldspar	3.9	1.3	8.2	-2.0	8.6	---	5
Biotite	18.6	7.3	42.3	14.0	8.1	26.0	30
Chlorite	---	---	---	---	13.7	6.0	15
CO2-gas	310.0	310.0	450.6	570.0	110.4	224.0	
Calcite	0.0	0.0	116.4	115.0	95.6	100.0	96
Kaolinite	-129.6	-133.2	0.0	-33.0	-84.8	-34.0	-41
Gibbsite	-16.9	---	---	---	---	-42.0	---
Smectite	---	0.0	-130.8	-81.0	0.7	-26.9	---
Goethite	-23.9	0.0	-54.6	0.0	-48.2	---	---
Halite	0.0	0.0	16.0	16.0	0.0	0.0	---
gypsum	0.0	0.0	15.0	15.0	1.0	0.0	---
Silica	---	---	---	---	---	0.0	---
Interlayer charge	0.5	0.33	0.5	0.33	0.52	0.52	0.52
Percent montmorillonite	---	0.0	12.5	0.0	0.0	0.0	0.0
Interlayer-K	---	0.000	0.252	0.000	0.320	0.320	0.320
Plagioclase An	38.2	38	38	38	27	27	27
Plag./K-feldspar	46.14	32.79	21.47	21.47	10.01	---	16.60
K-feldspar/Biotite	0.210	0.348	0.193	0.193	1.059	---	0.167
Fe/Mg (Biotite)	1.088	0.000	1.088	0.000	1.330	1.330	1.330

1) Bowser and Jones [ephermal springs] using average sierran biotite (Dodge and others, 1969), (2) Garrels and Mackenzie (1967) [perennial springs] using pure phlogopite, (3) Bowser and Jones [perennial springs] using average sierran biotite (Dodge and others, 1969), (4) Garrels and Mackenzie (1967) [ephermal springs] using pure phlogopite, (5) Bowser and Jones [Loch Vale model 1]—See table 5, (6) Mast and others (1990) [Loch Vale], (7) Clow and Drever (1996) data for 1990 only.

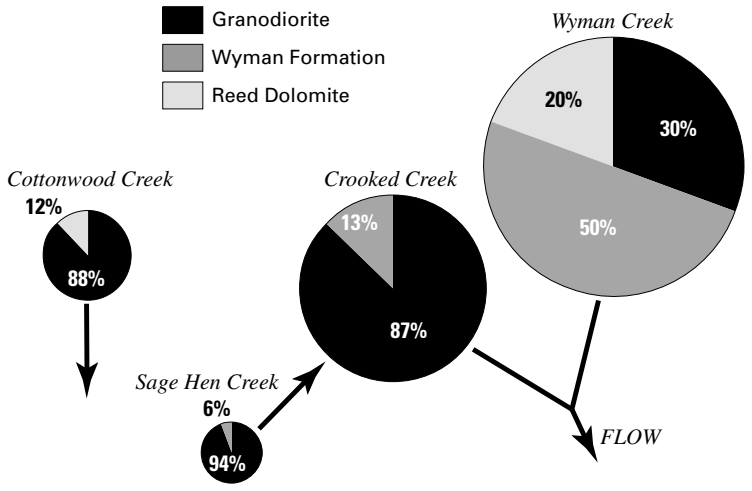

Fig. 4. Schematic illustration of drainage basins, percentage lithologies, and geographic drainage relationships for the watersheds in the Inyo Mountain, CA.

ide (goethite) mass transfer is significant, reflecting the spread in Fe/Mg ratios in the primary minerals. Definite differences in proportion of clay phases, and in smectite solid solution and interlayer charge exist in these balances, which can be further investigated for their hydrologic implications. In each comparison, our spreadsheet approach has achieved additional appraisal of primary-phase dissolution and product formation without sacrificing close quantitative similarity in mass transfer for the major reactant mineral phases.

Inyo Mountains, California

Lithologic differences among adjacent watersheds with similar but sparse vegetation influenced by the same climate should help better isolate the effects of lithology on the chemistry of weathering solutions. The question of whether the effects of silicate hydrolysis can be seen in watersheds dominated by carbonate rocks is also important. For these reasons we chose for study four adjacent watersheds on the eastern slopes of the White-Inyo Range of east-central California. The watersheds considered were Cottonwood Creek, Sage Hen Creek (Marchand, 1971), Crooked Creek, and Wyman Creek (Jones, 1965). In these watersheds Sierran Mesozoic granodiorites and adamellites are intruded into lower Paleozoic and late Precambrian sedimentary rocks dominated by dolomite, sandy argillites, and limestone (Ernst and others, 1993). Cottonwood Creek is the northernmost watershed and drains into Fish Lake Valley, Nevada. Among the other streams, Sage Hen Creek is a small, upstream tributary of Wyman Creek and Crooked Creek that joins Wyman Creek at the mountain front in northwest Deep Springs Valley, California. The relationship between the drainage areas and underlying lithic units is shown schematically in figure 4. Drainage basin areas and outcrop areas are listed in table 7. A discussion and comparison of each drainage basin follows.

The silicate mineral assemblages considered are similar to those used in the previous examples of watersheds underlain by plutonic rocks (Mast and others, 1990; Garrels and Mackenzie, 1967), and include plagioclase, K-feldspar, biotite, kaolinite, silica/quartz, goethite, and dolomite. As in the Sierran/Loch Vale cases, gypsum and halite are shown in the final mass balances as a means of correcting the sodium and calcium of stream waters for the sulfate and chloride content of rainfall.

TABLE 7

Summary of drainage areas and lithologic characteristics of the four watersheds in the Inyo Mountains. Shown are areas (in Km^2) and percentage of each lithology

Area (km^2) and (%)	Cottonwood Creek	Sage Hen Creek	Crooked Creek	Wyman Creek
Granodiorite	---	---	50.76 (87%)	23.83 (30%)
Adamellite	4.73 (83%)	2.58 (94%)	---	---
Wyman fm..	0	0.16 (6%)	7.51 (13%)	39.11 (50%)
Reed Dolomite	0.65 (12%)	0	0	15.28 (20%)
Total Area	5.38	2.74	58.28	78.22

Water analyses were obtained from published data and modified by subtracting snowmelt from average stream-water compositions. Differences between solute concentrations (water minus snow) are shown in table 2. Unlike recent watershed studies where annualized values are available, the data here are from either single samples (Marchand, 1971) or relatively few samples over a two-year period (Jones, 1965). Given the sparse vegetation in the area, and its dominance by coniferous species, we have assumed that biological dynamics exert a minor influence on the stream chemistry. The similarity of analyses from Wyman Creek sampled over a two-year period support the approach.

Comparable chloride concentrations in precipitation and stream waters suggest minimal evaporative concentration of precipitation; thus, raw data were used for mass-balance calculations. These restrictions raise questions about this analysis, but the results provide important insights into weathering processes, and especially the relative contributions of different lithologic types to the chemistry of the waters.

Cottonwood Creek.—Essentially two lithologic units underlie Cottonwood Creek. Cretaceous intrusives consisting of adamellite constitute 88 percent of the watershed (Marchand, 1971). The remaining portion of the watershed is underlain by the Reed Dolomite, a relatively pure dolomite. The creek drains intrusive rocks of the Cottonwood pluton, mapped as adamellite by Emerson (1966). The Mg/Ca ratio of the creek waters suggests that dolomite dissolution dominates the stream chemistry. However, as will be shown, subtraction of the dolomite "overprint" yields water compositions that are very similar to Sierran spring waters (Garrels and Mackenzie, 1967).

Marchand (1974) reported similar mineral compositions (probe-analyzed) of an adjacent pluton (Sage Hen pluton). Because the biotite compositions have Fe/Mg ratios of nearly one, we used an average of analyzed biotites with similar Fe/Mg ratios from nearby Sierra Nevada plutons (Dodge and others, 1969). Plagioclase compositions reported by Marchand (1974) are intermediate oligoclase (An-20), yet reported work on other nearby plutons in the area (Ernst and others, 1993) suggests compositions ranging from adamellite to granodiorite. Consequently, we considered a somewhat broader range of plagioclase compositions, from An-20 to An-40, similar to expected values for rock types in all four watersheds. Marchand (1974) also reported the presence of thin, siliceous tuff beds and soils in the drainage basin, suggesting silica glass as a possible reactant. The silica likely came from rhyolitic volcanic activity to the northwest in the Mono and Long Valley regions. These areas have been volcanically active in the Pleistocene, and their ashes are recognized in a number of Pleistocene to

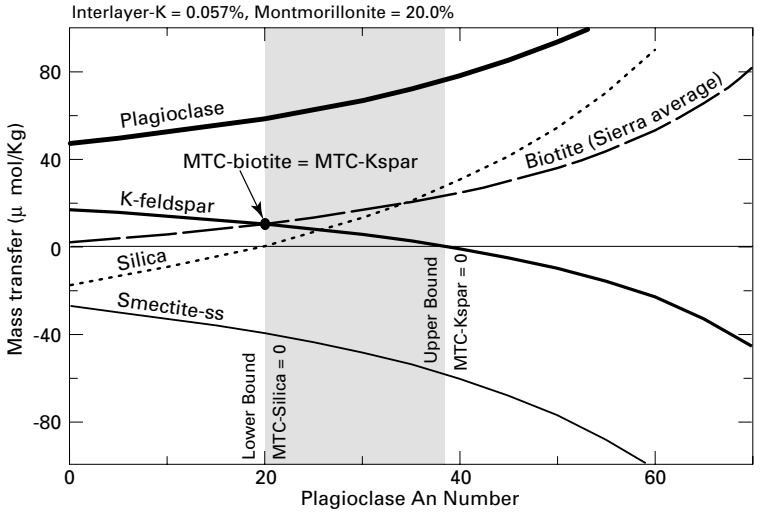

Fig. 5. Mineral mass transfer coefficients versus plagioclase composition for Cottonwood Creek waters. The box defines the upper and lower plagioclase composition limits where MTC-K-feldspar equals MTC-Biotite (arrow) and MTC-Silica are zero. Smectite composition and interlayer-K used in the model are shown in upper left.

Holocene lake sediments (Sarna-Wojcicki and others, 1993), including nearby Owens Lake.

Because of the sub-mature nature of the metasediments and the semi-arid climate, kaolinite *could be* present as an original sediment component (reactant), but, it is not likely to be a substantial contributor to the mass balances. Thus, we considered model mass-balance solutions that include combinations of silica, smectite, and/or kaolinite only as possible mineral reaction products. Possible product pairs kaolinite-smectite, and smectite-silica were considered as compatible, but silica-kaolinite pairs were rejected as incompatible (Kittrick, 1969, 1977). In as much as Marchand (1974) noted the presence of siliceous tuff beds in the watershed, we chose to emphasize the smectite/silica models over smectite/kaolinite models as more geologically reasonable. It should also be noted that *both* phases could contribute to the weathering in the watershed, but from differing protolithic substrates. Exposed adamellite could produce kaolinite/smectite weathering products alongside silica/smectite produced in or near the tuff beds or siliceous soils. Thus, our criteria for satisfactory mass-balance models in Cottonwood Creek included small positive or zero MTC's for silica or small, but negative MTC's for kaolinite.

In Cottonwood Creek, dolomite dissolution dominates the composition of the waters, with dolomite MTC's ranging from five to ten times those of comparable silicate mass transfers. With increasing anorthite content of plagioclase, dolomite MTC's decrease and feldspar MTC's increase, owing to the increased amount of calcium supplied by plagioclase. The coupled derivation of both K and Mg from increased weathering of biotite *decreases* the amount of potassium obtained from the dissolution of K-feldspar, thereby *decreasing* its MTC with *increasing* An-content of plagioclase. Above An-38, the K-feldspar MTC becomes negative, indicating the improbable precipitation of K-feldspar, and thus providing an upper bound on the dissolving plagioclase composition (fig. 5). Further, the mass-balance models are indeterminate without knowledge of the interlayer-K or beidellite-montmorillonite (Mg) content of the mixed or mixed-layer clay product. Thus, these variables were used to explore the mass-balance model possibilities.

TABLE 8

Critical plagioclase An-number crossover points (phase MTC = 0) for silica and biotite as a function of percent montmorillonite in dioctahedral smectite solid solution at two values of interlayer-K. Values calculated for average Sierran biotite composition with Fe/Mg = 1.09 (Dodge and others, 1969). Values calculated for Cottonwood Creek waters (Marchand, 1971)

COTTONWOOD CREEK DATA

Model = Silica + Smectite		Interlayer-K = 0.0		Interlayer-K = 0.2	
Biotite Fe/Mg	Percent Montmorillonite	An. No.at MTC-Silica=0	An. No. at MTC-K-feldspar=0	An. No.at MTC-Silica=0	An. No. at MTC-K-feldspar =0
1.09	0.0	33.2	39.4	45.9	52.2
1.09	10.0	25.4	37.3	36.5	50.1
1.09	20.0	17.6	35.0	27.2	47.9
1.09	30.0	9.8	32.5	17.9	45.5
1.09	40.0	2.1	29.8	8.7	42.8
1.09	50.0	0.0	26.8		39.8
1.09	60.0	0.0	23.7		36.6
1.09	70.0	0.0	20.2		32.9
1.09	80.0	0.0	16.4		28.8
1.09	90.0	0.0	12.2		24.3

Biotite data from Sierran average (Dodge and others, 1969)

Critical phase MTC cross-over points were examined as a function of montmorillonite percentage and interlayer-K, and the results are shown in table 8. Shown are plagioclase compositions for the points where the MTC's of silica and kaolinite equal zero for smectite compositions ranging from 0 percent to 50 percent montmorillonite and for interlayer-K compositions of 0.0 and 0.2 percent.[10] The upper and lower bounds of plagioclase compositions are given by the points where the MTC's go to zero for K-feldspar and silica respectively. For an actual plagioclase composition of An-20 for Cottonwood Creek, the range of possible smectite compositions is restricted and is shown in shading in the table. With minor modifications, these restrictions similarly apply to the subsequent model solutions for other nearby watersheds.

On the assumption that smectite compositions are similar across all four watersheds in the area, a beidellitic smectite composition was presumed for the Cottonwood Creek model, in accordance with more severely limited ranges of interlayer-K and montmorillonite percentage dictated by the models for the Sage Hen, Crooked, and Wyman Creek drainages. The minimum montmorillonite percentage in smectite solid solution is calculated to be 16.9 percent at zero percent interlayer-K. Any added interlayer-K in the smectites would produce negative MTC's for silica, an unlikely case considering the abundant siliceous tuff exposed in parts of the watershed (Marchand, 1974). Thus, a reasonable smectite composition compatible with a plagioclase composition of An-20, and biotite with Fe/Mg $>$ 1.0, is with 20 percent montmorillonite in solid solution. If the MTC for silica is set at zero at 20 percent montmorillonite, the interlayer-K is determined to be 0.057 percent. Higher interlayer-K would produce a *negative* MTC for silica, again unlikely. To accommodate the likelihood that silica MTC's are positive, the montmorillonite content of the smectite must be slightly higher. However, montmorillonite percentages much above 40 percent require either unreasonably high interlayer-K contents to keep the silica MTC positive, or such low interlayer-Ks that MTC's for silica exceed those for K-feldspar. The analyzed biotites for Sierran adamellites and granodiorites (Dodge and others, 1969) fit the K-Mg requirements well.

Our best mineral mass-balance model for Cottonwood Creek is bounded at the points where the MTC's of kaolinite (or silica) are zero at plagioclase with a composition of An-20 (fig. 5). For these conditions the sole products are beidellitic smectite and goethite. MTC ratios of biotite to K-feldspar are approximately one, and plagioclase-MTC/K-feldspar-MTC is approximately six at this composition, results consistent with our experience from other case studies.

Sage Hen Creek.—Sage Hen Creek is the southernmost of the watersheds studied in the Inyo Mountains, and is underlain predominantly by adamellite of the Sage Hen Flat pluton (Ernst and others, 1993), and siliciclastic sediments of the Wyman Formation (including minor limestone interbeds). Dolomite is virtually absent. The stream-water analysis was taken from Marchand (1971).

Modeling of mineral dissolution controls on these water compositions using the same mineral assemblage as for Cottonwood Creek yielded unsatisfactory results, reflecting differences in the weathering reactions for this nearby watershed. In as much as dolomite is a minor contributor (if at all) to the chemistry of Sage Hen Creek waters, it was eliminated from mass balance models. Instead, calcite was taken as the carbonate phase, consistent with its occurrence in the Wyman formation outcropping in the drainage basin.

As in the case of Cottonwood Creek, the most reasonable mass-balance results for Sage Hen Creek were obtained using beidellitic smectite and goethite as the major product minerals, with very small amounts of amorphous silica as a reactant or product

[10] Results are similar for kaolinite/smectite models, but for reasons already stated, we favor the silica/smectite models as more geologically realistic.

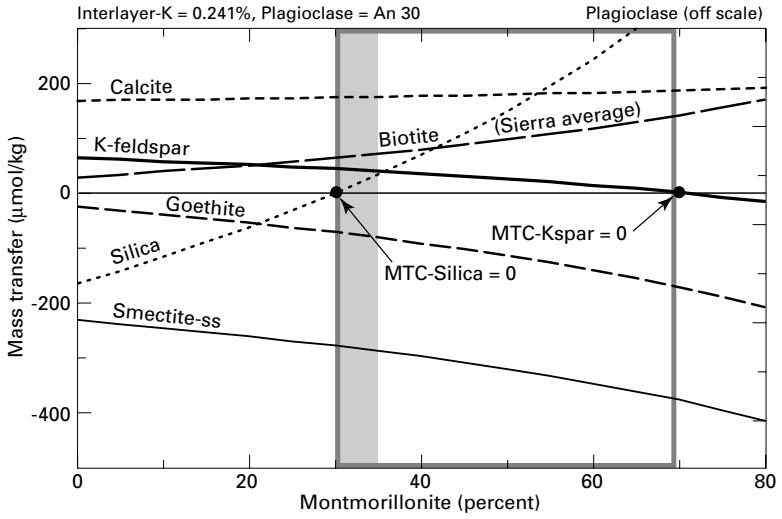

Fig. 6. Mineral mass transfer coefficients versus dioctahedral smectite composition for Sage Hen Creek waters. Satisfactory smectite compositional boundaries are shown bounded at MTC-silica = 0 and MTC-K-feldspar = 0 (unshaded box). More reasonable limits are shown in hachured area upper bounded at smectite composition where MTC-silica < MTC-K-feldspar. Plagioclase composition and interlayer-K used in the model are shown in upper left.

phase, depending on the anorthite content of plagioclase, the percent montmorillonite in solid solution in smectite, and its interlayer-K content. Compared to the Cottonwood Creek results, the Sage Hen Creek models required higher An-numbers (An-30) for plagioclase (Emerson, 1966), and slightly higher interlayer-K and montmorillonite content in the smectite to eliminate otherwise impossible analytic solutions. Figure 6 shows the mass transfer coefficients as a function of percent montmorillonite at plagioclase An-30, the composition reported for the Sage Hen Flat pluton (Emerson, 1966). An upper limit where K-feldspar MTC equals zero is at 70 percent montmorillonite, and a lower limit based on silica MTC equals 0 is at 30.9 percent montmorillonite. Clearly silica MTC's would be excessively large at the high montmorillonite percentage, and a more realistic range of composition would be between a MTC-silica of zero and MTC-silica less than MTC-K-feldspar. Thus, reasonable compositions would be in the range of 30 to 36 percent montmorillonite.

