

# Chemical Weathering in the Loch Vale Watershed, Rocky Mountain National Park, Colorado

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Mineralogic, hydrologic, and geochemical data were used to determine the source of solutes to surface waters draining the Loch Vale Watershed (LVWS), an alpine-subalpine drainage located in the Front Range of Colorado. The flux of dissolved solids from LVWS is primarily controlled by interactions between snowmelt and materials derived from the local bedrock; the biomass has only a minor effect on solute budgets except for ammonium. LVWS is underlain by Precambrian granite and gneiss, the major minerals include quartz, microcline, plagioclase, biotite, and sillimanite. Small amounts of calcite were found along hydrothermally altered zones in the bedrock. Mass balance calculations indicate that the weathering of calcite contributes nearly 40% of the cations derived within the basin. The importance of calcite weathering in LVWS is a result of its chemical reactivity and the high rate of physical erosion in this alpine environment. The average cationic denudation rate in the drainage (390 eq/ha/yr) is similar to long-term rates in forested Adirondack watersheds (500–600 eq/ha/yr), but much lower than the average for the North American Continent (3800 eq/ha/yr). Surface waters in LVWS are susceptible to acidification should acid deposition from the atmosphere increase.

## INTRODUCTION

Acid deposition and its negative impacts on forest and aquatic ecosystems in the eastern United States is currently a topic of increasing concern. Although precipitation in the western United States is not yet considered acidic, industrial and urban development pose a threat to pristine ecosystems. High-elevation drainages in the alpine and subalpine zones of the Rocky Mountains are considered some of the most acid-sensitive in the west [Roth *et al.*, 1985; Omernik and Griffith, 1986]. These systems are characterized by thin acidic soils, steep slopes, and unreactive bedrock types which result in dilute surface waters with alkalinities typically below 100  $\mu\text{eq/L}$ . Because of limited soil water contact in these areas the chemical weathering of bedrock minerals is the primary process by which incoming acidity is neutralized. Therefore an understanding of this process is important for predicting how these ecosystems will respond to possible future increases in acid deposition from the atmosphere [Drever and Hurcomb, 1986].

In this paper we examine the geochemical processes controlling surface water chemistry in the Loch Vale Watershed (LVWS), an alpine-subalpine drainage basin located in the Front Range of Colorado. The Loch Vale Watershed is similar to other high-elevation drainages in the Rocky Mountains and is representative of the most sensitive of these systems to acid deposition [Baron *et al.*, 1987]. Although there is presently no indication that Loch Vale has suffered damage from atmospheric acidity, there is growing evidence of acid deposition at this and other high-elevation sites in the Rocky Mountain region [Heit *et al.*, 1984; Kling and Grant,

1984; Lewis *et al.*, 1984; Harte *et al.*, 1985; Baron *et al.*, 1986; Litaor, 1986].

## STUDY AREA

The Loch Vale Watershed (LVWS) is an alpine-subalpine drainage basin located in Rocky Mountain National Park approximately 80 km northwest of Denver, Colorado (Figure 1). The northeast facing drainage covers 860 ha and ranges in elevation from 3110 m at the watershed outlet up to 4010 m along the Continental Divide. Average annual precipitation rates range from 75 to 100 cm/yr, with greater than 70% of that occurring as snow. Over 80% of the watershed consists of bare rock surfaces and active talus slopes. Tree line occurs at approximately 3300 m, above which vegetation is represented by alpine tundra and meadow. The lower 6% of the basin is covered by a mature forest of subalpine fir (*Abies lasiocarpa*), Engelmann spruce (*Picea engelmanni*), and limber pine (*Pinus flexilis*). The most extensive soils in the basin are found in forested areas and are described as medium- to coarse-textured Cryoboralfs developed in glacial till and bedrock [Walthall, 1985]. These soils are typically less than 50 cm deep and are extremely acidic, with pH values between 3.3 and 4.2.