Because silica contributions are probably small, we used a silica MTC of zero to explore the range of possible smectite compositions (fig. 7A, B). An iterative procedure was used to solve for interlayer-K and percent montmorillite for plagioclase/K-feldspar MTC ratios of 5, 10, and 20, and MTC-silica equal to zero. The resulting range of smectite compositions were surprisingly limited. For the Sage Hen Flat plagioclase composition, possible mass-balance solutions were limited to a range of 26 to 39 percent montmorillonite and 0.16 to 0.37 percent interlayer-K. Taking the more typical range of plagioclase/K-feldspar MTC ratios of 10-20, the smectite compositions are even more restricted, amounting to 26 to 31 percent montmorillonite and 0.16 to 0.24 percent interlayer-K.

A small, but positive MTC for silica would be consistent with the suggested dissolution of ash from the Bishop Tuff (Marchand, 1974), and would require slightly higher An-numbers (and/or higher montmorillonite percentages in smectite, or slightly lower interlayer-K contents), as well as reduce the amount of calcium required from microcrystalline calcite assumed to be derived normally from felsic plutonic rocks (Fritz, 1975; White and others, 1999b). A plagioclase composition versus MTC plot for

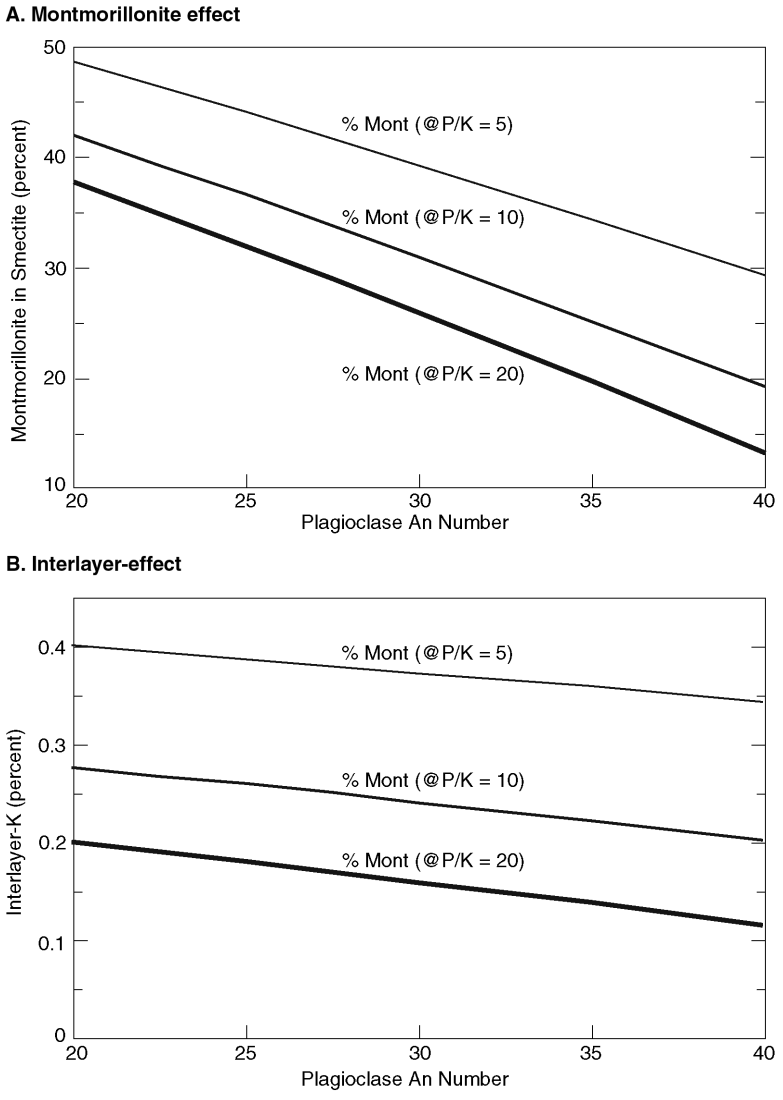

Fig. 7. Range of possible montmorillonite and interlayer-K contents of dioctahedral smectite as a function of plagioclase composition for Sage Hen Creek waters. Lines are drawn for MTC *ratios* of plagioclase (P) to K-feldspar (K) of 5, 10, and 20, the range of values typically found in watershed and ground water case-studies in this article. (A) Plagioclase versus % montmorillonite content of the smectite solid solution. (B) Plagioclase versus interlayer-K in the smectite.

30.9 percent montmorillonite, and an interlayer-K of 0.241 in the smectite is shown in figure 8. The preferred mass balance model results for Sage Hen Creek are compared with those for the other Inyo Mountain watersheds in table 9.

Clearly, confirmation of the preferred mass-balance solution requires better chemical characterization of clays in the watershed. However, the detection of 20 to 30 percent montmorillonite in smectite would not be possible with powder x-ray diffraction techniques, instead requiring high-resolution analytical electron microscopy (Banfield and others, 1991a, 1991b). Despite such uncertainty, the mass balance results are remarkably similar to those obtained for the ephemeral Sierra Nevada

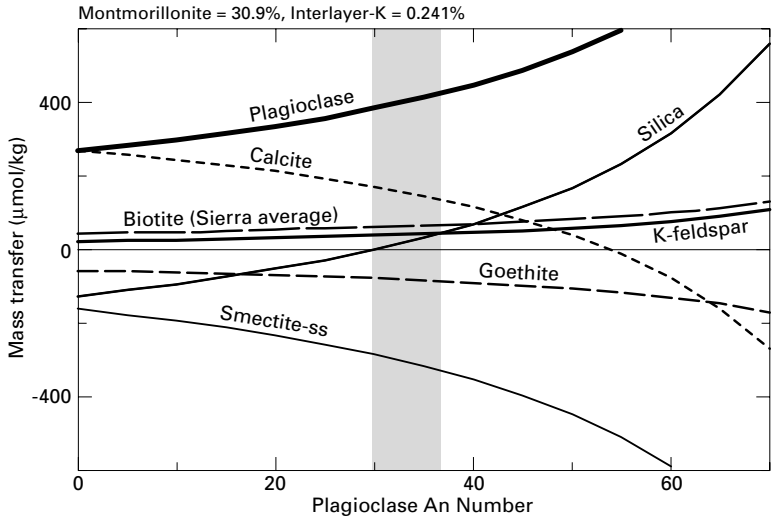

Fig. 8. Mineral mass transfer coefficients versus plagioclase composition for Sage Hen Creek waters. Hachured area represents plagioclase stability range based on MTC-silica = 0 and MTC-silica less than MTC-K-feldspar. Smectite composition and interlayer-K used in the model are shown in upper left.

TABLE 9

Best fit mass balance models for the four watersheds in the Inyo Mountains, CA

	Mass Transfer Coefficients (μmol)			
PHASE	Cottonwood Ck.	Sage Hen Ck.	Crooked Ck.	Wyman Ck.
Plagioclase	58.5	383.7	745.5	566.0
K-feldspar	9.9	38.4	74.6	60.9
Biotite	10.1	60.6	281.8	194.2
Silica	0.0	0.0	0.0	0.0
Kaolinite	0.0	0.0	0.0	0.0
Smectite-ss	-40.5	-283.9	-699.9	-511.4
Goethite	-12.7	-77.7	-363.6	-250.5
Halite	2.8	2.8	92.1	50.4
Gypsum	27.9	90.4	204.5	404.3
Dolomite	609.2	---	---	415.7
Calcite	---	171.7	700.6	676.4
CO_2	1343.4	734.6	1997.5	2566.2
Plagioclase An-No	20	30	35	35
% montmorillonite	20.0	30.9	38.7	35.0
Interlayer-K	0.057	0.241	0.327	0.250
Plagoiclase/K-feldspar	5.90	10.00	10.00	9.29
K-feldspar/biotite	0.99	0.63	0.26	0.31
Fe/Mg (Biotite)	1.09	1.09	1.09	1.09

spring water discussed earlier. Notably, the solute calcium/sodium ratio is higher than predicted from the plagioclase stoichiometry, and requires additional sources of calcium (for example, microcrystalline calcite as at Loch Vale, and in Wyman Formation limestone beds). In addition, the MTC's for K-feldspar and biotite are comparable, and the plagioclase/K-feldspar MTC ratio is similar to the Sierran and Loch Vale cases (approximately 10 to 20).

Crooked Creek.—Crooked Creek is a tributary to Wyman Creek (Jones, 1965), and drains an area composed largely of Mesozoic adamellite-granodiorite of the Cottonwood pluton (Ernst and others, 1993). Plagioclase compositions are listed as An-29, very similar to the Sage Hen Flat Pluton (Emerson, 1966). Given the similarity in watershed lithology, the water compositions for Crooked Creek should be similar to Sage Hen Creek, but with higher solute concentrations reflecting the larger area of the watershed. As with Sage Hen Creek, calcite, not dolomite, was included as a reactant mineral phase. As expected, total MTC's for Crooked Creek are higher, consistent with its greater drainage area, yet mass transfer ratios are similar to Sage Hen Creek.

A mineral-phase assemblage identical to that for the Sage Hen Creek case was used, but to keep the MTC-silica at or slightly greater than zero, we were forced to use slightly higher montmorillonite percentages and interlayer-K content in the smectites (37.7 percent and 0.327 percent respectively) at An-35 plagioclase. Again, an iterative process was used to determine the compositions corresponding to a silica MTC of zero, a plagioclase/K-feldspar MTC ratio close to 10, and a biotite/K-feldspar MTC ratio approximately equal. Interestingly, using a plagioclase composition of An-35 would bring the smectite composition closer to that derived for the Sage Hen Flat composition, compatible with more granodioritic rocks in the watershed. The slightly higher anorthite content of plagioclase is in accord with the work of Ernst and others (1993), indicating that the pluton dominating the Crooked Creek drainage is more granodioritic in composition.

The preferred mass-balance model results are compared with those for the other Inyo Mountain watersheds in table 9 using these latter values. The MTC versus plagioclase composition plots are similar to those for Sage Hen Creek.

The trend toward higher-percent montmorillonite and interlayer-K in product smectite correlating with larger drainage area and greater outcrop of Wyman Formation metasediments is noteworthy. We cannot rule out the possibility that smectites are from mixed source rocks, derived from both the weathering of granodiorite and from the late Precambrian metasediments, each different in composition. Thus, our mass-balance results could reflect mixed solutes derived from igneous biotite and/or sedimentary biotite, possibly chloritized. Clearly, a more detailed mineralogical description of the rocks from both the Sage Hen and Cottonwood plutons and their weathering would be required to further develop the mass-balance results.

Wyman Creek.—Compared to the other watersheds considered, Wyman Creek drains the largest area. It includes runoff from Sage Hen Creek, including sub-basins that are underlain by various percentages of plutonic rocks, and Precambrian/Cambrian sedimentary rocks including limestone, dolomite, shale, and sandy argillites. The geologic constraints would predict that Wyman Creek waters should yield mass-balance results intermediate between the dolomite-dominated waters of Cottonwood Creek and the granodiorite-dominated waters of Sage Hen or Crooked Creeks, and that is precisely what is observed.

Mineral-phase assemblages similar to, but in different combinations, compared to other Inyo Mountain drainages were used. The experience from the mass-balance analysis of Crooked and Sage Hen Creeks supports the prevalence of smectite in the clay-weathering product. With MTC's for kaolinite and silica set to zero, the mass-balance matrix reduces in dimension, allowing consideration of both dolomite and calcite together in this mixed sedimentary/plutonic setting. Satisfactory models were

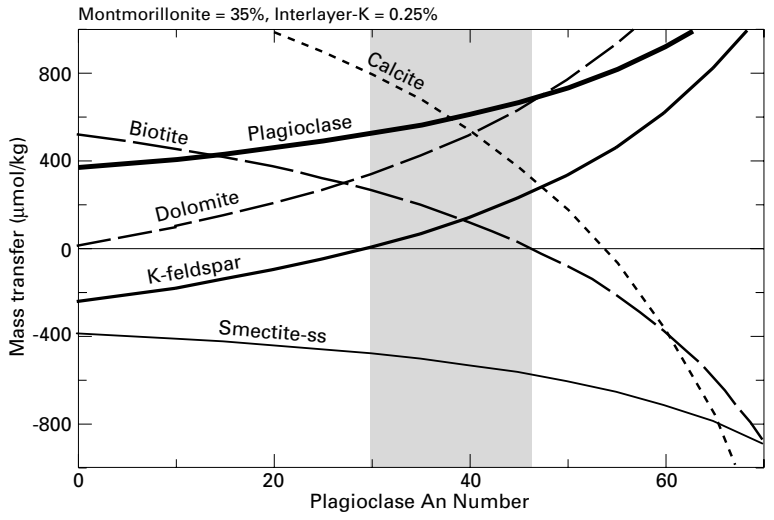

Fig. 9. Mineral mass transfer coefficients versus plagioclase composition for Wyman Creek waters. Range of possible plagioclase compositions based on lower bound where MTC-K-feldspar = 0 and upper bound where MTC-biotite = 0 (hachured area). Smectite composition and interlayer-K used in the model are shown in upper left. Note that both calcite and dolomite are included in this model.

obtained with similar percent montmorillonite, interlayer-K, and plagioclase An-numbers, as compared to other watersheds, especially Crooked Creek.

The range in anorthite composition of plagioclase possible in mass balances for the Wyman Creek watershed is surprisingly limited. As with the other Inyo Mountain Watersheds, the lower and upper limits are the points where the MTC's for K-feldspar and biotite are zero (figs. 9 and 10). Note that intermediate between the two limits, the

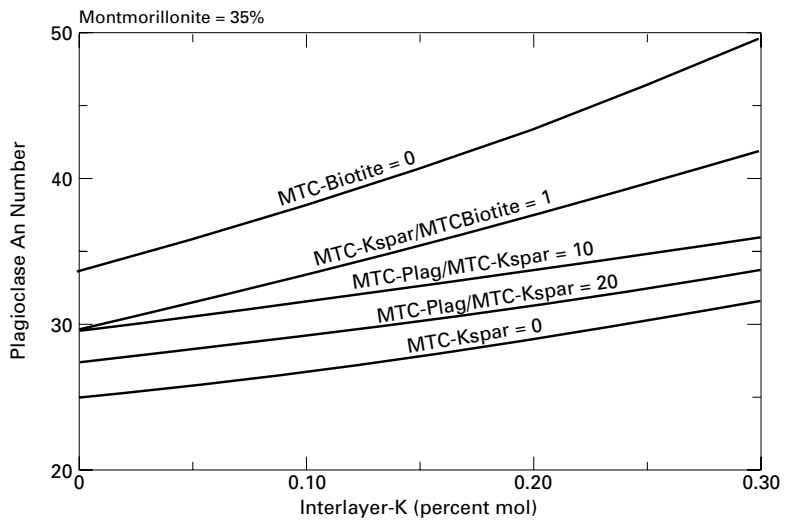

Fig. 10. Wyman Creek model mass balance solutions as function of An-number and interlayer-K. Upper and lower plagioclase compositional limits based on same criteria as figure 9. Plotted also are lines where MTC-biotite = MTC-K-feldspar and MTC ratios of plagioclase to K-feldspar are 10:1 and 20:1. Calculated for smectite composition of 35% montmorillonite.

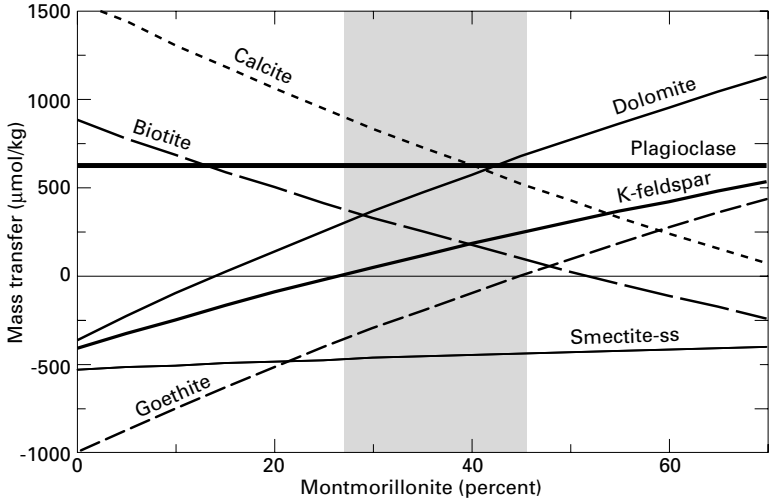

Fig. 11. Mineral mass transfer coefficients versus smectite solid solution composition for Wyman Creek mass balances. Upper and lower bounds on possible smectite compositions are where MTC-goethite and MTC-K-feldspar are each equal to zero, respectively.

MTC ratio of biotite/K-feldspar is near one, and plagioclase/K-feldspar MTC ratios are near 10.

The smectite composition is further restricted (fig. 11), showing that permissible smectite compositions are between 27 and 45 percent montmorillonite (based on cross-over points for K-feldspar and goethite, respectively). The upper and lower limit boundaries were calculated as a function of interlayer-K content for a 35 percent montmorillonite to demonstrate the compositional limits for the smectite. Finding a unique analytical solution is clearly not possible, yet mineral MTC restrictions suggest mineral compositions of approximately An-35 plagioclase, smectite with 35 percent montmorillonite, and 0.25 percent interlayer-K as the best average composition for the Wyman Creek watershed.

These compositional relationships emphasize the complex compositional dependence and mutual interdependencies in mineral mass balances, and their resulting constraints (figs. 9 and 11). Although it is not possible to find a unique analytical solution for the mass transfers considered, it is clear that definite *limits* to the range of possible solutions can be determined by consideration of the mineral composition variables controlling these results.

Despite the obvious overprint of the dolomite and calcite from the sedimentary rocks in the drainage basin, the silicate mass-balance results for Wyman Creek are similar to those obtained from the Sage Hen and Crooked Creek drainages. Further, the mass transfer coefficients (MTC's) for the phases that supply calcium (that is, calcite, intermediate plagioclase, and dolomite) are approximately equal, indicating the important role of carbonate minerals in the calcium (and magnesium) content of natural waters. Despite their lower mass abundance, the higher dissolution rate of carbonates, compared to silicates, influences the water composition well out of proportion to their mass abundance.

Considering the four watersheds in the Inyo Mountains as a whole, a surprisingly coherent model of hydrochemical evolution emerges, despite some concerns and limitations in the analytical data for the waters. The four basins offer a significant range in underlying geologic character, and yet provide a reasonably consistent set of model results (table 9). Moreover, a plot of drainage area versus stream water ionic strength

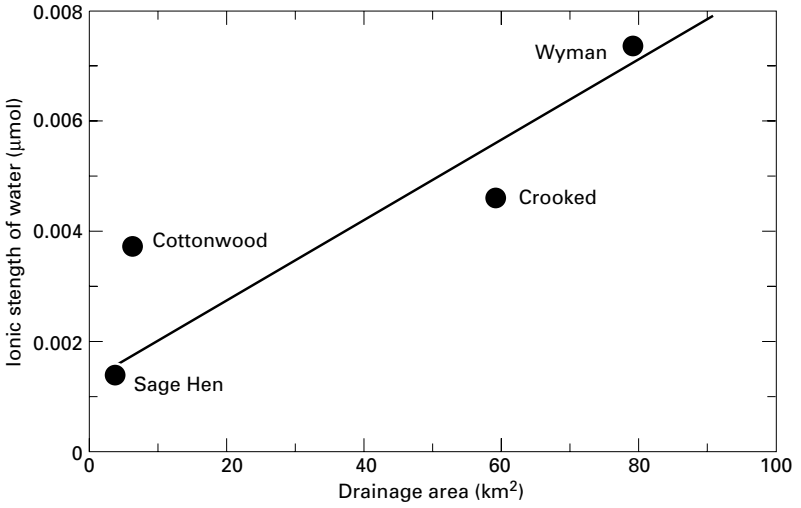

Fig. 12. Drainage area versus ionic strength of stream waters for selected watersheds in the Inyo Mountains, CA. Note offset point for Cottonwood Creek, reflecting additional solutes from carbonate dissolution.

(fig. 12) shows a reasonably linear correlation among Crooked, Sage Hen, and Wyman Creeks. Cottonwood Creek shows an anomalously high ionic strength, and this is likely due to the dominance of carbonate rock dissolution on the total chemistry of the water. The increasing order of total mineral mass transfers in the waters (fig. 13A) is appropriate for silicate weathering-dominated systems (for example, Sage Hen, Crooked, and Wyman Creeks). After removing the solutes contributed by carbonate dissolution (dolomite and calcite) in the Cottonwood Creek waters, the remaining solutes attributable to silicate weathering (fig. 1B) appear comparable to those from the kaolinite-dominated springs in the Sierras and Loch Vale watersheds (Garrels and others, 1975; Mast and others, 1990).

It is evident that the relative MTC's of carbonate minerals compared to silicate minerals are not in accordance with what would be predicted from laboratory-determined values. Velbel (1993a) pointed out that the MTC ratios of mineral pairs could be used as a measure of the *relative* dissolution rates of minerals under field conditions. Results from the Inyo Mountains invite comparison. Table 10 lists computed MTC ratios for the selected watersheds in the Inyo Mountains, and for laboratory-based ratios. Values listed were summarized from various sources (Drever, 1997b; Appelo and Postma, 1996; Blum, and Stillings, 1995; Busenberg and Plummer, 1982; and Plummer, 1977). Regardless of qualifications in the direct comparison of these rates, with one exception, all of the field-based carbonate/silica ratios are within a factor of two of each other and differ from laboratory-based rates by several orders of magnitude (Blum and Stillings, 1995; Busenberg and Clemency, 1976; and Chou and Wollast, 1984; Chou, 1985).

Two major possibilities may explain the differences between these field and laboratory-based estimates. First, the relative effective surface areas of the silicate and carbonate rock terrains are important. If, in fact, the laboratory and field-based rate ratios are assumed correct, and the calcite/plagioclase rate ratio differences are solely due to relative surface areas, it would imply that the carbonate rocks have significantly lower surface area than the silicates. This would be reasonable if the surface areas of the carbonate-rock terrains are controlled by fracture density, and if silicate-terrain surface areas are determined more by individual mineral grains. Secondly, the fact that

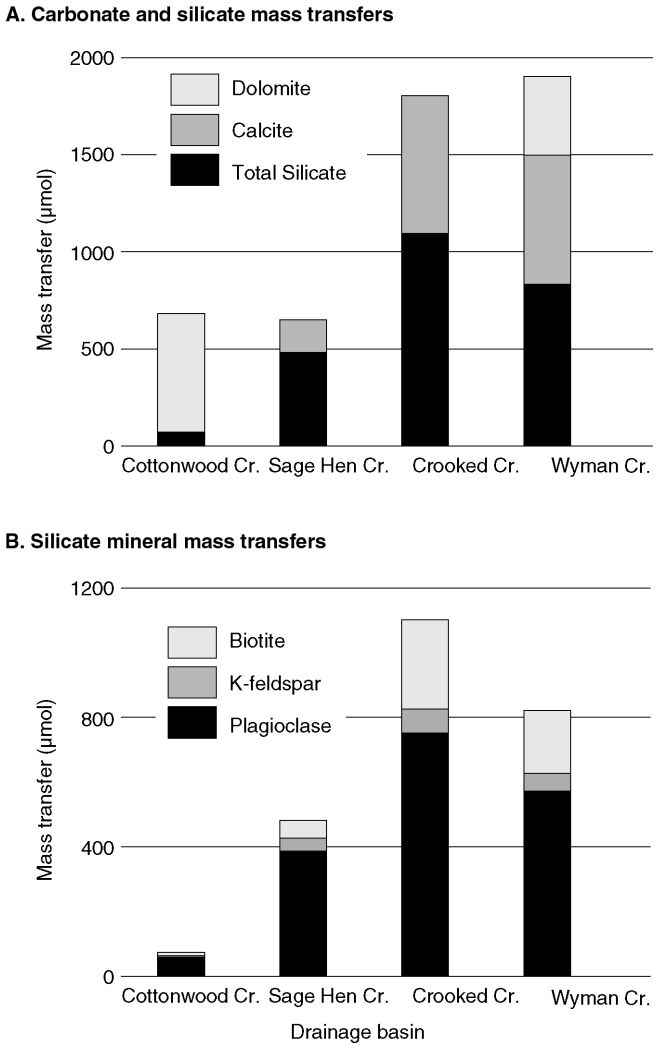

Fig. 13. Comparison of mineral mass transfers for selected watersheds in the Inyo Mountains, CA. (A) Comparison of dolomite, calcite, and total silicate contributions. (B) Comparison of minerals in silicate fraction only.

dissolution rates are, in part, determined by the degree of undersaturation of phases, "affinity effect" (Lasaga, 1995), would lead to smaller calcite/plagioclase dissolution rate ratios if the waters of the Inyo Mountain streams are at or near carbonate saturation.

Note that the critical mass-balance analysis for these waters depended strongly on detailed consideration of the geology of the watersheds, including petrography and mineralogy of the underlying rocks. For instance, the lithologic distribution in the catchments, and seemingly subtle, yet critical, differences in plagioclase compositions in the different plutons, were key factors in providing an internally consistent set of mass-balance solutions among the basins. These solutions would obviously be improved further by added mineralogic information on soils and metasediments.

TABLE 10

Mass transfer coefficient ratios for the watersheds in the Inyo Mountains, CA, in comparison to laboratory-based experiments

MTC Ratios	Cottonwood Ck.	Sage Hen Ck.	Crooked Ck.	Wyman Ck.	Lab-based
Plag/K-feldspar	5.91	9.99	9.99	9.29	2.10
K-feldspar/Biotite	0.98	0.63	0.26	0.31	1.00
Calcite/Plag.	--	0.45	0.94	1.20	80.00
Dolomite/Plag.	10.41	--	--	0.73	0.80
Calcite/Dolomite	--	--	1.00	1.63	100.00

APPROXIMATE LAB-BASED DISSOLUTION RATE (moles/cm2/sec)		
Calcite	2.00E-14	Appelo and Postma (1996)
Dolomite	2.00E-16	Appelo and Postma (1996)
Plagioclase	2.50E-16	Blum and Stillings (1995)
K-feldspar	1.20E-01	Blum and Stillings (1995)
Biotite	2.00E-17	White and others (1999)

Catoctin Mountain, Maryland

Based on the results of the studies of the watersheds in the Inyo Mountains, it was expected that the mass-balance approach should provide consistent results from adjacent watersheds having similar geologic, but more humid climatic settings, with greater seasonal variation in surface runoff and stream chemistry. We chose an example from one of the United States Geological Survey's calibrated watershed studies focused on understanding acid-rain effects on weathering in the northeastern United States. The site consists of two lithologically similar, adjacent watersheds in the Catoctin Mountain area of central Maryland (Katz and others, 1985). The two basins are of comparable area (Hauver Branch, 550 ha; and Hunting Creek, 1040 ha), and are underlain by albitized, low-grade metavolcanic rocks of the Blue Ridge Province. An all-season state highway crosses the larger basin, and is subject to winter road-salt application. Local roads, having only a small load with low traffic and seasonal use, cause minimal impact on Hauver Branch, the smaller basin. The bedrock contains major amounts of chlorite, epidote, albite, and actinolite with much lesser amounts of calcite, quartz, K-feldspar, or biotite. Weathering products are dominated by kaolinite and goethite.

The chemistry of the stream water changes with seasonal variation in the level of the water table (Rice and Bricker, 1995). When ground-water levels fall below the regolith-bedrock interface, the concentrations of calcium, magnesium, sodium, alkalinity, and silica increase, and concentrations of sulfate decrease. Acker and Bricker (1992) demonstrated the relatively rapid weathering of the Catoctin metabasalt, regardless of whether it is driven by carbonic acid weathering in the bedrock or by sulfuric acid deposition near the surface.

Our spreadsheet-based mass balances generally agree with the results of Katz and others (1985) from the Hauver Branch watershed, but not for Hunting Creek. Results are not directly comparable, inasmuch as they used a mineral/solute matrix of reduced dimension (six versus our ten). However, both sets of analyses (Katz, 1989; Katz and others, 1985) indicate that consideration of additional sources of calcium and potassium are required in these watersheds for reasons that will be discussed below.

TABLE 11

Comparison of mass transfer coefficients from Hauver Branch and Hunting Creek based on data from Katz and others (1985). Road-salt mass balance is shown for pure halite

	Hunting Creek 1982	Hunting Creek 1983	Hauver Branch 1982	Hauver Branch 1983
PHASE	1982	1983	1982	1983
Albite	-271.1	-120.0	-50.1	48.0
K-feldspar	52.1	94.8	14.1	20.8
Actinolite	206.0	243.4	118.4	156.2
Chlorite	-30.2	-6.9	57.6	33.0
Pyrite	51.5	125.0	110.5	162.0
Calcite	212.8	680.7	235.0	533.2
Kaolinite	139.7	19.5	-39.6	-67.4
Goethite	-463.5	-611.8	-347.3	-474.3
CO2-Gas	1327.2	1569.3	1045.0	1146.8
Halite	1411.3	1670.0	469.3	528.0

Concentrations in Kg/Ha. Negative concentrations for precipitates.

The larger Hunting Creek drainage differs principally from Hauver Branch in the much higher concentrations of chloride and sodium in the stream waters, a result of winter road salt application along Maryland State Route 77 that passes through the watershed. Using the data from Katz and others (1985), comparative mass-balance results from both watersheds were calculated for 1982 and 1983 and are shown in table 11.

Applying mass-balance calculations with the same mineral assemblages used in the Hauver Branch watershed to the Hunting Creek basin would require *precipitation* of albite and chlorite, thermodynamically impossible under low temperature conditions. Further, despite the fact that K-feldspar occurs only as a trace mineral in either basin, mass balances demand significant weathering contributions from K-feldspar (or biotite) from among the reported bedrock minerals. Thus, explanations of these data require either an additional mineral source for calcium and potassium and/or a sodium sink. Given that sodium is typically conservative in weathering solutions, and that sodium-bearing weathering products have not been identified in such environments, the suggestion of a sodium sink must be rejected. However, added calcium and potassium can be supplied from either or both of two alternate sources: (1) secondary constituents of road salt, or (2) the long-term loss of vegetation in the drainage areas.

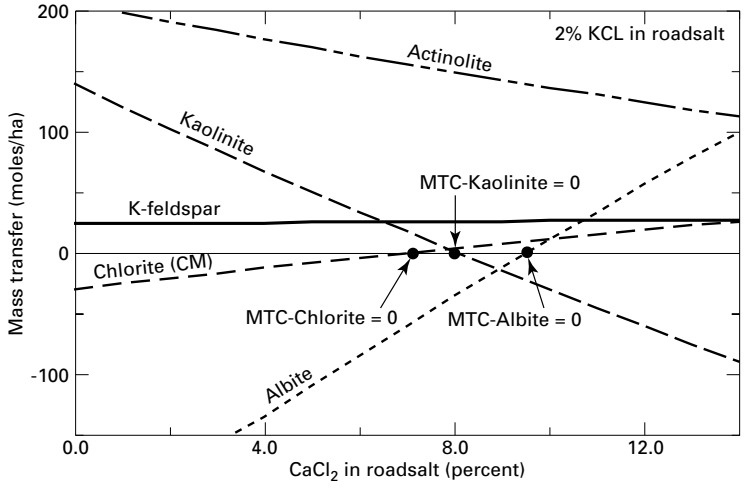

Fig. 14. Mineral mass transfer coefficients for Hunting Creek watershed (1982) versus percent $CaCl_2$ in road salt (with two percent KCl). Note that MTCs for both albite and chlorite should be positive, limiting the lower concentration of $CaCl_2$ to 9.6 percent.

The large chloride loading for Hunting Creek from the use of winter de-icing agents provides a source of sodium, calcium, and probably potassium. Katz and others (1985) estimated that 10 to 20 percent of the total ion equivalents in subsurface waters could come from this source. To explore the road-salt contribution we devised a mass-balance phase, informally termed "road salt," as a mixed mineral consisting dominantly of halite with small and variable percentages of sylvite (KCl) and antarcticite ($CaCl_2 \cdot 6H_2O$), the latter reflecting a calcium additive commonly used for de-icing under colder temperature conditions. Considering halite-antarcticite mixes only in Hunting Creek for the years 1982 and 1983 would require 10.6 and 3.7 mole percent calcium chloride, respectively, in the road salt to reduce the mass-transfer coefficient for albite from negative (a weathering product) to zero.

Sylvite (KCl) is present in small quantities in commercial road salt. By adding two percent KCl to the road salt mix, the amounts of $CaCl_2$ required to reduce the MTC for albite to zero are lowered to 9.5 and 2.7 percent for these same years cited above. Mineral mass transfers for the water year 1982 were calculated, and are shown in figure 14 as a function of percent $CaCl_2$ at a fixed 2-percent KCl. The very low modal abundance of K-feldspar in the watershed (Badger, 1989) suggests its contribution to stream water potassium would be very small (Katz and others, 1985). Thus, alternate sources of potassium are suggested.

Due to the relatively large road salt loading in Hunting Creek (tables 11, 12), the potassium contained in road salt can significantly affect mass-balance calculations, and the mass transfer terms for K-feldspar, chlorite, and albite. Analyzed rock-salt data (Stewart, 1963) suggest 1 to 2 percent KCl is not unreasonable. However, concentrations ranging from 3.7 to 5.7 mole-percent KCl would be required to reduce the K-feldspar MTC to nearly zero (for the 1982 and 1983 samples, respectively). At higher $CaCl_2$ concentrations, the required KCl would be even greater (4.1 to 6.2 mole-percent at 10-percent $CaCl_2$). This dependency is illustrated in figure 15, where, the effect of $CaCl_2$ on the albite MTC, and the percent KCl required to reduce the K-feldspar MTC are shown for 1982-83. Clearly even more $CaCl_2$ would be required to produce albite mass transfers greater than zero, and that would require even more KCl to reduce the MTC-K-feldspar to reasonably low levels. Allowing for a small contribution of calcium and even less potassium from road salt can help resolve, but not eliminate the problem.

TABLE 12

Revised mass transfer coefficients with road-salt correction for 6.5% $CaCl_2$ and 3.5% KCl. Paired columns are a comparison of mass balance solutions using calcite or epidote. (Compare with table 11.)

	Hunting Creek		Hauver Branch	
	(HC-1)	(HC-2)	(HB-1)	(HB-2)
PHASE	kg/ha	kg/ha	kg/ha	kg/ha
Albite	139	139	130	130
K-feldspar	40	40	3.4	3.4
Actinolite	188	154	139	112
Chlorite	26	47	44	59
Pyrite	125	125	162	162
Calcite	**688**	**---**	**535**	**---**
Epidote	**---**	**252**	**---**	**196**
Kaolinite	-116	-388	-110	-322
Goethite	-501	-686	-440	-583
CO2-Gas	1561	2250	1144	1680
"Roadsalt"	1568	1468	496	596

HC = Hunting Creek, HB = Hauver Branch

Sources of sulfate are equally ambiguous. Katz and others (1985), Katz (1989), and Rice and Bricker (1995) suggested that precipitation and dry fall could account for the major sulfate input in the watersheds. However, a factor of two difference in sulfate loading per unit area between the two watersheds is inconsistent with atmospheric sources for all the sulfur. Moreover, pyrite in the bedrock strongly suggests that it is an added source of sulfate through oxidation. Thus, we used pyrite as a reactant phase for the calculations shown in tables 11 and 12. It is also worth noting that using low $CaCl_2$ percentages produces negative MTC's for pyrite, a thermodynamically improbable result under surface-weathering conditions, and provides an effective *lower bound* on the range of allowable $CaCl_2$ concentrations.

Reasonable balances can also be achieved by using a fictive phase "atmospheric precipitation"(atm. ppt.) representing the input of sulfate balanced by hydrogen ion and not calcium. Yet whether sulfate is derived primarily from atmospheric precipitation (wet fall and dry fall) or from pyrite oxidation will appear only in the magnitude of the pyrite and goethite mass transfer coefficients. Through-fall calcium sulfate could

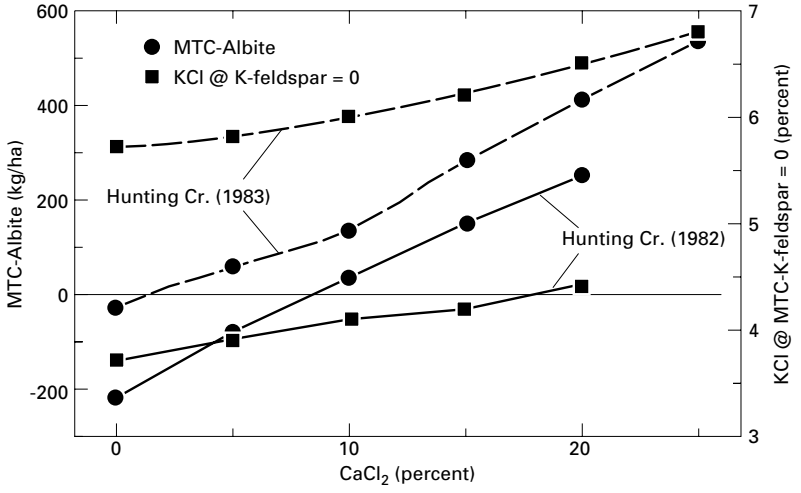

Fig. 15. Effect of $CaCl_2$ in road salt on MTC-albite and minimum percent KCl in road salt required for positive K-feldspar mass transfer coefficients. Data for 1982 and 1983 in Hunting Creek watershed.

provide an additional calcium source, and thereby reduce the input from other calcium-bearing minerals, such as calcite, actinolite, or epidote. Moreover, an added source of calcium would also reduce the ratio of amphibole to chlorite, and bring it more in line with what might be expected from silicate modal abundances.