## METHODS

Precipitation and surface waters in LVWS have been monitored by the National Park Service since 1983 as part of the Aquatic Effects Research Program of the National Acid Precipitation Assessment Program. Wet-only precipitation is collected on a weekly basis using an Aerochemetrics wet/dry precipitation collector in participation with the National Acid Deposition Program (NADP). Stream discharge is measured continuously with a Parshall flume and stilling well located at the watershed outlet. Stream samples for chemical

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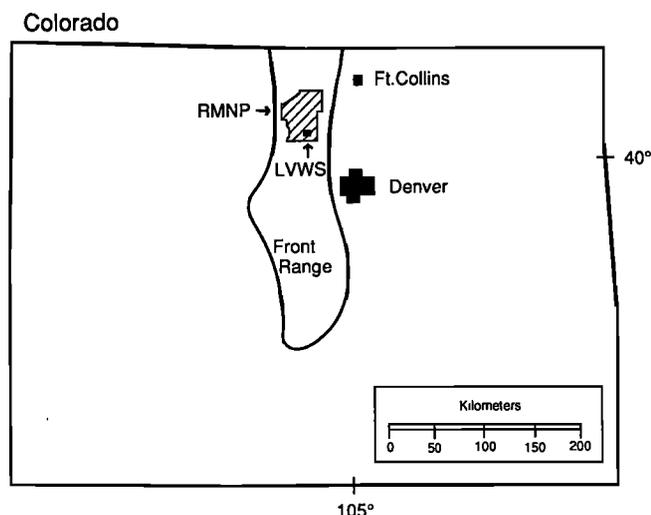


Fig. 1. Location of Rocky Mountain National Park and the Loch Vale Watershed within the Front Range, Colorado.

analysis were collected weekly except during the peak of the snowmelt event in spring when samples were collected daily. Details of collection and analytical procedures are given by *Baron et al.* [1987] and *Lockard* [1987]. The mineralogy and chemistry of soils were determined by X ray diffraction and bulk chemical analysis [Mast, 1989]. Twenty-five thin sections were used to determine bedrock mineralogy by means of optical and cathodoluminescence microscopy. Individual mineral compositions were determined by electron microprobe analysis.

#### BEDROCK AND SOIL MINERALOGY

LVWS is underlain by a biotitic gneiss and the Silver Plume Granite, both Precambrian in age. The mineralogy and chemistry of the two units are very similar although relative mineral abundances do vary slightly. The major minerals are quartz, An<sub>27</sub> plagioclase, microcline, biotite, and sillimanite. Minor and accessory minerals include ilmenite, magnetite, cordierite, orthopyroxene, zircon, and apatite [Cole, 1977]. In both outcrop and thin section there is evidence of hydrothermal fluid infiltration along fractures and joints. The alteration assemblage includes sericite ± epidote which replaces plagioclase and chlorite which replaces biotite. Cathodoluminescence microscopy revealed that small to moderate amounts of calcite also occur with the alteration assemblage (Figure 2). When seen under transmitted light, the calcite is nearly impossible to identify because



Fig. 2. Cathodoluminescence photomicrograph showing fine-grained calcite (white areas) along a hydrothermally altered zone in gneiss. The large white grains outside the altered zone are plagioclase. Photomicrograph is 3.5 mm across.

of its fine grain size and occurrence with other alteration products such as sericite. Calcite was also found along grain boundaries and microfractures in the granite in what otherwise appears to be mineralogically unaltered rock. The carbonate content of whole rock samples, determined by coulometric titration of CO<sub>2</sub> liberated from powdered samples with HCl, ranged from 0.005 to 0.4 wt % CaCO<sub>3</sub>. X ray diffraction data for over 50 soil and sediment samples show the most common clay mineral assemblage to include a mixed-layer smectite-illite clay and kaolinite as well as detrital mica, chlorite, quartz, and feldspar. Minor amounts of vermiculite, hydrobiotite, and gibbsite were also observed in some soils. Selective extractions with Na<sub>2</sub>CO<sub>3</sub> [Follet et al., 1965] and sodium-citrate-dithionite [Jackson, 1956] solutions suggest that amorphous or poorly crystalline aluminum and iron hydroxides are also present in soils. In the <2 μm fraction of 15 soil samples, extractable aluminum ranged from 1.7 to 6.0 wt % Al<sub>2</sub>O<sub>3</sub> and 3.5 to 9.2 wt % Fe<sub>2</sub>O<sub>3</sub>. The average chemical compositions of bedrock and soil minerals are given in Table 1.