Vegetation effects should be considered as alternate sources of potassium and calcium in the Catoctin Mountain watersheds. Short-term (less than one year) variations in stream chemistry from the two basins are typical for many streams in vegetated regions, and reflect the dynamics of annual plant growth and decomposition (Likens and others, 1994, 1998; Taylor and Velbel, 1991; Velbel, 1995). For a forest at steady state with respect to its total biomass, the flow-weighted, mean annual composition should vary little from year to year. If, on the other hand, forest biomass was either increasing in response to changing local climatic conditions, nutrient loading, or recovery from deforestation, or decreasing from the effects of plant disease or atmospheric loading (for example, acid precipitation), the flow-weighted, annual mean composition should vary from year to year in response to these changes.

The record of plant diseases and insect infestations may provide evidence for local vegetative loss, despite a general observation that biomass is accumulating in watersheds of the eastern United States (Velbel, 1995). Puckett (oral communication) indicated that a severe oak blight infestation was evident in nearby Virginia about the time of the studies reported by Katz and others (1985). In a later application of mass-balance considerations to soil water and springs in the area, Katz (1989) estimated that the net contribution of total ion equivalents from biological processes ranged up to 20 percent.

It is important to note that our recognition of the implications for biomass contributions of potassium and calcium initially came solely from mass-balance analyses attempting to use $CaCl_2$ and KCl additions to road salt. Further analysis of the range in mass transfers over seasonal to multi-year periods (Rice and Bricker, 1995) resulted in increased understanding of the role of vegetation on major ion dynamics. This experience has suggested that mineral mass balances can be sensitive indicators of biomass changes, even when these changes are not fully evident from field observations.

Hauver Branch, the Catoctin watershed less affected by road salting, has been monitored continuously since 1982. O'Brien and others (1997) used a mass-balance

approach to summarize ten years worth of observations from this, as well as four other mid-Atlantic watersheds, and included improved mineral analyses based on the work of Badger (1989). As with earlier work (Katz, 1989; Katz and others, 1985) discrepancies in the expected contribution of particular cations relative to the abundance and reactivities of minerals identified suggested other solute sources for the streams, especially in the case of calcium and potassium.

For Hauver Branch, the contribution of calcium from bedrock weathering is determined by actinolite-amphibole, and epidote, or calcite. Published dissolution kinetic data would suggest that calcite and, to a lesser extent, amphibole are significantly more reactive than epidote (Sverdrup and Warfvinge, 1995). However, the abundances given by O'Brien and others (1997) for epidote (24 percent) and amphibole (2.4 to 9.8 percent) relative to calcite (<2percent) suggest that these silicates could be important calcium sources, especially considering the low modal percentage of calcite in the watersheds. Thus, we calculated mass balances using epidote (as well as actinolitic amphibole) instead of calcite as a key calcium-bearing bedrock phase. The epidote and calcite balances were calculated separately, so as not to increase the mass balance matrix beyond ten. The results are shown in table 12. Use of either of these phases does not significantly alter the mass-transfer coefficients for the feldspars, but it does modify the proportions of the product phases, so that more kaolinite is produced (and CO_2 consumed) using epidote.

Because of the more specific consideration of Fe and Al, the 10 by 10 matrix in our models leads to a reversal of the relative mass transfers for amphibole and chlorite as compared with the 6 by 6 matrix used by Katz and others (1985), but not compared with their later published calculations (Katz, 1989). Note that the Si/Al ratios of the primary silicates used in our analysis are all greater than or equal to one. Because kaolinite (Si/Al=1) is the only silicate included in the weathering product assemblage, an excess of solute silica must be produced, and the stream silica values are in accordance with this effect.

In the absence of specific mineral analyses for mass-balance calculations, idealized compositions have often been employed, that is, the so-called "plausible phases" (Parkhurst, 1982). The question arises as to how important are precise mineral analyses, especially considering the number of samples necessary to be statistically representative of a given watershed. O'Brien and others (1997) attempted to evaluate the effectiveness of mass-balance models using a comparison of idealized mineral chemistry and analytically determined phase compositions (Badger, 1989) for samples from the Hauver Branch watershed. Their comparison was based on a 10-year mean of precipitation and stream flow analyses, and mass balances calculated by NETPATH. Their data were processed using a correction technique that allows for reverse exchange of sodium for calcium on mineral surfaces in soils due to road salt (Shanley, 1994) by reference to the $Na+/SiO_2$ ratio in uncontaminated groundwater.

Using data from O'Brien and others (1997), we calculated spreadsheet mineral mass balances with both idealized and analyzed mineral data. This effort reproduced the problems seen in comparing the relative mass-transfer coefficients in the original model with modal analysis of the metabasalt, that is, too little albite and too much K-spar compared with the mafic minerals, and too much amphibole relative to chlorite. However, utilizing the *mineral* composition-based correction of Shanley (1994) that relates the Na flux to the Na/SiO_2 ratio of bedrock plagioclase, the Na output of the watershed was increased over the chloride equivalent by an amount equal to 1/3 the SiO_2 flux (the ratio in albite), and an equivalent amount subtracted from the output of Ca & Mg in the stream. This appears to neglect silica derived from other silicates (for example, chlorite and actinolite), but actually assumes that this SiO_2 is incorporated in kaolinite. To avoid an ionic imbalance associated with the mean data used by O'Brien and others (1997), and to examine the effects of annual climatic

TABLE 13

Comparison of NETPATH-based mass balances from O'Brien and others (1997) for idealized and analyzed mineral composition with results from spreadsheet analysis. Note: O'Brien and others used a 7 × 7 matrix vs the 10 × 10 matrix used in here. Both sets of data use Shanley (1994) Na ion-exchange corrections for road salt, but with different Na/Si factors

Calculation Source:	O'Brien et al., 1997 (NETPATH)		This paper		
Mineral Composition:	Idealized mineral compositions	Probe-analyzed minerals (Badger, 1989)	Idealized mineral compositions	Probe-analyzed minerals (Badger, 1989)	
Albite	494	421	269.0	286.3	
K-feldspar	---	---	26.5	8.3	
(Biotite)	36	---	---	---	
Actinolite	102	179	28.0	32.3	
Chlorite	46	224	62.1	159.4	
Calcite	795	676	437.6	416.2	
(K-montmorillonite)	---	-127	---	---	
Kaolinite	-311	-405	-214.7	-347.7	
Goethite	---	---	-293.9	-527.2	
Pyrite	---	---	239.2	81.4	
CO2-gas	2482	2600	1060.8	1082.1	
Road salt	---	---	584.5	584.5	<--Pure NaCl

Units: mol/ha/yr.

Albite/(Actinolite + Chlorite) =	3.34	1.04	2.99	1.49	
Albite/K-feldspar =	---	---	10.2	34.5	

variation, our balances were computed on the salt-corrected data for each of the 10 years of record, and were then averaged (table 13). Although differential mineral weathering rates prevent absolute comparisons (as illustrated by the relatively large MTC's for the very small amount of calcite in the rocks), the resulting mass transfer coefficients were more consistent with silicate modal ratios for the metabasalts. In a nearby watershed, Logan and Dyer (1996) obtained similar mass-balance results through estimation of the pre-salt-contaminated solute Na composition by calculation from an average cation ratio of area waters, rather than from the feldspar Na/SiO_2 ratio.

As with observations at Loch Vale (Clow and Drever, 1996), interannual mass transfers were correlated with the precipitation record. From 1982 through 1992, elevated levels of dissolution in Hauver Branch were generally obtained for wet years, and minimum amounts for dry, especially if similar annual climatic conditions occurred successively (fig. 16).

Final results from our models are compared with the NETPATH mass balances of O'Brien and others (1997) in table 13. Differences are due to several factors. Most obvious is their use of only seven mineral phases, whereas our spreadsheet employs ten. Moreover, they used a slightly different set of phases for their idealized versus analyzed mineral composition runs (biotite in one case and K-smectite in the other). The mass balances employed by O'Brien and others (1997) used an evaporation factor of 2.2 to correct for runoff ratio, which should result in MTC's roughly twice the magnitude we calculated; however, the ratio of their mineral mass transfers to ours is not the same for all phases, ranging from 1.2 to 5.5. Finally, there are differences in the mafic mineral assemblages used. The mass transfers for goethite, pyrite, as well as the reactant minerals, cannot be the same because original Fe/Mg ratios were different. Despite these variations, the ratios for feldspar, total mafic minerals, and calcite remain broadly

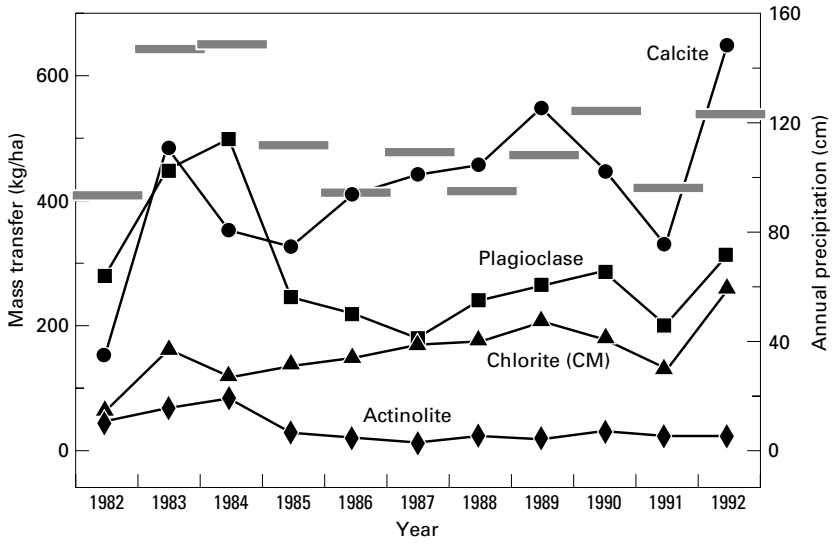

Fig. 16. Mineral mass transfers for Hauver Branch watershed from1982 through 1992. Also plotted is annual precipitation (bars). Based on spreadsheet mass balances obtained from O'Brien (1997) data corrected for road salt (Shanley, 1994).

similar in the results from O'Brien and others (1997) and ours. As noted earlier, the balance derived from the analyzed mineral compositions is also the most consistent with the relative modal abundance for the mafic minerals. These results suggest the superiority of the specifically analyzed mineral compositions, and emphasize the importance of obtaining this type of data for the best mass balances.

GROUNDWATER STUDIES IN SEDIMENTARY ENVIRONMENTS

The mass-balance cases described up to this point were drawn from calibrated watershed studies or surficial spring systems where the detailed hydrology can be complicated, but the bedrock lithologies are relatively well-defined. The study of ground-water systems avoids the heterogeneity and variable organic conditions of soils, and dampens short-term climatic, biologic, or anthropogenic effects. On the other hand, clastic, silicate aquifers generally add compositional complexity to the mineral-water interaction in crystalline bedrock. Source materials for these aquifers are mineralogically diverse, and although largely dominated by relatively few silicate phases (that is, quartz, K-feldspar, and plagioclase), other minor minerals can exert considerable control on the resulting water compositions. Moreover, and perhaps more important, is the fact that the mineral assemblage, being a mechanical mixture from various sources, provides a wide range of compositions for even the same phase. For example, heterogeneous crystalline source rocks can range in plagioclase composition from albite to labradorite. Because mass balances are algebraically limited (number of phases = number of solute constraints), special modifications to allow for compositional variability and phase diversity must be found. The following two examples of clastic ground-water aquifers do not permit assumptions of mineralogic homogeneity, but illustrate the advantages of flexibility in the spreadsheet method for examining mineral controls on solute evolution along a flow path.

Vekol Valley, Arizona

Ground water in crystalline or siliciclastic terrains, such as at Vekol Valley, Arizona, provide suitable conditions to examine the effects on silicate mass balances of

sufficient reaction time and surface exposure, compositional variation in silicate reactants and products, and open versus closed systems. Where there are a number of wells along a well-defined flow path, the effects of distance, topography, variable recharge, and lithologic change can be evaluated by comparison of well pairs along the presumed flow path. If independent evidence for ground water-flow rates and mineral grain-size distribution is available, the mass transfer data can be used to estimate field-based mineral dissolution rates.

Robertson (1991) presented an extensive analysis of groundwater evolution in intermontane basins of southern Arizona employing NETPATH (Plummer and others, 1991) mass balance. Models were developed from chemical analyses of waters collected from wells along general flow paths for selected topographically closed basins based on the difference between water compositions observed in recharge areas and water compositions determined for down-gradient wells. Reactant and product mineral phases used in the models and their average chemical compositions were chosen to be consistent with overall basin geology.

Robertson (1991) chose Vekol Valley, one of 6 from the 72 identified basins in Arizona, as typical of the topography and geology of many of the arid basins in the south-central part of the state, and the valley is representative of a predominantly ground water drainage basin developed in a variety of crystalline rock types and extensive alluvium derived therefrom. The Vekol Basin is bounded on the east by schist, granite, and andesite of the Table Top and Vekol Mountains and on the west by andesite, basalt, and schist of the Sand Tank Mountains where the most abundant recharge occurs. The alluvial aquifer consists of several hundred feet of sand and gravel overlain throughout much of the basin by thick silt and clay. Ground-water flow is toward the center and thence southward out of the basin. Reactions were modeled starting with average rainfall and including three wells along a flow path from close to the mountain front on the west to near the center of the basin, referenced as Vekol-1, Vekol-2, and Vekol-3 in the following text.

Robertson (1991) concluded that the ground-water compositions in the Vekol Valley are dominated by hydrolysis reactions of recharge waters with plagioclase and mafic silicate (represented by the pyroxene, augite), plus precipitation of calcite down gradient, and the formation of montmorillonitic smectite, leading to increased pH and depletion of alkaline-earth cations in the central valley ground water. Robertson's (1991) mass balance utilized a small amount of ion-exchange to account for a portion of the decrease in calcium and increase in sodium concentrations.

Ground-water chemical data is presented in table 2. Several characteristics of the well-site mineralogy and water chemistry are particularly relevant to mass-balance analysis. The clastic plagioclase feldspars range from andesine through bytownite; Robertson (1991) suggested that andesine (An-45) was the mean reactive composition. Other detrital phases include quartz, potassium feldspar, muscovite, and minor pyroxene (augite). Clay fractions are dominated by mixed-layer smectites, with minor kaolinite and muscovite. Calcite was observed in most samples. Importantly, the water temperatures in all three wells were greater than 35°C, which should accelerate mineral weathering reaction rates.

Hydrochemical changes down gradient along the Vekol Valley flow path are larger than those typical of the watershed studies discussed earlier. The waters are predominantly sodium bicarbonate type, with calcium and chloride the next most abundant ions. Concentrations of sodium, chloride, sulfate, and potassium all increase down gradient, whereas alkalinity, magnesium, and calcium all decrease. Silica concentrations remain relatively constant. The large increase in chloride suggests dissolution of older, buried playa salts, but inasmuch as sodium concentrations increase to approximately twice the level of chloride, additional sodium sources are necessary.

TABLE 14

Saturation indices for critical minerals in ground water from Vekol Valley, Arizona

	SATURATION INDICES		
Phase	VEKOL 1	VEKOL 2	VEKOL 3
Albite	-1.13	-1.02	-0.88
Anorthite	-3.05	-3.57	-3.53
K-feldspar	-0.44	-0.41	0
Kaolinite	2.61	1.23	2.9
Gibbsite	0.15	-0.46	0.34
Ca-Montmorillonite	1.63	0.07	1.79
Calcite	-0.08	-0.1	-0.87
Talc	1.63	2.1	-2.19
Halite	-7.52	-6.69	-7.42

Saturation indices for waters were calculated using PHREEQC (Parkhurst and Appelo, 1999), and results are shown in table 14. Plagioclase is undersaturated over its entire compositional span, and K-feldspar indices range from slight undersaturation to near equilibrium in well Vekol-3. Calcite indices were calculated to be near equilibrium in the shallower wells and slightly undersaturated in well Vekol-3. Small changes in pH or PCO_2 between collection and analysis of waters at the 36+ degree temperatures reported can account for such a discrepancy (Robertson, oral communication), and this becomes a factor in the interpretation of the mass-balance results.

Several reasonable mass balances were obtained for all three Vekol Valley well pairs. These balances considered multiple mineralogical variables, including plagioclase composition, interlayer-K content of the mixed-layer smectite, dioctahedral smectite solid solution (beidellite to montmorillonite), and composition of augitic pyroxene. Use of Robertson's representative plagioclase (An-45) and his analyzed augite composition, variable smectite composition, interlayer-K, and the presence of other minor minerals, were important to obtain satisfactory mass balances. Cross-over points on the mass transfer versus feldspar or smectite composition plots define the upper and lower bounds for mass-balance solutions (for example, where augite MTC's go from positive (possible) to negative (impossible)). The most reasonable models are summarized in table 15 and plotted as a function of plagioclase and dioctahedral smectite solid solution in figures 17 and 18. Mineral mass transfers for all three well pairs are presented graphically in figure 19.

Not surprisingly, the mass transfers between wells indicate that the bulk of the weathering takes place in the upper segments of the flow path, and the amounts of plagioclase and potash feldspar reacted, as well as the amount of smectite formed, are very similar for these segments. Further, the ratios of plagioclase to K- feldspar are within the range found in the Sierra and Loch Vale examples. The quantities of augite dissolved, CO_2 consumed, and iron oxide formed are similarly diminished for the interval between Vekol-2 and Vekol-3 wells (nearly an order of magnitude smaller).

The mass balances indicate that calcite deposition takes place throughout the system, with the largest mass transfers between the up gradient well pairs. Following comparatively rapid dissolution of ferromagnesian minerals in the shallow up gradient portion of the aquifer noted by Robertson (1991), the ground water flow continues at depths below significant atmospheric or soil zone sources of CO_2. Thus, additional reaction takes place effectively in a closed system, dissolved CO_2 is reduced, and mass transfer is diminished.

TABLE 15

Comparison of spreadsheet mass balance results with values calculated by Robertson (1991). Significant differences arise from his use of silica and ion-exchange as "phases", in contrast to our use of smectite of variable composition

	VEKOL VALLEY, ARIZONA					
	Rainwater->Vekol-1		Vekol-1 -> Vekol-2		Vekol-2 -> Vekol-3	
PHASE	This paper	Robertson	This paper	Robertson	This paper	Robertson
Plagioclase (An45)	2620	1330	2651	2330	278	10
K-feldspar	325	60	358	170	135	90
Augite	323	510	80	280	2	50
Silica	---	-630	---	-440	---	-170
CO2-gas	920	---	274	---	144	---
Smectite_ss	-2249	-1060	-2146	-1820	-312	-40
Palygorskite	36		0	---	12	---
Calcite	-2170	-1580	-1751	-1730	-310	-180
Goethite	-282	-250	-56	-20	-20	-20
Halite	25	20	1326	1330	282	280
Gypsum	55	50	479	480	238	240
Ion Exchange	---	350	---	90	---	80
Interlayer Chg	0.50		0.50		0.50	
% Montmorillonite	53.50		53.50		53.50	
Interlayer-K	0.15		0.15		0.15	
Plagioclase An Number	45		45		45	
Plagioclase/K-feldspar =	8.06	22.17	7.41	13.71	2.06	0.11
K-feldspar/Augite =	1.01	0.12	4.49	0.61	62.34	1.80
UNITS in μmoles/Kg rock/year						

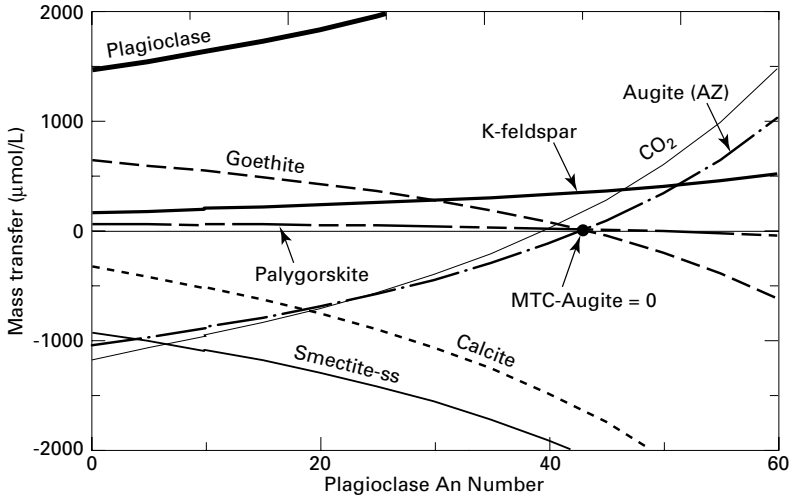

Fig. 17. Mineral mass transfer coefficients versus plagioclase composition for well pair Vekol-1 to Vekol-2. Smectite composition: 53.5% montmorillonite, 0.15% interlayer-K. Augite MTC < 0 below An-43.

Mass transfers for halite and gypsum reflect the solute dissolution along the flow path indicated by increases in Na, Cl, and SO_4 down gradient. Considering the climate and geomorphic history of the area (Robertson, 1991), this suggests that the ground waters are traversing older and/or buried playa or other saline deposits. In as much as the only Na-bearing phases in the mass balances are reactants, all the sodium from weathering ends up in the fluid. Because the principal Na-source mineral is plagioclase, the plagioclase mass-transfer coefficients are driven by the changes in solute sodium in the ground water.

Mass balances including the chain-structure clay, palygorskite, and zeolites (erionite and clinoptilolite, the latter giving slightly more reasonable results than the

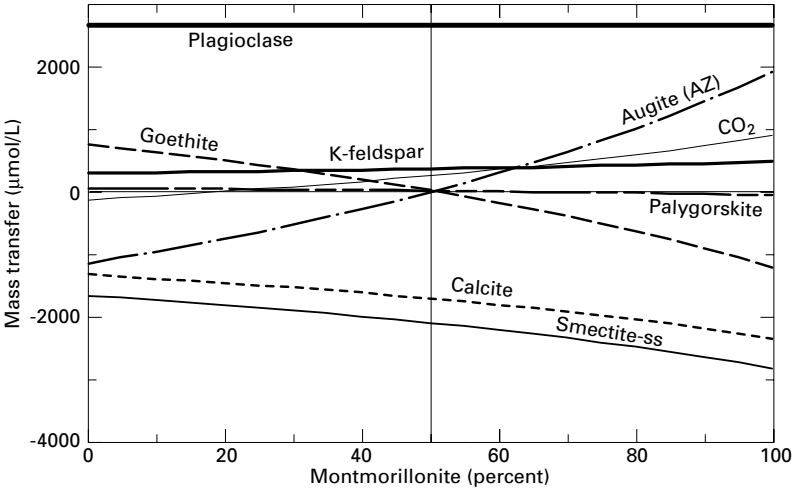

Fig. 18. Mineral mass transfers versus smectite composition for well pair Vekol-1 to Vekol-2. For 0.15% interlayer-K and An-45 plagioclase. Vertical line is lower montmorillonite percent allowed (~50%).

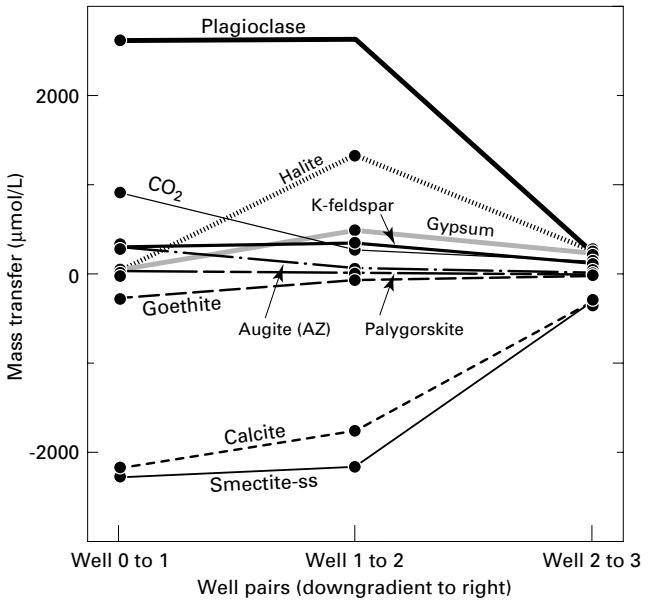

Fig. 19. Mineral mass transfers compared for all three well pairs. Note increase in halite and gypsum mass transfers between wells Vekol-1 and Vekol-2 and significant decrease in all mineral mass transfers at the farthest downgradient well pair, Vekol-2 to Vekol-3. (Not all phases are plotted for purposes of clarity.)

former), gave acceptable mass-balance solutions. However, palygorskite is typically found in surficial closed basin environments (Jones and Galan, 1988). Montmorillonite/beidellite ratios and interlayer-K content of smectite adjusted to small, positive palygorskite MTC's for all well pairs (table 15) provided the most reasonable of all mass balances considered.

The percentage of montmorillonite end-member in our dioctahedral smectite solid-solution model can increase, due to either actual interstratification (Jones, 1986; Banfield and others, 1991a, 1991b) or physical mixing of two clay phases. The smectite thus represents the product not only of plagioclase weathering, but of augite as well. It serves as the principle sink for magnesium and silica, as well as aluminum, in the mass balance. Robertson (1991) considered several smectite compositions, but presented mass-balance results only for a mixed dioctahedral-trioctahedral 2:1 clay phase. If true interstratification is accompanied by reduced layer charge, the exchangeable calcium thus displaced increases the amount of calcite precipitated per unit reaction in the model. This displacement may be augmented by potassium uptake in clay associated with increased K-feldspar dissolution where this mineral is more abundant. The weathering K-feldspar will not contribute any magnesium. It will cause a lower Si/Al ratio in the smectite composition as compared with the primary mafic silicate alone (3:1 versus 8.5:1 for the pyroxene composition used here), requiring a less montmorillonitic smectite in the balance. Thus, as with the watersheds in the Inyo Mountains discussed earlier, the Vekol Valley mass balances are constrained by the relative abundance, and specific mineral composition of plagioclase, K-feldspar, and mafic minerals in the source areas.

Examination of figures 17 and 18 reveals how sensitive the mass-balance solutions are to plagioclase composition, and to the montmorillonite/beidellite ratio of the clays and their interlayer-K composition. The critical MTC cross-over points for augite and

palygorskite fall surprisingly close to Robertson's suggested plagioclase composition (An-44.5). Mass-balance smectite compositions require significant Mg and Si content and are lower bounded at 43 percent montmorillonite[11] (fig. 18). In fact, the mass-balance results are surprisingly limited. Careful consideration of critical MTC cross-over points and their upper and lower limits leaves little possibility for other compositions. Consideration of other ferromagnesian minerals such as hornblende and/or biotite would not converge to any acceptable mass balance.

As noted earlier, the mass balances required calcite precipitation for all well pairs. This is consistent with calculated saturation indices at or near equilibrium in the ground water. Although the calcite saturation index for the distal well pair (Vekol 2-3) indicated slight undersaturation, analytical uncertainties in the pH and CO_2 data related to sampling and temperature change (Robertson, oral communication) leave this question unresolved.

As mentioned earlier, Robertson's (1991) mass balances used a small amount of ion exchange to help explain the inverse sodium-calcium concentrations, although he also suggested that such a process *should not* be required to explain the geochemical evolution of these waters. Similarly we rejected using exchange in the mass balance as neither necessary nor theoretically defensible. Although there is a notable increase in the sodium proportion of solutes down gradient (probably attributable in part to older saline playa sediments), it does not reach sufficient concentration in the present ground water to induce much cation exchange. Indeed, it can be argued that ion exchange is not important in aquifer materials where most of the clay was generated under current hydrologic conditions. Because hydrolysis of primary silicates is much slower than ion exchange reactions, mass transfer coefficients of newly formed clays are far too small to provide any reasonable amount of added cation exchange capacity to the aquifer. Physically transported smectite deposited in an alluvial basin is effectively pre-exchanged and not a significant source of solute sodium or calcium uptake. Ion exchange is only important when younger ground water displaces older water of different chemistry, and in sediments with a large proportion of minerals with significant exchange capacity (for example, freshwater displacing interstitial waters in marine shales), but such conditions do not exist in any of our case studies.

Trout Lake, Wisconsin

The ground-water-dominated, clastic sediment site in the Trout Lake area of northern Wisconsin is comparable in complexity to the Vekol Valley. The area is within Vilas County in north-central Wisconsin, and has been the subject of hydrochemical, physical and biological studies since 1981 as part of the NSF Long-Term Ecological Research (LTER) Program (Magnuson and Bowser, 1990).

The geologic setting for ground water in this lake-rich area is in moderately thick (~50 m) glacio-fluvial sediments overlying relatively impervious, crystalline, Precambrian bedrock. The aquifer consists of mechanically-generated, sand-sized silicate mineral grains derived from granitic to gabbroic intrusive rocks, metavolcanic, and metasedimentary Precambrian rocks from the Canadian Shield. Quartz constitutes over 90 percent of the mineral mass, yet the remaining fraction contributes virtually all solutes from mineral weathering (table 16). The local glacial drift is further characterized by its lack of clastic carbonate minerals, most notably calcite (Kenoyer and Bowser, 1992b). Therefore, models for the evolution of these waters should be consistent with the lack of calcite, and with plagioclase compositions appropriate for the glacial drift, and with mineral reactions compatible with presumed mineralogical differences between the silt and the sand layers above and below.

[11] Normal X-ray diffractograms of clay minerals from clastic mixtures are not able to distinguish between beidellite and montmorillonite. Detailed determination would require multiple observations by high resolution analytical electron microscopy (for example, Banfield and others, 1991).

TABLE 16

Summary of microprobe-analyzed minerals and their modal percentages in Trout Lake area aquifer, Wisconsin. Data after Kim (1996)

SUMMARY OF MINERAL COMPOSITION AND ABUNDANCE IN TROUT LAKE AREA SEDIMENT

Minerals	Mineral Formulas	Modal percent	Compositions		
			Average	Lowest	Highest
Quartz	SiO_2	76.4			
K-feldspar	$(K_{0.91}Na_{0.08}Ca_{0.01})(Al_{1.03}Si_{2.96})O_8$	10	Ab8-Or92	Albite 0	Ab 56
Plagioclase	$(Na_{0.77}Ca_{0.17}K_{0.02})Al_{1.19}Si_{2.82})O_8$	2.2	An17-Ab83	An 0	An 61
Amphibole	$Ca_{1.85}Na_{0.35}K_{0.12}(Mg_{2.33}Fe_{2.14}Al_{0.65})(Si_{6.94}Al_{1.06})O_{22}(OH)_2$	0.9		40[a], 0.6[b]	85, 2.4
Pyroxene	$(Mg_{0.85}Ca_{0.62}Fe_{0.48}Al_{0.05}Na_{0.02}Ti_{0.02})(Si_{1.96}Al_{0.04})O_6$	0.6	63[c], 5.9[b]		
opx	$(Mg_{1.08}Fe_{0.71}Ca_{0.17}Al_{0.03}Ti_{0.01})(Si_{1.99}Al_{0.01})O_6$			51[c], 3.6[b]	73[c], 20.6[b]
cpx	$(Mg_{0.78}Ca_{0.74}Fe_{0.40}Na_{0.02}Al_{0.06}Ti_{0.02})(Si_{1.96}Al_{0.04})O_6$			63[c], 0.6[b]	90[c], 1.95[b]
Epidote	$Ca_{2.0}Al_{2.2}Fe_{0.8}Si_3O_{12}(OH)$	0.7	Zoisite 77%	Zoisite 60%	Zoisite 95%
Chlorite	$(Fe_{2.38}Mg_{2.09}Al_{1.43}Ti_{0.01}Ca_{0.01}K_{0.01})(Si_{2.73}Al_{1.27})O_{10}(OH)_8$	1			
Biotite	$K_{1.96}Na_{0.01}(Fe_{2.84}Mg_{2.48}Al_{0.51})Al_{2.18}Si_{5.82}O_{20}(OH)_4$	<0.1			
	TOTAL	99.2			

a : Ca + Mg atomic % in octahedral sites of amphibole

b : Mg/Ca ratio

c : Ca + Mg atomic % in octahedral sites of pyroxene

Studies presented here are based on results of samples from a network of 36 ground water-monitoring wells (at depths ranging from 2-20 meters) on a 120 meter wide isthmus of land, and along a ground-water flow path between two lakes, Crystal Lake and Big Muskellunge Lake (fig. 20A). The isthmus separates the two lakes; Crystal Lake is up gradient and Big Muskellunge is down gradient, with approximately one meter of head difference between them. Critical to understanding the mineralogic control on the chemistry of waters moving through the isthmus sediment is a low angle, up gradient dipping, one-meter thick silt layer through which the ground water moves (Kenoyer and Bowser, 1992a, 1992b; Kim and others, 1999). These lakes are part of the North Temperate Lakes, Long-Term Ecological Research study site in Vilas County, in northern Wisconsin. Hydrogeologic and geochemical studies from these wells have been described in several earlier studies (Kenoyer, 1986; Kenoyer and Bowser, 1992a, 1992b; Kim and others, 1999; Bullen and others, 1996).

Earlier arguments for the evolutionary controls on the chemistry of the ground water were presented in Kenoyer and Bowser (1992b) using the geochemical forward modeling approach (PHREEQE) (Parkhurst and others, 1990). Results were consistent with the lack of carbonate mineral control on water compositions (Bullen and others, 1996). Kim (ms, 1996) focused on a more detailed mineralogic characterization of the glacial sediments, and this information combined with the mass-balance analysis allows us to: 1) re-examine the earlier results; 2) provide an independent test of the previous conclusions; and 3) examine the relationship between Ca/Na ratios of weathering solutions and chemical controls on waters from mixed-phase, clastic systems. Results shown here are only broadly similar to those presented earlier (Kenoyer and Bowser, 1992a), and benefit from more confidence in flow-path definition and more detailed analyses of mineralogy and chemistry.

The mass-balance analysis presented here is based on samples from a network of wells in a groundwater plume of water from Crystal Lake flowing in a shallow, unconfined aquifer between the two lakes (fig. 20B). Ground-water from four wells (K-87, K-70, K-71, and K-5) along a flow streamline was analyzed to determine the geochemical evolution trends. The sample from the well nearest Crystal Lake (K-87) was considered as the input water and samples from the down gradient wells (K-71 → K-70 → K-5 respectively), were considered as the evolved water. Refinements of ground water flow models were constrained by isotopic data ($\delta^{18}O$) and allowed the selection of wells along a streamline or flow path (Bullen and others, 1996; Kim and others, 1999). The mass-balance modeling approach used is similar to the Vekol Valley case, where we have attempted to find a consistent set of reactions and mass transfers reflecting the mineralogy of the aquifer sediments not only between paired wells, but across all well pairs considered in the analysis.

A summary of chemical changes along the flow path is shown in figure 21 as a function of distance from Crystal Lake and is based on the work of Kim (ms, 1996). Differences in chloride concentrations among ground-water samples were assumed to be due to either analytical uncertainty or residual effects of road-salt contamination from a time when a local all-season road was constructed across the area (Kenoyer, 1986). Therefore, chloride concentrations were set to zero in the mass-balance calculations (the changes are small, and do not significantly alter the ion balances). In general, the solute concentrations increase down the flow path, with more rapid changes occurring in the middle section, reflecting the larger surface area of the silt compared to the medium to coarse-grained sands that bound it.

To illustrate the changes down gradient, sodium and magnesium are plotted as a function of calcium in the plume centroid water (as defined by the $\delta^{18}O$ of the water) (fig. 22). Interestingly, the Ca/Mg ratio of the waters is nearly constant. In contrast, solute sodium concentrations increase through the silt zone, but within the error of

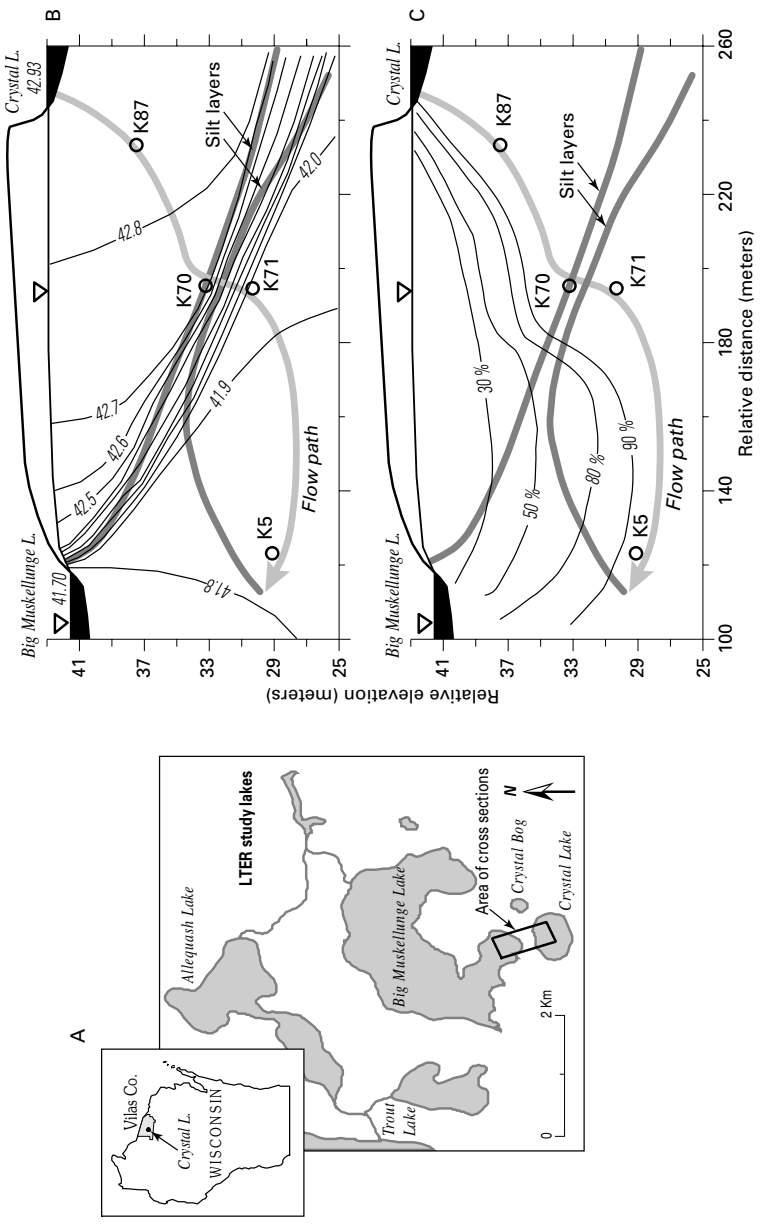

Fig. 20. Index map and cross section of isthmus between Crystal Lake and Big Muskellunge Lake, Wisconsin. (A) Location map showing location of study transect between Crystal and Big Muskellunge Lakes. (B) Hydraulic head contours (in meters) are based on data from 30 wells. Also shown are two silt layers with lower hydraulic conductivity and the modeled flow path based on data of Kim and others (1999). (C) Contours of percent lake water recharge to ground water based on conservative isotopic mixing of $\delta^{18}O$ in samples from 30 observation wells. Silt layers and flowpath also shown. Based on data of Kim and others (1999).