#### GEOCHEMICAL MASS BALANCE

Mass balance calculations were used to interpret both mechanisms and rates of mineral weathering in LVWS. Of the techniques used to determine the weathering rates of geologic materials, mass balance studies are generally considered the most reliable means of calculating weathering

TABLE 1. Chemical Composition of Bedrock and Soil Minerals Measured by Electron Microprobe and Bulk Chemical Analysis

Mineral	Composition
Oligoclase	Ca <sub>0.27</sub> Na <sub>0.73</sub> Al <sub>1.27</sub> Si <sub>2.73</sub> O <sub>8</sub>
Biotite*	(K <sub>0.98</sub> Mg <sub>1.00</sub> Fe <sub>1.33</sub> Ti <sub>0.18</sub> Al <sub>0.33</sub> )(Al <sub>1.35</sub> Si <sub>2.65</sub> )O <sub>10</sub> (OH) <sub>2</sub>
Chlorite	(Mg <sub>1.81</sub> Fe <sub>2.72</sub> Al <sub>1.39</sub> )(Al <sub>1.23</sub> Si <sub>2.77</sub> )O <sub>10</sub> (OH) <sub>8</sub>
Calcite	CaCO <sub>3</sub>
Smectite-illite†	(K <sub>0.32</sub> Ca <sub>0.10</sub> )(Fe <sub>0.25</sub> Mg <sub>0.39</sub> Al <sub>1.47</sub> )(Al <sub>0.46</sub> Si <sub>3.54</sub> )O <sub>10</sub> (OH) <sub>2</sub> ·nH <sub>2</sub> O
Kaolinite†	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>

\*Some biotite contained up to 2% F, but Cl was not detected.

†Clay compositions were determined by bulk chemical analysis.

rates on a watershed scale [Velbel, 1985; Clayton, 1986]. The mass balance approach involves determining input-output budgets for dissolved constituents in surface waters and can be expressed as

$$[\text{Output}] - [\text{Input}] = [\text{Weathering} \pm \Delta \text{ exchange pool} \pm \Delta \text{ biomass}]$$

where [Input] represents elements added to the watershed in precipitation and [Output] represents dissolved constituents leaving in catchment in stream water or groundwater if subsurface flow is significant. In undisturbed forested catchments, annual changes in the biomass and soil exchange pool are often assumed to be negligible, and the above expression is reduced to the simpler case where the difference between inputs and outputs represents solutes contributed by mineral weathering. Provided the stoichiometries for individual weathering reactions are known, these expressions can be solved to yield reaction rates for individual minerals as a function of time and total surface area of the watershed [Velbel, 1986].

Two important assumptions were made in applying the mass balance technique in this study. First, the biomass represents a steady state situation, so that on an annual basis the uptake of elements in new growth is approximately equal to the release of these elements by decay [Arthur and Fahey, 1990]. There are a number of reasons for suspecting that the effects of biological uptake should be minimal: (1) The forest in LVWS is mature and has never been logged, (2) tree cores indicate no major fires or other disturbances over the last 450 years [Baron and Bricker, 1987] and, (3) forest vegetation covers less than 7% of the watershed area, so small fluctuations in biomass should not significantly affect solute budgets.

The second assumption is that the release of cations from the soil exchange complex is small compared to the net cation flux from the watershed. Although there is evidence that acid levels in precipitation are higher than historic levels, precipitation is by no means chronically acidic, and it is doubtful that present inputs are sufficient to cause a net loss of cations from exchange sites. Clayton [1988] reports that present levels of atmospheric acidity in Idaho (70 mol/ha/yr) are insufficient to cause cation stripping in forested watersheds in the Idaho Batholith. Acid inputs to Loch Vale average 140 moles/ha/yr, and although twice the loading rates in Idaho, they are 5–10 times lower than hydrogen loading rates in eastern catchments where cation stripping has been documented. In addition, the combination of a sparse soil cover over the drainage and the release of large volumes of water during spring snowmelt minimizes soil water contact, thus reducing the influence of exchange reactions on net cation fluxes.