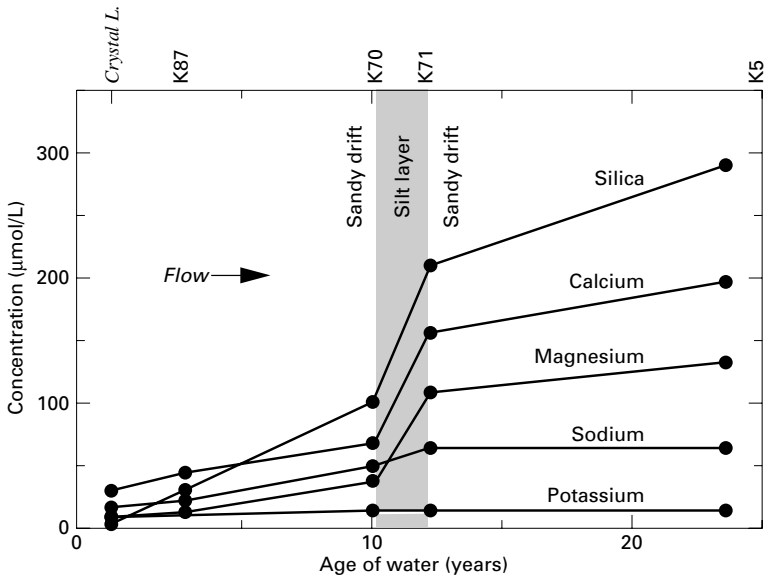

Fig. 21. Change in water chemistry with time along the flow path shown in previous figure. Note the rapid increase in solutes across the silt layer and the near-constant sodium concentration downgradient of the silt.

analysis, sodium concentrations remain nearly constant down gradient of the silt layer. Because feldspar is the only solute sodium source and no sodium sink mineral(s) exist(s), this observation has important implications for plagioclase weathering.

Phases and phase compositions used for the mass-balance analysis are listed in table 16. Initially, optical microscopic studies yielded plagioclase compositions with an average anorthite content of An-45 (Kenoyer and Bowser, 1992a). However, more recent electron microprobe analysis of a larger number of grains determined a range

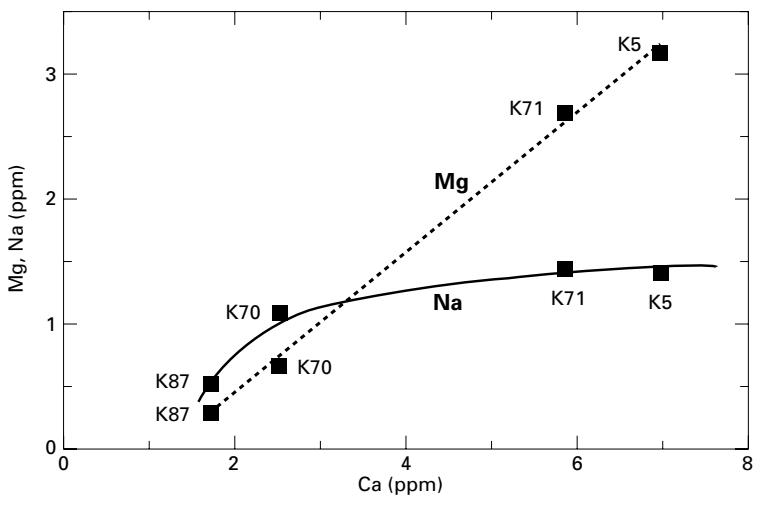

Fig. 22. Plot of sodium and magnesium versus calcium concentration in wells along flow path, showing near-linear increase in magnesium and leveling of sodium concentration down gradient.

TABLE 17

Saturation indices for critical minerals in ground water in the Trout Lake area, Wisconsin

	SATURATION INDICES			
WELL --->	"K87"	"K70"	"K71"	"K5"
MINERAL PHASE	UPGRADIENT	PRE-SILT	POST-SILT	DISTAL
Anorthite	-9.98	-6.22	-3.99	-3.6
Albite	-7.53	-4.12	-2.72	-2.28
K-feldspar	-3.84	-0.74	0.56	0.95
Kaolinite	4.19	6.79	4.68	5.97
Ca-Montmorillonite	-1.08	3	1.49	3.04
Gibbsite	1.21	1.86	0.63	1.13
CO2(g)	-2.23	-2.38	-3.9	-3.29
Fe(OH)3(a)	-1.92	-1.09	2.46	3.06
SiO2(a)	-1.67	-1.02	-0.85	-0.7

of plagioclase compositions from nearly pure albite to labradorite, with a mean composition of approximately An-17 (Kim, ms, 1996). Similarly, large compositional ranges were observed for amphibole, biotite, chlorite, and pyroxene grains, reflecting the lithic heterogeneity of the source region. This increases the number of mineral phases beyond the number of solute constraints (10), and different approaches are needed to resolve these mass-balance model limitations.

This "multiple-phase composition" problem is typical of most sedimentary aquifers or alluvial soils, and complicates the interpretation of solute balances derived by silicate hydrolysis in these common geologic environments. It is important to note here that the application of mass balances to calibrated watersheds and ground-water flow systems is strongly biased in favor of watersheds or aquifers with a uniform and simple lithology. With plagioclase as an example, our approach to the multi-composition limitation is to characterize the mineral used in the mass-balance calculations according to what we defined earlier as the *mean reactive composition* of the mixture of plagioclases, an estimate of a dissolution rate-adjusted mean chemical composition for plagioclase, or simply the single plagioclase composition whose congruent dissolution would yield a water of the same Ca/Na ratio (expressed as the calcium mole fraction for the mineral, that is, An-number). Similarly, we used the fictive phases biotite-chlorite and hornblende-pyroxene in models.

The chemical speciation and mineral equilibrium model PHREEQC (Parkhurst, Thorstenson, and Plummer, 1990) was used to evaluate the saturation state of waters from each well with respect to the critical mineral phases. Results are shown in table 17. With the exception of goethite in the well K87-K70 pair, all mass transfers are consistent with calculated saturation indices.

The saturation indices indicate that K-feldspar closely approaches equilibrium along the flow path, and the mass-transfer coefficients are correspondingly small. Actual supersaturation of K-feldspar is even indicated in the down gradient wells, suggesting formation rates sufficient to allow precipitation within the transit time for waters between the wells. Unfortunately, sediment samples from these wells were not

TABLE 18

Summary of mass balance results from ground water in well pairs in Trout Lake area, Wisconsin

Int-Chg = 0.50 100.0 % Montm. Int-K = 0.000 An = 20.0	Mass-Transfer Coefficients		
	Wells pairs		
	K87 -> K70	K70 -> K71	K71 -> K5
Plagioclase	31.57	18.96	0.00
K-feldspar	0.23	0.51	-1.47
Hornblende	13.32	105.60	44.54
Chlorite	3.37	20.66	0.10
CO2-gas	89.08	335.91	141.30
Goethite	-28.47	-154.74	-37.98
Smectite_ss	8.89	-90.31	-10.53
Kaolinite	-36.93	-24.59	-13.78
Halite	0.00	0.00	0.00
Pyrite	-0.35	0.63	-2.06

units: μmol/L

Using Kim (ms, 1996) analyzed chlorite.

available to confirm these intriguing results, although a similar outcome was described for the coastal sand aquifer near Coos Bay, Oregon by Magaritz and Luzier, (1985).

The mass transfers for plagioclase are even more dramatic. The data for the down gradient wells show a near-constant sodium concentration, yet continued increase in dissolved calcium. Under reducing conditions, a paired iron-sodium exchange model was considered (Bowser and Jones, 1998) and subsequently rejected. Because of the leveling of the sodium concentration at the distal end of the flow path, the mass-transfer coefficients for plagioclase go to zero (table 18). Therefore, the increases in calcium between these two wells must be due to continued dissolution of mafic minerals, and not plagioclase. Plagioclase dissolution is effectively shut down.

This observation is consistent with recently published work on the "affinity effect" (for example, $\Delta G_{reaction}$ for plagioclase dissolution) wherein dissolution rates are significantly reduced on approach to mineral equilibrium. Burch and others (1993), and Taylor and others (2000) addressed this phenomenon for albite and laboradorite, respectively, and suggested that dissolution rates decreased at saturation indices as much as four orders of magnitude away from equilibrium. Our plagioclase saturation indices fall within the range they indicated.

Satisfactory mass-transfer coefficients for the ferromagnesian minerals are obtained in our analysis. Hornblende dominates over chlorite. The choice of hornblende and chlorite compositions was remarkably critical, and only the compositions shown in table 16 produced mass-balance model solutions consistent with the observed saturation indices. Slight changes in Fe/Mg ratios (and coupled shifts in Mg/Al, Mg/Ca, and Si/Al ratios) produced mass-balance coefficients incompatible with these minerals as only solute sources and not weathering products. The results for the distal well pair K-71/K-5 indicate that hornblende alone is responsible for the observed solute increases, which corresponds to the largest undersaturation calculated by Bullen,

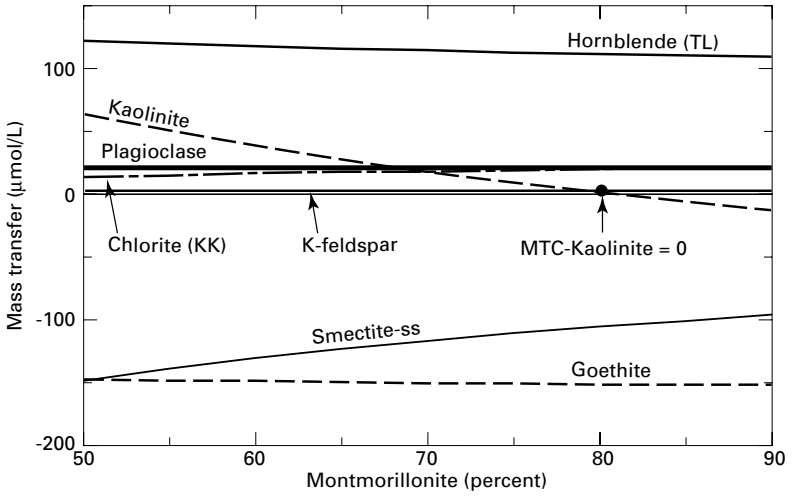

Fig. 23. Mineral mass transfer versus dioctahedral smectite composition with An-30 plagioclase. Note MTC-kaolinite < 0 is restricted to greater than 80% montmorillonite. Modeled for wells K70 to K71 bounding the silt layer.

Krabbenhoft, and Kendall (1996) for any of the silicate assemblage. These observations are unique to systems we have studied so far.

Goethite precipitation is required by the mass balances for all three well pairs, yet the saturation indices suggest dissolution of iron oxides between the up gradient wells K-87 to K-70. In contrast, analysis of total iron (by atomic absorption spectrophotometry on acidified samples) indicates a loss over this interval. These differences could result from changes in the partitioning of iron between organically bound and inorganic forms. Interestingly, such changes only show up in the sign and magnitude of the goethite mass-transfer coefficients; all other mineral mass transfers are unaffected.

The model results fit the geologic setting and source minerals well. Magnesian chlorite is abundant and ubiquitous in Archean source rocks reflecting low to medium grade metamorphism. Although chlorite mass transfers were low compared to hornblende, the chlorite Mg/Fe ratio is key to a suitable mass-balance solution. More iron-rich chlorites invariably produced negative primary mafic mineral mass-transfer coefficients. On the other hand, the relatively large mass-transfer coefficient for chlorite in the silt is geologically reasonable. Chlorite and hornblende are found in relatively unaltered lithic fragments in the sand units, whereas in the silt, the grains are commonly disaggregated particles, providing relatively larger surface area, and thence reactivity, for chlorite.

End-member montmorillonitic smectite and kaolinite dominate the reaction products. More beidellitic (aluminous) smectite compositions invariably led to incompatible mass transfers between the clays and primary silicate phases (fig. 23) (for example, negative MTC's for reactants, or positive MTC's for products). Note that the inferred greater proportion of montmorillonite in smectite solid solution is driven by mass-balance considerations, not by direct mineralogic evidence. Mafic mineral dissolution in the silt layer is considered as a stepwise intergranular diffusive process driven by local concentration gradients, such as proposed by Wood and others (1990). Under these conditions, cations can be very locally distributed into smectite, as demonstrated by Banfield and others (1991a). The calculated dissolution of smectite in the up gradient well pair K-87/K-70, and the later precipitation of smectite in the down

gradient wells are consistent with the saturation indices (table 17). The implications of these results are that some detrital or pedogenic smectite was available in the shallow glacio-fluvial sediments after deglaciation, perhaps aeolian smectite transported from Cretaceous shales to the west, as suggested earlier (Borchardt, 1977; Kleiss and Fehrenbacher, 1973).

Studies such as at Trout Lake involving coupled chemical and physical-based flow models, and the use of several well pairs, have allowed us to better define silicate reactions, stability and kinetics in a field setting. In effect, the multi-compositional approach has provided additional constraints with which more informative mass-balance models can be determined.

DISCUSSION

Mass Balance, General

Mass balance is simply a budget. It describes solute fluxes into and out of a catchment, or between wells along a common flow path, and assigns changes in solute concentrations to specific sources or sinks. Where not subject to anthropogenic pollution, and on a sufficiently long time scale, mineral weathering is the dominant source of solutes in many surface and near-surface environments. Exchange sites and biomass simply represent interim storage that may or may not be in steady state over time. In keeping with this view for all of the example watersheds considered here, the mass-balance technique employed has emphasized mineral compositional factors. Therefore, this general discussion will deal primarily with mineralogical aspects of solute distribution.

Every catchment chosen to demonstrate the spreadsheet mass-balance technique has exposed special features related to reactions involving rock-forming silicates. This is a reflection of the compositional variability and range of crystal-structural constraints in these minerals. It also tests the flexibility of the spreadsheet approach in handling multiple phases and solute species, and wide-ranging response to changes in input values.

Unique in our approach to mass balances is the exploration of mass-balance solutions over mineral compositional space for both reactant and product phases (for example, plagioclase and clay minerals). This has allowed us to demonstrate that although unique mass-balance solutions are rarely possible, there are severe restrictions to the range of possible mineral compositions that satisfy these conditions. Use of consistent sets of phases among multiple watersheds in similar protolithic settings and climate or multiple well pairs along a ground-water flow path further restricts the range of possible analytical solutions and significantly improves our confidence in the mass-balance results. We used this to advantage in the Inyo Mountain Watersheds, the Vekol Valley wells, and the Trout Lake wells.

Employing models to re-examine the mass-balance results derived in these studies has emphasized the interconnection of the mineral compositional influences on the solute concentrations, particularly for the major solute cations (Ca, Mg, Na, and K). These concentrations are coupled by their ratios in the complete mineral assemblage; that is, in both reactant and product mineral phases. Often the major solute ratios in the water are just as profoundly, though indirectly, affected by the relative amounts of more insoluble elements in the mineral assemblage, especially the Si/Al ratio. Generally in small, dilute-water, silicate catchments, the influential product phases are 1:1 (kaolin-type) clays or the simple oxy-hydroxides of Al, Si, and Fe^{3+}, but calcium and perhaps magnesium may be involved in carbonates, and minor, but significant levels of Ca, Mg, and K can be associated with interlayer uptake in 2:1 (mica-type) clays.

The case studies analyzed provide some useful insights into the principal processes of mineral weathering in both watershed and groundwater systems. Generally, the important influences fall into two categories: a) largely mineralogic factors which

include reaction kinetics and solution saturation, and b) factors that are more related to physical or environmental parameters. Of the latter, the dominant controls are hydraulic conductivity, grain size, surface area, and climate.

Comparative mass transfer coefficients for what we consider our best mass balances are summarized in table 19, together with the mineralogic information used for each analysis. Comments to follow consider various important geologic and geochemical controls in the context of the case studies presented.

Mineralogic Factors

Generation of satisfactory mass balances normally assumes that identifiable minerals in the soil regolith or aquifer are all involved in the reactions. Clearly, this is not always so, and a key problem of mass-balance analysis is to identify which phases are actually involved in controlling water compositions. For example, a number of rare, trace minerals are most likely present in *all* soils and aquifers, yet their mass contribution to total solutes is insignificant. In other cases, the water and solutes are derived from mixtures of nearby but disparate local soil environments. For instance, in the Luquillo Mountains of Puerto Rico, diorite bedrock weathers in two distinct zones (White and others, 1998). Plagioclase and hornblende are the principal reactants of the bedrock-saprolite interface, whereas biotite and quartz weathering dominates the bulk of the regolith. Chemically, plagioclase and hornblende constitute the major controls on stream water composition, and biotite and quartz exert the primary influence on pore-water composition. In our two ground-water examples, such situations range from simple flow deepening that essentially closes the overall system to CO_2 at Vekol Valley, to the complex change of aquifer texture and mineral composition in the ground-water flow system at Trout Lake. The assemblage of products and reactants in our mass balance for the Catoctin watersheds remains consistent through significant shifts in annual climate.

Inherent in understanding the mineral influence on natural water chemistry are questions about dissolution mechanisms. Mass-balance analysis generally assumes that the ratios of solute species are concordant with stoichiometric ratios in the dissolving mineral phases, but some have suggested that the fluid and solid element ratios are not necessarily the same (Nesbitt and Young, 1984). Mass-conservation considerations would then demand that product phases (likely clay minerals or amorphous protoclays) are generated that reflect incongruent reactions.

Departures from bulk mineral stoichiometry at surfaces of weathered feldspars were used to argue that dissolution was controlled by homogeneous reactions at near-neutral pH conditions and by heterogeneous dissolution under low pH conditions (Muir and others, 1989; Nesbitt and others, 1991; Nesbitt and Muir, 1988; Nesbitt and Young, 1984). The work addressed the nature of the surface residuum forming on feldspars during dissolution and to what degree such "coatings" or "leach layers" affect mechanisms and rates of dissolution. Velbel (1996) has maintained that interfacial reaction is rate-determining and therefore, slower than transport through a secondary mineral coating. This question is especially pertinent for the Trout Lake example because of the apparent "shutdown" of plagioclase dissolution along the flow path, as revealed in the Na balance. Although somewhat less dramatically, the same effect can be seen for plagioclase in the final segment of the Vekol Valley flow path. In this case the augite MTC decrease may be due, in part, to simple loss of the phase by complete dissolution.