#### Chemical Budgets

Five years of hydrologic and chemical data were used to calculate the input-output budgets for LVWS. Annual budgets were calculated for a 12-month period beginning November 15, rather than a normal calendar year, to ensure that all precipitation stored in the winter snowpack is removed from the basin as streamflow in the same 365-day period. Precipitation input is calculated by multiplying the measured concentration of each species in the weekly NADP sample by the volume of precipitation incident over

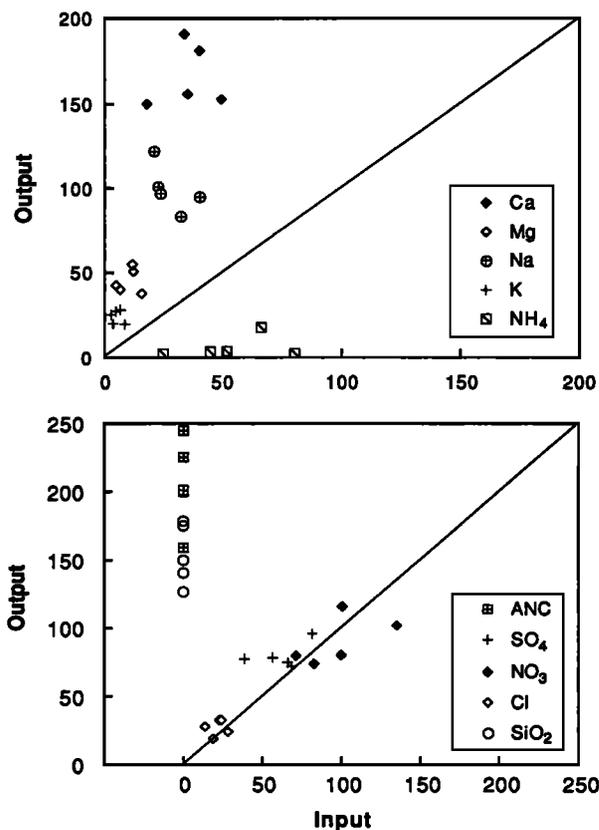


Fig. 3. Five years (1984–1988) of annual inputs versus annual outputs of major chemical species, expressed in moles/hectare/year.

the watershed for that week. These weekly inputs are then summed over the year to yield loading rates in units of moles per hectare of watershed per year. Similar results for outputs were obtained by multiplying weekly discharge at the flume by the appropriate weekly solute concentration; results were obtained more frequently when daily stream water samples were taken in spring. In LVWS the largest source of error in the chemical budgets is related to accurately determining the hydrologic budgets for the watershed, in particular, measuring the input of snow during winter months. Average annual discharge from LVWS over the 5-year study period was  $5.2 \times 10^6 \text{ m}^3$ , with an estimated error of  $\pm 10\%$ . Estimates of the average annual input to the system range from  $7.8 \times 10^6 \text{ m}^3$  to  $14.1 \times 10^6 \text{ m}^3$  of water per year. The minimum estimate is the actual measured value, while the maximum estimate includes corrections for the catch efficiency of the Belfort rain gage and snow that drifts into the catchment from outside the watershed boundaries [Baron and Denning, 1990]. Independent estimates of water input using chloride budgets and the WRENSS hydrologic model [Charter and Swanson, 1989] yield an intermediate value of  $9.5 \times 10^6 \text{ m}^3$ , which is probably the best estimate of average precipitation input to the system over the 5-year study period [Baron and Denning, 1990].

To illustrate more clearly how various inorganic species behave as they pass through the watershed, 5 years of annual inputs, calculated using the measured precipitation volume, are plotted against outputs in Figure 3. Elements which plot on the diagonal line represent conservative behavior, those

TABLE 2. Weathering Reactions Used in Mass Balance Calculations

Reaction	
	<i>Biotite to Mixed-Layer Smectite-Illite</i>
(R1)	$1.15 \text{ Bio} + 0.10 \text{ Ca}^{2+} + 0.49 \text{ H}_4\text{SiO}_4 + 1.21 \text{ O}_2 + 2.13 \text{ CO}_2 + (0.73 + n)\text{H}_2\text{O} \rightarrow \text{Smect} + 0.76 \text{ Mg}^{2+} + 0.81 \text{ K}^+ + 1.28 \text{ FeO(OH)}_{(s)} + 2.13 \text{ HCO}_3^- + 0.21 \text{ TiO}_{2(s)}$
	<i>Chlorite to Mixed-Layer Smectite-Illite</i>
(R2)	$1.39 \text{ Chlor} + 0.10 \text{ Ca}^{2+} + 0.32 \text{ K}^+ + 0.31 \text{ H}_4\text{SiO}_4 + 1.78 \text{ O}_2 + 3.74 \text{ CO}_2 + n\text{H}_2\text{O} \rightarrow \text{Smect} + 2.13 \text{ Mg}^{2+} + 3.53 \text{ FeO(OH)}_{(s)} + 3.74 \text{ HCO}_3^-$
	<i>Oligoclase to Kaolinite</i>
(R3)	$\text{Olig} + 1.27 \text{ CO}_2 + 4.82 \text{ H}_2\text{O} \rightarrow 0.64 \text{ Kaol} + 0.27 \text{ Ca}^{2+} + 0.73 \text{ Na}^+ + 1.46 \text{ H}_4\text{SiO}_4 + 1.27 \text{ HCO}_3^-$
	<i>Kaolinite to Aluminum Hydroxide</i>
(R4)	$\text{Kaol} + 5 \text{ H}_2\text{O} \rightarrow 2 \text{ Al(OH)}_{3(s)} + 2 \text{ H}_4\text{SiO}_4$
	<i>Nitrogen Assimilation</i>
(R5)	$X \text{ NH}_4^+ + Y \text{ NO}_3 + (X - Y) \text{ HCO}_3^- \rightarrow \text{Organic} - \text{N}$
	<i>Calcite Dissolution</i>
(R6)	$\text{Calcite} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}^{2+} + 2 \text{ HCO}_3^-$

which fall above indicate an internal source within the watershed and those below a sink. In general, a net loss of base cations, dissolved silica, and alkalinity and a net gain of nitrogen have occurred from this watershed system. Weathering of bedrock minerals presumably accounts for the dissolved solids in excess of the amount introduced in precipitation. Chloride, sulfate, and nitrate exhibit roughly conservative behavior, suggesting that they are primarily of atmospheric origin and relatively unaffected as they pass through the watershed. Turk and Spahr [1990] found wet deposition to be the primary source of sulfate and chloride for a number of high-elevation lakes along the Colorado Front Range. Small amounts of sulfate may be generated by the oxidation of sulfide minerals, although pyrite was observed only rarely in thin sections of gneiss. Ammonium is the only species with significantly higher inputs than outputs, indicating a net gain of nitrogen to the watershed. The exact mechanisms by which ammonium is removed from surface waters in LVWS are presently unknown. A major fraction of the ion is probably assimilated by aquatic organisms and eventually accumulated in lake sediments or lost from the system by physical washout.

### Chemical Weathering

To interpret the sources of solutes to surface waters draining LVWS, we followed an approach similar to that used by Garrels and Mackenzie [1967]. In Table 2 are presented a set of weathering reactions consistent with mineralogic and chemical data discussed above. Because the chemistry and mineralogy of the granite and gneiss are essentially identical, the same weathering reactions apply for both bedrock units. The results of mass balance calculations using average input-output budgets for 1984–1988 are presented in Table 3. The first line in Table 3 lists chemical inputs calculated using the precipitation volume measured at the NADP station in the watershed. Precipitation inputs in the second line are corrected slightly so that chloride budgets balance. The behavior of chloride in LVWS should be relatively conservative, as there is a negligible contribution from weathering (the concentration in biotite is less than 0.01%), and it is probable that precipitation inputs are underestimated because of problems related to accurately measuring snow inputs in alpine areas [Baron and Bricker, 1987]. In addition, this correction is consistent with the