Calculated mass-transfer coefficients can be directly related to mineral dissolution rates if the minerals are sufficiently undersaturated to follow the linear dissolution rate law (Blake and Walter, 1999), wherein the rate constant is equated to the solute flux per unit area of the dissolving solid per unit time. To utilize this relationship, the mass balance must be obtained in flux rather than concentration units (White and others, 1996). However, Gislason and others (1996) indicated that the free energy of reaction

TABLE 19

Summary of the most reasonable mass balance results obtained for the six case studies. Mineral mass transfer ratios are shown at bottom of table.

	SIERRAN	SIERRAN	LOCH VALE	INYO MTS	INYO MTS	INYO MTS	INYO MTS	CATOCTIN	VEKOL	VEKOL	VEKOL	TROUT LAKE	TROUT LAKE	TROUT LAKE
	EPHEMERAL	PERENNIAL	Loch Vale	Cottonwood Ck.	Sage Hen Ck.	Crooked Ck.	Wyman Ck.	HAUVER (avg)	Well 0->1	Well 1->2	Well 2->3	K87-K70	K70-K71	K71-K5
Interlayer Charge	0.5	0.5	0.5	0.50	0.50	0.50	0.50	---	0.50	0.50	0.50	0.5	0.5	0.5
Pct. Montmorillonite	---	12.5	0.0	20.00	30.90	38.70	35.00	---	53.47	53.47	53.47	100.0	100.0	100.0
Interlayer-K	---	0.252	0.330	0.057	0.241	0.327	0.250	---	0.150	0.150	0.150	0.000	0.000	0.000
Plagioclase An-No	38.2	38	27	20.00	30	35	35	0	45	45	45	20	20	20
Plagioclase	178.00	175.8	86.3	58.5	383.7	745.5	566.0	269	2620	2651	278	31.57	18.96	0.00
K-Feldspar	3.90	8.2	8.6	9.9	38.4	74.6	60.9	26.5	325	358	135	0.23	0.51	-1.47
Biotite	18.60	42.3	8.1	10.1	60.6	281.8	194.2	---	---	---	---	---	---	---
Chlorite	---	---	13.7	---	---	---	---	62.1	---	---	---	3.37	20.66	0.10
Hornblende	---	---	---	---	---	---	---	---	---	---	---	13.32	105.60	44.54
Actinolite	---	---	---	---	---	---	---	28	---	---	---	---	---	---
Augite	---	---	---	---	---	---	---	---	323	80	2	---	---	---
Calcite	0.00	116.4	95.6	---	171.7	700.6	676.4	437.6	-2170	-1751	-310	---	---	---
Dolomite	---	---	---	609.2	---	---	415.7	---	---	---	---	---	---	---
Co2-Gas	310.00	450.6	110.4	1343.4	734.6	1997.5	2566.2	1060.8	920	274	144	89.08	335.91	141.30
Kaolinite	-129.60	0.0	-84.8	0.0	0.0	0.0	0.0	-214.7	---	---	---	-36.93	-24.59	-13.78
Smectite	---	-130.8	0.7	-40.5	-283.9	-699.9	-511.4	---	-2249	-2146	-312	8.89	-90.31	-10.53
Palygorskite	---	---	---	---	---	---	---	---	36	0	12	---	---	---
Gibbsite	-16.90	---	--	---	---	---	---	---	---	---	---	---	---	---
Goethite	-23.90	-54.6	-48.2	-12.7	-77.7	-363.6	-250.5	-293.9	-282	-56	-20	-28.47	-154.74	-37.98
Silica	---	---	---	0.0	0.0	0.0	0.0	---	---	---	---	---	---	---
Pyrite	---	---	---	---	---	---	---	239.2	---	---	---	-0.35	0.63	-2.06
Gypsum	0.00	15.0	1.0	27.9	90.4	204.5	404.3	---	55	479	238	---	---	---
Halite	0.00	16.0	0.0	2.8	2.8	92.1	50.4	---	25	1326	282	0.00	0.00	0.00
Road Salt	---	---	---	---	---	---	---	584.5	---	---	---	---	---	---
	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	mol/ha/yr	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L
Plag/K-spar	45.64	21.47	10.00	5.91	9.99	9.99	9.29	9.29	8.06	7.41	2.06	137.17	37.06	0.00
Kspar/Biotite	0.21	0.19	1.07	0.98	0.63	0.26	0.31	0.31	---	---	---	---	---	---
Fe/Mg-Biotite	1.09	1.09	1.33	1.09	1.09	1.09	1.09	1.09	---	---	---	---	---	---

("affinity") for silicates could be related to suppression of dissolution rates at much greater undersaturation levels than previously realized (as documented in the laboratory dissolution experiments on albite (Burch and others, 1993) and labradorite (Taylor and others, 2000). Despite the problems of solution saturation, differential kinetics, and variable physical parameters (for example, effective surface area, hydraulic conductivity), comparative MTC's readily obtained from the spreadsheet technique certainly provide at least a semi-quantitative estimate of the relative dissolution rates of mineral phases used in successful mass balance calculations. In predominantly silicate terrain, they probably work best for small upland watersheds of the sort considered here.

The disparities between weathering rates calculated from total solute fluxes and those based on individual mineral dissolution can be considered by straightforward comparison of the mass-transfer coefficient ratios obtained from spreadsheet models. Just as Sr isotope (Blum and others, 1993), Rb/K, and Na/K (Bullen and others, 1998) ratios have been used to ascertain comparative dissolution rates of coexistent minerals with contrasting elemental compositions, the MTC ratios derived for primary silicates, such as plagioclase and biotite, can be compared for watersheds in similar lithologic settings, as with our watersheds in the Inyo Mountains. Using such ratios takes advantage of the Velbel (1993a) observation that key mineral pairs will show similar *relative* rates of weathering, despite variation in absolute values. Thus, the MTC ratios for the major rock-forming minerals of the granitic rocks in the Sierra Nevada and Loch Vale examples are broadly similar, despite the fact that one is based on a spring (ground-water) system and the other on a stream flow system. Similarly, the weathering rate ratios from the Inyo Mountains and Catoctin Mountain sites are generally similar after allowance for the respective contributions of carbonate minerals and road salt (table 19).

White and Blum (1995) have maintained that silica, as well as sodium, are essentially conserved in solution during weathering. This would appear to hold only where there is continuous solute transport and primary silicate dissolution is entirely congruent; that is, where there is complete flushing of the constituents released to solution by dilute water hydrolysis. Certainly in the formation of smectite or vermiculite from feldspar or mafic silicate, such as in all our crystalline-rock drainage basins, a significant portion of the silica released from the reactant phase is retained in the solid mineral product. The transport effect can be seen in the comparison of adjacent catchments by Yuretich and others (1996), whereby the stream fed by more rapid ground-water transport (and acidic pH) shows a positive correlation of SiO_2 with total cations and acid-neutralizing capacity. This suggests congruent dissolution with kaolinite rather than smectite as a product, whereas the watershed with deep ground-water sources shows about 50 percent higher cation denudation without a close relation to silica flux. Yuretich and Batchelder (1988) have recommended the general use of silica fluxes as indicators of weathering rate, but Drever (1997b, 1997c; Drever and Stillings, 1997) noted that solute silica can be irregularly affected by adsorption-desorption reactions and plant uptake, even in very dilute catchments. All of the watershed mass balances obtained in our examples require the formation of silicate product phases. None are compatible with the idea of completely conservative solute silica. Nevertheless, consistent ratios of SiO_2 to other major cations can be useful.

Product phase importance.—Even where mineralogical characterization of watershed lithology has been recognized as important, it commonly has been difficult to quantify. Characterization of product minerals is especially difficult, requiring analysis of very fine-grained soils and regolith dominated by iron and aluminum oxides and chemically complex clay minerals. The clay mineral composition of soils is diverse, typically involving mixtures of minerals of widely ranging chemical composition whose origin may range from truly pedogenic to residual detritus or aeolian sediment. Thus, the

mere presence of some fine-grained minerals in soils is not, *a priori* proof of their involvement in local weathering environments (Miller and Drever, 1977). Instead, consideration of product phases is in part based on information on the crystallinity and relative reactivity of clay minerals, whether or not they are product or reactant phases involved in the local weathering environment, or, for that matter, whether they are involved in the weathering at all. In a study of recent basalt weathering in an Iceland watershed, Moulton and others (2000), used the chemical analyses of the finest soil fraction to represent weathering products in their mass balance calculations, because of the lack of mineralogically definitive x-ray diffraction data.

One of the features of our spreadsheet model is the ease with which concomitant compositional variations in multiple silicate reactant and product phases can be assessed. This is particularly well-illustrated in our Inyo Mountains, Vekol Valley, and Trout Lake examples. Although solute mass balances are not in themselves constrained by mineral equilibria, the reaction sequence down a flow path was used to derive compatible assemblages with which to achieve a suitable mass balance.

As observed in our case studies for weathering under near-neutral pH conditions, the mineral reaction sequence coincides with the leaching of base cations (Na, Mg, K, & Ca) and silica relative to alumina and ferric iron. There are two main reaction pathways:

1. calcic plagioclase and alkali feldspar → beidellitic smectite → kaolinite[12] → gibbsite,
2. ferromagnesian mineral (pyroxene, amphibole, mafic mica) → montmorillonitic smectite (or vermiculite) → kaolinite (+ goethite) → gibbsite.

As weathering reactions proceed, there should be a consistent increase in product phases, and, as is seldom recognized mineralogically, an increase in the products of product-phase alteration. This was illustrated in the study of biotite alteration to kaolinite (with some vermiculite and interstratified intermediates) in the regolith of the Luquillo Mountains of Puerto Rico (Murphy and others, 1998). Multiple mass-balance sequences for such situations can be readily obtained, compared, and evaluated with the spreadsheet, as demonstrated in our test cases.

However, the evident simplicity of the mass-balance approach can hide added complexities of mineral dissolution under field conditions, and the non-steady-state character of such settings can be difficult to assess. Based on comparison of bulk chemical analyses of fresh and slightly altered bedrock, Miller and Drever (1977) suggested that most of the weathering of large volumes of andesite was partial dissolution without the formation of identifiable clay. This is consistent with the general observation that crystallization kinetics of complex layer silicates (that is, 2:1 clays) under surface conditions are considerably slower than primary mineral dissolution (Cama and others, 2000). However, systematic allowance for compositional variations in major reactant (for example, plagioclase) and product (for example, smectite) phases alone permits an instructive range of mass-balance solutions. This is especially well shown in our examples from the watersheds in the Inyo Mountains and Loch Vale.

The calcium problem.—Solute analysis of streams and springs in crystalline-rock terrain typically show that these waters have higher Ca/Na ratios than can be predicted by congruent dissolution of the plagioclase feldspars in the bedrock, which, as emphasized in our case studies, is normally the most obvious and predominant source of these elements. This situation in small watersheds has been referred to as the "calcium problem" (implied by Paces, 1983; Mast and others, 1990; specifically stated by Bowser & Jones, 1993). Such a condition indicates that there are either additional

[12] In the spreadsheet analysis we do not distinguish between kaolinite and halloysite, because the only difference is hydration water.

sources of calcium, an unidentified sodium "sink" (Na-bearing weathering product), or that plagioclase dissolution is incongruent with respect to calcium and sodium. In addition, as argued by Bowser and Jones (1993), the Ca excess may be at least partially attributed to structural aberrations in the plagioclases themselves.

The dissolution rate of plagioclase increases gradually with increasing Ca content, with a marked increase in the rate above An-75 (Blum, 1994). Blum (1994) cited the TEM work of Inskeep and others (1991), suggesting that non-stoichiometric plagioclase dissolution can be explained by preferential dissolving of calcium-rich exsolution phases. Even without detailed observations of crystal structure, White and others (2001) concluded that faster plagioclase weathering in granitic bedrock of the southeastern United States could be related in no small part to higher anorthite content. Thus, differential dissolution of microscopically unmixed plagioclase grains can be expected to produce waters with higher Ca/Na ratios than anticipated from bulk compositional considerations. However, Clayton (1986) pointed out that selective weathering of calcic portions of zoned plagioclases could yield waters with Ca/Na ratios *no higher than that of the most calcic portion of the mineral.* Furthermore, the influence of the more rapidly dissolving calcium-rich plagioclases on increasing solute Ca/Na ratios can be retarded or reversed by solute cation build-up and the formation of a more relatively aluminum-rich weathering product such as kaolinite.

Other silicate-mineral sources of calcium may be important. Calcium-bearing silicate phases in crystalline or siliciclastic rocks are commonly minor in abundance (for example, epidote-zoisite), or contain lesser amounts of Ca (for example, amphibole). In addition, independent sources of calcium in the biomass are usually limited to surficial recharge. Efforts to explain the differences in Ca/Na ratios of weathering solutions led to the postulate of micro-crystalline calcite occurring with the plagioclase (Garrels and Mackenzie, 1967). This was actually verified by petrographic analysis of micro-fractures in the Loch Vale granodiorite (Mast and others, 1990). Their mass-balance calculations indicated that total mass-transfer coefficients for plagioclase and calcite were approximately equal, despite the large differences in the modal percentages of these two minerals in the source rock. This difference was attributed to a much larger rate-constant for dissolution of calcite than plagioclase in this weathering environment and the greater surface area of calcite. Subsequently, White and others (1999b) have demonstrated by flow-through column experiment and analysis of CO_2 in granitoids that excess Ca can commonly be attributed to calcite in micro-fractures, disseminated grains, and replacement of calcic cores in plagioclase.

Affinity effects also play a role in comparative MTC's of carbonate minerals and calcium-bearing silicates. Surface waters and shallow ground-water commonly have calcite saturation indices at or near zero, reflecting the more rapid dissolution of calcite (and/or dolomite). Dissolution rates of these minerals may approach zero under these conditions, and continued dissolution of calcium-bearing silicates can lead to carbonate precipitation.

Even in situations where calcite is demonstrably absent, such as at the Trout Lake site, the calcium problem is persistent, with the excess calcium derived from amphibole and from a small but identifiable more calcic plagioclase from Archean diabasic rocks that contribute to the glacial debris in the area.

The calcium problem is common in numerous published watershed studies, and appears in the mass-balance modeling of all our catchments developed on plutonic rocks. Resolution of the problem demands a multi-element approach considering all sources contributing to the weathering fluids. Likens and others (1998) argued for selective loss of calcium from plagioclase without noting that higher Ca/Na ratios would require a residual phase enriched in sodium. This reflects the potential pitfalls of taking a single-element approach to weathering without consideration of solute ratio linkages in the dissolution of associated silicate minerals.

An alternate solution to the calcium problem is to suggest that one or more sodium-bearing minerals are involved in weathering reactions. Thus, sodium conservancy and the question of its role in *product* mineral phases is critical. Because plagioclase is such a ubiquitous reactant in silicate rocks, obtaining a watershed mass balance *without* invoking an unlikely sink for Na (such as the Na-smectite used by Furman and others, 1998), can be very difficult. The temptation to call upon ion exchange is contrary to the fundamental premise in natural dilute water systems that alkaline-earth cations or K are strongly preferred over Na on surface or interlayer exchange sites (Appelo and Postma, 1996). In the Trout Lake example, Bullen and others (1996) have suggested that the formation of inhibitory iron oxyhydroxide coatings may retard sodium release to solution but a more likely explanation is the inhibition of the plagioclase dissolution rate as it approaches equilibrium, referred to earlier (Burch and others, 1993; Taylor and others, 2000; Gislason and others, 1996). In addition, alkali cations like sodium can decrease the rate of feldspar dissolution by competing for reactive sorption sites at the feldspar surface, as has been demonstrated experimentally (Stillings and Brantley, 1995; Strandh and others, 1997; Blake and Walter, 1999). At Catoctin Mountain, however, the loss of sodium can be attributed to reversal of normal exchange selectivity by abnormally high, road salt-induced concentrations of NaCl.

Carbonate overprints.—As illustrated in the mass balances derived for the watersheds in the Inyo Mountains, the contribution of silicate dissolution in the presence of a large carbonate mineral weathering flux can be successfully differentiated even when the data are limited, with due caution about small differences in large numbers. Moreover, the mass balances for the watersheds in Inyo Mountains illustrate the value of comparison of multiple watersheds and their settings, and the importance of product phase variation, including specific crystal-chemical aspects, such as the composition of clay mineral solid solution and interlayer chemistry.

Perhaps the most difficult case is where dolomite (± calcite) is present in the watershed or aquifer. The coupled calcium and magnesium in the dolomite and sources of calcium from plagioclase and Ca/Mg-bearing silicate minerals makes it difficult to easily solve for the relative mass transfers of these critical phases. Only with exceptionally well-characterized mineral compositions in relatively simple lithologic settings will satisfactory mass-balance solutions be derived. This is evident in at least one of the watersheds in the Inyo Mountains (for instance, Wyman Creek).

Inasmuch as the global calcium balance plays such a key role in the carbon budget at geologic time-scales (Berner, 1999), it is important to improve our knowledge of the sources <u>and</u> sinks of calcium at these global scales. The general assumption of near quantitative solubilization of calcium under global weathering conditions is not born out by watershed and groundwater aquifer scale studies discussed herein, where calcium is, at least in part, retained in silicate weathering products (Bowser and Jones, 1993). However, the ubiquity of small, but highly reactive, amounts of calcite even in plutonic rock terranes, as illustrated in mass transfer coefficients comparable to the major rock-forming silicates (note particularly the calcite/plagioclase ratios for Sierra/Loch Vale and Catoctin), must be taken into account.

Potassium imbalance.—Imbalances in calcium and potassium, both of which are prone to significant involvement in surficial biologic processes, emphasize a preference for compositional data from groundwater or subsoil pore fluids to most clearly distinguish the mineralogic role in watershed mass balances. Thus, confidence in the implications of our results to mineralogic control of natural water chemistry in the cases of the Sierran springs, or the groundwaters of the Vekol Valley and the Trout Lake area is justified.

In addition to calcium excess in the solute balances for crystalline catchments, potassium fluxes often appear to be greater than might be expected from the

abundance of the most obvious potash-bearing minerals, feldspar and mica, in the source rocks (particularly in ferromagnesian lithologies). This suggests alternate sources of K, which might be in ultrafine matrix material or in widely, distributed trace concentrations in major mineral phases. In weathering or general water-rock interaction, however, this potassium can also be retained by alteration products in soils, clays, or the biomass, and is subsequently released at varying rates depending on hydrologic and climatic conditions. The recycling of potassium and other inorganic nutrients can strongly influence pore-water chemistry in shallow regolith, as shown in the Luquillo Mountains of Puerto Rico (White and others, 1998), or in the Catoctin watersheds underlain by K-poor greenstones (Katz, 1989; Katz and others, 1985; O'Brien and others, 1997).