TABLE 3. Mass Balance Calculations Using Average Chemical Budgets for 1984–1988

Reaction	Ca	Mg	Na	K	SiO <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>	NH <sub>4</sub>	NO <sub>3</sub>	SO <sub>4</sub>	Cl	Weathering Rate, mol/ha/yr
Measured input	35	10	28	5	0	0	108	53	98	62	21	
Cl-corrected input	46	13	36	7	0	0	141	69	127	81	28	
Biotite to smectite-illite	-2	20		21	-12	56						26 biotite
Chlorite to smectite-illite	-1	13		-2	-2	23						6 chlorite
Feldspar to kaolinite	23		63		126	110						86 feldspar
Kaolinite to Al(OH) <sub>3</sub>					42							21 kaolinite
Nitrogen assimilation								-63	-36			
H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup> = H <sub>2</sub> CO <sub>3</sub>						-138	-138					
Calcite dissolution	100					200						100 calcite
Calculated output	166	46	99	26	154	224	3	6	91	81	28	
Measured output	166	46	99	24	154	206	3	6	91	80	28	

Units of dissolved constituents produced(+) or consumed(-) are mol./ha/yr.

TABLE 4. Molar Ca/Na Ratio in Stream Water and Plagioclase From Watersheds Underlain by Felsic Bedrock Types

Surface Water (Ca/Na)	Plagioclase (Ca/Na)	Reference
1.67	0.37	this study
1.00	0.11–0.43	Miller [1961]
1.53*	0.61	Garrels and Mackenzie [1967]
1.22	0.33–0.43	Marchand [1971]
0.93	0.00	Katz et al. [1985]
0.83	0.23	Clayton [1986]
0.97	0.28†	Creasey et al. [1986]
3.85	0.33–1.22	Drever and Hurcomb [1986]
1.53	0.29†	Paces [1986]
0.33	0.11	Cooper et al. [1987]
3.25	0.33	Giovanoli et al. [1988]

\*Perennial springs.

†Whole Rock.

intermediate estimate of precipitation input given by *Baron and Denning* [1990]. In the third and fourth lines the remaining magnesium and potassium are assigned to the weathering of biotite and chlorite to a mixed-layer smectite clay containing approximately 30% illite layers. Both biotite and chlorite reactions are written so that aluminum and iron are conserved in a solid phase. Enough plagioclase is then altered to kaolinite to yield the observed sodium outputs. Sodium was used as a limiting factor because plagioclase is the only significant source of this element in the watershed. Then a small amount of kaolinite is altered to gibbsite to account for the dissolved silica concentrations observed at the outlet. In the seventh and eighth lines, corrections are made for biological assimilation of ammonium and nitrate according to the net reaction given in Table 2, and the excess hydrogen is reacted with bicarbonate. Finally, the remaining calcium and bicarbonate are assigned to the dissolution of calcite. These reactions are then summed to yield the calculated stream water chemistry shown at the bottom of Table 3. Weathering rates of individual minerals in moles/hectare/year are tabulated in the last column of Table 3.

A rather unexpected result of the proposed weathering model is that nearly 40% of the total cations derived within the basin are apparently contributed by the dissolution of calcite. Weathering of a carbonate mineral is not only implied by the mass balance calculations but is supported by the observation of calcite in thin section using cathodoluminescence microscopy. It is surprising that the weathering of calcite, which makes up much less than 1% of the bedrock, is nearly as important as the dissolution of plagioclase which is considerably more abundant.

From the success of mass balance calculations made by *Garrels and Mackenzie* [1967] to interpret the chemistry of ephemeral springs in the Sierra Nevada, it is often assumed that calcium and sodium in waters draining granitic rocks are derived from the weathering of plagioclase. In LVWS the plagioclase composition necessary to account for the observed Ca/Na ratio in stream water would have to be 60% anorthite, which is inconsistent with the measured value of 27%. In recent years, several studies have investigated the relationship between mineral weathering and the chemistry of surface waters draining silicate terrains. In many of these studies the measured Ca/Na ratio is much higher than the observed ratio in the bedrock plagioclase (Table 4). The

excess calcium has been attributed to incongruent feldspar dissolution or to the presence of trace amounts of highly weatherable minerals in the local bedrock. In LVWS, mass balance calculations indicate that the most likely source for the calcium is a reaction which is stoichiometrically similar to calcite dissolution, releasing only calcium and bicarbonate to solution.