Ion exchange.—Because clay minerals are a primary source of exchange capacity in most natural materials, cation exchange on clays has been invoked to account for varying degrees of compositional change in silicate-solute mass balances. However, in contrast to many models proposed for forested catchments (Bassett, 1997), we have shown that the role of cation exchange is minimal, except where significant mixing of solutions of different reactive history is involved (none of which are included in our six examples). The basic assumption is that new silicate surface is created by weathering more slowly than cation exchange rates. Also assumed is that the creation of new exchanger surfaces in the course of weathering is quantitatively much too small to provide all the exchange capacity demanded by mass-balance considerations. Clays derived from local weathering should be considered as "pre-exchanged."

In silicate-dominated watersheds with significantly developed soil or alteration zones, such as the Sierra Nevada or Catoctin catchments considered here, or in the Panola Mountain, Georgia, saprolite considered by White and others (2000), springs, soil solutions, or shallow groundwaters can reflect shorter reaction times and intermediate products as compared with longer-term effluents from the basin. Drever (1997a) stated,

> ". . .as the composition of the soil solution changes, ions will be exchanged between the solid phase and the solution. If the soil solution does not change with time, adsorbed ions will not change either, and ion exchange will make no net contribution to the solute budget."

Further supporting such an argument, Velbel (1993d) commented that:

> ". . .the minimal contribution of cation exchange to watershed solute budgets cannot be proven, but is strongly suggested by the fact that rates calculated by the geochemical mass balance method give relative rates (rate ratios) which compare most favorably with relative rates determined in laboratory kinetic studies of mineral weathering. . .in other words, cation exchange is a negligible influence on solute output. . ."

Increasing the hydrogen ion available to promote silicate hydrolysis is a major consequence of anthropogenically-induced acidification. The reservoir of exchangeable ions in rock and soil is generally very large compared to the annual acid input from the atmosphere, and where the H^+ additions exceed the exposure of fresh silicate mineral surface, there is an overall depletion of base cations (Drever, 1997a, 1997b, 1997c; Drever and Stillings, 1997). We would emphasize that, at the same time, such protonation reactions also affect crystal structural bonds and lead to formation of new phases of different stoichiometry, surface, and dissolution properties, generally an irreversible process. Because of the fundamental nature of associated phase alteration, this so-called "H^+ exchange" is more accurately described as a secondary *and irreversible* stage of weathering, adding mineral-structure cations (especially silica) to the total solute flux.

Two fundamental differences between "exchange" and "weathering" reactions are rate and reversibility. True cation exchange reactions are rapid, whereas dissolution of silicates ("weathering") is relatively slow (Velbel, 1996). In addition, true cation exchange is completely reversible, inasmuch as no structural change takes place in the substrate. In contrast, silicate dissolution reactions are irreversible, reflecting the

differential solubility of the principal structural cations of rock-forming minerals, silicon, aluminum, and ferric iron. Thus, if the aqueous input is providing H^+ (for example, acid precipitation) or cations preferred by the exchanger, such as Ca^{++} (as is the case with normal fresh waters), the displaced cations will indeed reflect a pre-existing "exchange complex" at product mineral surfaces, rather than structural cations derived from primary silicate alteration. Though these cations have been obtained from precursor silicate mineral dissolution, their proportions are dictated by selectivity at surfaces and the solubilities of secondary weathering products, instead of the stoichiometry of the primary mineral assemblage. Yuretich and others (1996) evaluated such contributions by the measurement of exchangeable cations in representative samples from the watershed, and utilized an "exchanger" as a phase in the mass balance. Coupled with mineralogic estimates of the silica/sesquioxide status of the weathering products, this approach avoids the assumption of H^+ exchange proceeding on an inert substrate.

In accord with these comments, our view of mineral-water interaction in soils and regolith is similar to that for fresh bedrock, permitting use of product, as well as reactant, mineral composition and kinetic constraints in mass-balance calculations (Murphy and others, 1998). Such considerations better recognize the continuum of weathering and soil-forming processes, and allow a consistent treatment of mineral-water reaction, despite physically heterogeneous (porosity, surface area, grain-size, fracture) conditions as illustrated with the watersheds in the Inyo Mountains or with the step-wise infiltration, mass-balance treatment of weathering stages in the deep regolith of the Luquillo Mountains (White and others, 1998). This view also permits more ready separation of strictly mineralogic control from physical or biologically mediated processes, as was done with the Catoctin Mountain watersheds.

The fact that similar models are obtainable for both the watershed and ground-water case studies presented herein further emphasizes that exchange may have been over-emphasized in surface-water systems. The role of ion exchange (as opposed to irreversible silicate hydrolysis) in determining the composition of weathering-derived waters (even in areas highly affected by acid precipitation) is worthy of reevaluation.

Physical and Hydrologic Factors

Comparative mineral dissolution rates from laboratory and field experiments.—Data from the watersheds in the Inyo Mountains suggests that the differences between carbonate and silicate rates are determined more by contrasts in mineral surface area, rock fracture density, and undersaturation/saturation state of waters with respect to calcite and/or dolomite, rather than differences in fundamental dissolution rates of the minerals. On the other hand, the dissolution rate ratios among various *silicate* phases is in line with the arguments of Velbel (1993a) in favor of the similarity of such ratios (tables 10 and 19).

Blum and others (1998) noted that by far the largest uncertainty in comparing field and laboratory weathering rates is surface area. They noted that the rates calculated from granitic watershed fluxes fall within a factor of about 10, despite differences in catchment properties, similar to the limited range in mass-transfer coefficient ratios we found in our Sierra Nevada, Inyo Mountains, and Vekol Valley examples. Their explanations for the contrast between field and laboratory rates focused on three primary differences: (1) mineral-solid surface area increase at nearly the same rate as reaction-rate decrease; (2) the importance of increasing saturation state and/or Al inhibition (probably as related to product phase formation), such as with feldspars; and (3) the combination of immobile pore water (relative permeability or residence time) with the retardation effect of total solute accumulation. These factors, plus temperature and mineral-explicit kinetic data, are essentially the same as cited by Sverdrup and Warfvinge (1995) and White and others (2001). These findings are in line with the similarities in mass transfer coefficients we obtained for similar

lithologies, and support the contention of Velbel (1993a, 1993b, 1993c, 1993d) and Swoboda-Coberg and Drever (1993) that the recognized weathering rate discrepancies between field and laboratory are due primarily to physical effects.

Time scales of variation and comparative watersheds.—Seasonal variation of solute chemistry can be dramatic and characteristic of many watershed studies (Katz and others, 1985; Williams and others, 1993; Clow and Drever, 1996), reflecting seasonal effects on snowmelt accumulation, ground-water recharge/discharge, temperature, total precipitation, atmospheric loading, and soil/biota interaction. In contrast, saturated flow in ground-water systems is less vulnerable to such short-term variability. The solute dynamics in our two ground-water cases reflect this stability.

In watersheds, bioactive calcium and potassium are particularly dynamic and demonstrate the complex interaction of the inorganic and organic portions of the watersheds (Likens and others, 1998; Likens and others, 1994; Likens and Bormann, 1995). For these reasons, at least annualized values are recommended and generally used to minimize the effects of shorter-term processes (Drever, 1997a, 1997b, 1997c; Drever and Stillings, 1997). We have employed annualized data for our case studies where available or appropriate (for instance the Loch Vale and Catoctin Mountain watersheds). Several investigators have cautioned that even annualized budgets can be subject to longer-term effects, especially in catchment biomass due to deforestation, plant disease, recovery from clear cutting or burning, and climate change (Drever, 1997c; Neal and others, 1997; Velbel, 1985a, 1985b), a factor that we have recognized in the potassium and calcium balances in the Catoctin Mountain example using the spreadsheet approach.

Shorter-term mass-balance analyses are particularly vulnerable to these seasonal and storm-related effects. Differential residence times of fluids and temporal variation in mixing of fluids from different sources within the catchment are non-steady-state processes and tend to obscure an understanding of the mineral weathering impact on such waters. Because saturated flow in ground-water systems is less vulnerable to short-term variability, these types of flow systems are especially appropriate for mass-balance considerations. This has been demonstrated in detail in our Vekol Valley and Trout Lake case studies.

The effect of short-term process variations raises a question about the long-term significance of mineral mass-transfer coefficients calculated here for the watersheds in the Inyo Mountains, where shorter-term or infrequent sampling periods were used. However, these comparisons were derived from samples collected in adjacent catchments during the same season, and nonetheless give a good idea of relative weathering rates in different lithologic mixes under nearly identical climatic regimes. This suggests that mass-balance treatment of comparative watersheds can mitigate the effects of short-term variation, provided they are both driven by the same external variables (climate, biomass change, denudation rate). At the same time, however, the comparison of MTC's in the mass balances obtained for each of the ten years of annualized flux data for the Catoctin watersheds (fig. 16) reveals relations to climatic variations dependent on physical conditions, such as wetting and drying, as well as the relative dissolution rates of the weathering minerals.

Role of vegetation.—The role of the vegetation in controlling the dynamic cycling of critical bioactive elements such as calcium and potassium has long been recognized (Cleaves and others, 1970; Graustein, ms, 1981; Velbel, 1985a, 1985b; Likens and Bormann, 1995; Drever, 1997c; Drever and Stillings, 1997). Although many mass balance studies have assumed that the biomass is in steady state, this is particularly risky in forested catchments. Drever (1984) has pointed out that forests typically go through cycles of gradual biomass increase interrupted by some type of catastrophic loss. In the case of the Catoctin watersheds, the balance for potassium appears controlled in part by the biomass, and the influence of plants on the calcium budget in a large number of

watersheds has been emphasized (for example, Likens and others, 1998). A general biomass stoichiometry with a major base-cation proportion of 4Ca:2K:Mg has been presented by Schnoor and Stumm (1985), which compares favorably with the ratios employed by Velbel (1995) for other watershed mass balances. In a manner similar to our treatment of road salt at Catoctin Mountain, Taylor and Velbel (1991) used major rock-derived cation ratios in forest biomass to effectively introduce a "biomass" phase with averaged stoichiometry into the mass balances for seven of the Coweeta watersheds, and demonstrated differences of as much as a factor of four in overall weathering rates. Individual differences were most pronounced for those minerals, such as biotite, that contain major plant nutrient elements; whereas albitic plagioclase was little affected. For the bare basalt in the Skorradalur watersheds of western Iceland, Moulton and others (2000) determined mass transfer coefficients for plagioclase and pyroxene comparable to the values for feldspar and mafic minerals obtained in four of our six basin examples. For forested drainages, although sodium flux was very similar to that from the bare rock (the same Na solute conservancy seen in our studies), pyroxene mass transfer was increased to 4 to 5 times as much as feldspar. This reflects the increased weathering and Mg+ Ca uptake by the trees.

It is important to note that our mass-balance models revealed the probable role of biomass change at Catoctin Mountain *prior* to our fully investigating the evidence for such effects in the literature. The spreadsheet approach allowed us to easily vary the "biomass" composition, and provided a sensitive test of the relative importance of the biomass component of watershed solute fluxes.

Mass Transfer Comparisons

A comparison of the most reasonable mass balances achieved with our spreadsheet technique for each of the six case studies is presented in table 19. As done in earlier tables, the mass-transfer coefficients for reactant phases are shown as positive, and MTC's for products are given as negative. Overall, there is a positive correlation of total MTC values and CO_2 consumption with total solutes in the waters. Altogether, 20 phases were considered for each 10×10 matrix, with plagioclase, K-feldspar, a mafic phase, goethite, CO_2, and smectite or kaolinite utilized in all, and halite plus gypsum used in most of the mass balances. Not only were the best mass balances obtained with the same mineral assemblages for similar bedrock lithologies, but similar MTC ratio ranges were also maintained, despite variations in hydrology. The most specific mass-balance solutions were required for the siliciclastic ground-water systems, which were not as subject to short-term effects, but did contain more variable mineralogic constituents. In either case, suitable mass balances were achieved while retaining internal consistency in the watershed mineral assemblage.

Our investigations covered a range of lithologic, hydrologic, and climatic settings, yet the results are satisfyingly similar (table 19). The spreadsheet approach using reactant and product mineral compositions as variables to limit the range of possible mass-balance solutions provided much improved results. In large part our better understanding arose from the detailed consideration of the analyzed mineral compositions from the study area, and subtle but important improvements in added geologic constraints. Employing multiple watersheds and multiple ground-water sampling points from well-defined flow paths, and insistence on the same mineral weathering suites for related localities provided added constraints that improved our confidence in the mass-balance results. Use of the fictive phase and mean reactive phase concepts added further constraints that focused our model solutions.

By definition, mass-balance models demand that the sum of all mineral mass transfers and water composition changes must balance. Models that do not balance fail to do so because of inadequate information on the mineralogic, geologic, and ecological setting of the study area, incorrect knowledge of the composition of the mineral phases *demonstrably involved in the weathering reactions,* imprecise water analyses,

or lack of adequate model limitations, as in the case where the number of reacting phases exceeds the number of solute species.

SUMMARY AND CONCLUSIONS

The Features and Advantages of the Spreadsheet Mass-Balance Approach

The application of widely available spreadsheet format and calculations to the derivation of watershed mass balances promotes detailed and relatively rapid assessment of mineral composition effects on natural water chemistry. Use of 10 by 10 matrices of solute/mineral compositions permits sensitive testing of the response of mass-balance model results to variations in multiple mineral-phase assemblages and related chemistry. The method allows us to explore the hydrochemical influence of wide-ranging compositional variation in silicate minerals, particularly critical ubiquitous phases such as plagioclase, biotite, amphibole, pyroxene, and smectite clays. In addition, the concepts of fictive (combination) phases and of mean reactive composition permit us to increase the number of minerals in the matrix and the constraints on the mass-balance solutions. The ease and compositional adaptability of the spreadsheet technique permits ready multiple mass-balance comparisons of variable watershed inputs under similar climatic conditions, or causal delineation of hydrochemical changes between wells along flow lines. This is done with the assumption that similar details in mineral assemblages and compositions will satisfy all mass balances obtained under comparable hydrologic conditions.

Compositionally constrained mass balances can be obtained even where limited by thermodynamic stability considerations for specific minerals under weathering conditions. Plots of mass-transfer coefficients as functions of major mineral composition (especially the plagioclase Na/Ca ratio or dioctahedral smectite solid solution, that is, beidellite/montmorillonite ratio) afford definition of the range of mass-balance solutions in terms of compositional limits for dissolution or precipitation of critical phases in the assemblage. In addition to compositional variation of primary reactant minerals, provision can also be made for the effects of variable charge and exchangeable ion composition in product clays, Fe/Al oxyhydroxides, or amorphous silicate. These features commonly define a relatively narrow range of mass balances strongly restricted by the specific mineral reactants and products involved in the weathering environment, and can sometimes provide unique solutions.

At least qualitatively, multiple and remarkably similar mass-balance solutions can be derived for calibrated watershed and ground-water systems dominated by silicate hydrolysis. Solute derivation heretofore alleged to be largely the purview of soil and vegetation processes may be less influenced by such effects than fundamental rock (mineral) weathering reactions.

Principles and Results of Mass-Balance Assessment of Silicate Mineral Controls on Natural Water Chemistry

Under most weathering conditions, silicate hydrolysis is the most important process governing solute derivation from crystalline rock or clastic terrains, and its distinctive signature can be recognized despite overprints reflecting carbonate (calcite and dolomite) dissolution, road-salting, and/or biomass degradation.

All too often, field mineral-weathering studies characterize the reactant (primary rock-forming mineral) phases in much more detail than the product (soil mineral) phases, a fact that severely hampers mass-balance analysis and proper understanding of appropriate solute-determining reactions.

Cation exchange is a negligible influence on solute output, except in the case of mixing of waters contrasting strongly in concentration. Hydrolysis of silicate phases resulting from acid precipitation or generation in soil environments is not reversible, as required for true ion exchange, but is more accurately considered as second-stage

weathering, with product phases resulting from incongruent protonation reactions. Such reactions can be treated in mass balance the same as primary silicate dissolution.

Greater attention to a thorough compositional characterization of specific mineral assemblages involved in weathering environments (such as in studies by Drever, Velbel, or White) can significantly improve mass-balance models. The emphasis on variation in fluid compositions involved in weathering as compared to either reactant or product mineral phases restricts our ability to quantify weathering processes and/or controlling rates under field conditions. The use of idealized Mg end-member ferromagnesian mineral compositions in mass balances exaggerates the relative mass transfers of feldspar and mafic silicates. The problem is fundamentally one of mineralogic definition.

The effect of mineral compositional relations (expressed, for example, in multiple element ratios; Si/Al, Si/Fe, Na/Ca, Ca/Mg, Na/K, Fe/Mg) involved in multiphase weathering demands attention to major element links in solids and associated fluids. Focus on single elements or solute species without consideration of these synergistic connections can lead to simplistic or erroneous conclusions.

Mineral mass balances over a wide range of hydrologic and weathering conditions indicate that the complete solute conservancy of silica can be expected only where soils and/or groundwaters are dilute and well-flushed under temperate to tropic conditions. The formation of kaolinite or 2:1 layer silicate clays in situations with low hydraulic conductivity or less than continuous flow, such as under more arid conditions, argues against silica solute conservancy.

In crystalline rock or clastic silicate terrains, it is typical that plagioclase will sufficiently dominate the mineral mass balance to justify detailed consideration of its structural and related compositional variation. However, even with allowance for calcite weathering and/or precipitation disproportionate to its abundance, alternative sources of calcium are often demanded (the "calcium problem"). The important roles of amphibole, pyroxene, epidote/zoisite, and/or cycling through clay interlayers and vegetative biomass are thus exposed.

In accord with the conclusions of Graustein (ms, 1981), our mass balances produced no evidence for non-conservative solute behavior of sodium under a variety of weathering conditions in silicate terrains. Magnesium, an important solute in most weathering environments, is closely linked with sparingly soluble iron, and is regulated largely by weathering of ferromagnesian silicates (biotite, chlorite, amphibole, pyroxene) in non-carbonate terrains. Calcium/magnesium ratios in natural waters of crystalline watersheds depend on the Na/Ca ratios of plagioclase, and the Fe/Mg and Ca/Mg ratios of weathering ferromagnesian silicates. Potassium, like calcium, has a prominent silicate mineral source in feldspar, can be heavily involved surficially in vegetative biomass, and may be a constituent of anthropogenic additions (for example, road salt, fertilizer). Unlike calcium, potassium is an important constituent of phyllosilicates, both as reactant (for example, mica) and in product (2:1 layer clays). Mass-balance analysis needs to consider both primary mineral sources and product material sinks.

Mineral mass balance can aid recognition of degree of undersaturation ("affinity") or product nucleation effects on silicate kinetics, especially feldspar and clays. These influences can effectively shut down dissolution of otherwise soluble phases.

With proper attention to the details of mineral assemblages and the nuances of chemical composition, mass-balance analysis can reveal previously unrecognized effects of lithologic and/or hydrologic properties, interannual changes in vegetative biomass, buried evaporative saline residues, road-salting, and long term, or perhaps even seasonal, variations in flow paths, solute source, or fluid reservoir.

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