Although calcite was observed in LVWS, there are other possible sources of calcium which satisfy this stoichiometric constraint. Two recent studies suggest high Ca/Na ratios in surface waters draining granitic terrains are the result of incongruent release of cations with respect to the average feldspar composition of the bedrock [*Clayton*, 1988; *Velbel and Romero*, 1989]. Incongruent release of cations may be due to inhomogeneities within the mineral grains such as exsolution intergrowths or chemical zonation in crystals. *Gardner* [1983] termed this mechanism apparent incongruency, as it actually represents the congruent dissolution of more than one phase. Although this mechanism is more commonly observed in laboratory dissolution studies, it has been reported to control the chemistry of waters in a natural system [*Clayton*, 1986, 1988]. Clayton found that surface waters draining small catchments underlain by granitic rocks had a Ca/Na ratio of 0.83, considerably higher than the ratio of 0.23 predicted from the weathering of an An<sub>19</sub> plagioclase to kaolinite. Further investigation of plagioclase crystals in thin section revealed that the crystals were commonly zoned. He hypothesized that preferential weathering of the calcic rich cores was apparently controlling the Ca/Na ratio in surface waters. In LVWS it is doubtful that this mechanism supplies additional calcium to surface waters, as chemical zoning was not observed in the plagioclase.

Another mechanism of incongruent dissolution involves a preferential release of cations from the solid phase, as is observed during laboratory dissolution studies when freshly ground minerals first contact solution [*Chou and Wollast*, 1985; *Holdren and Speyer*, 1985; *Mast and Drever*, 1987]. This initial incongruency results from an exchange reaction between cations on the mineral surface for hydrogen ions in solution. As the reaction progresses, the release rate of dissolved components eventually reaches a steady state, and the dissolution reaction becomes congruent. This initial transient state is rather short (lasting of the order of minutes to days), and it is generally assumed that the steady state dissolution step is the main process controlling the weathering of feldspars in the natural environment [*Wollast and Chou*, 1985].

The dissolution of carbonate minerals introduced with eolian dust is another plausible source of dissolved calcium in surface waters. Two recent studies have documented the eolian transport of sedimentary materials from semiarid lowlands to high-elevation watersheds in the Sangre de Cristo Mountains using strontium isotopic ratios in surface waters, vegetation, and soils [*Gosz et al.*, 1983; *Graustein and Armstrong*, 1983]. *Litaor* [1987] studied the mineralogy and chemistry of eolian material collected in an alpine watershed approximately 40 km south of LVWS. The mineralogy of this material was not conclusive as to its origin, although a few (four over a 2-year period) samples contained calcite. *Turk and Spahr* [1990] propose that eolian deposition in the Front Range may be episodic and that relatively large amounts of dust from sedimentary basins to the west could be deposited during periods of drought and strong winds;

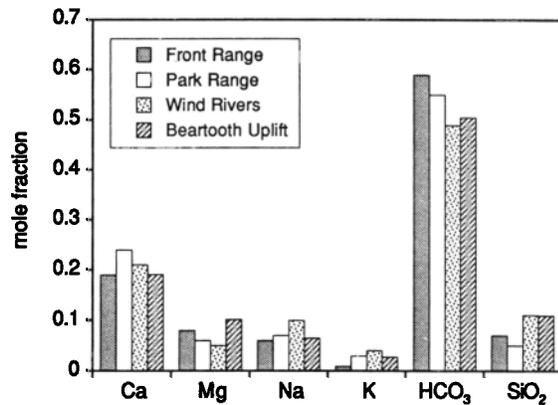


Fig. 4. Graph comparing relative abundance of major cations, silica, and alkalinity for high-elevation lakes in the Rocky Mountain region. Data for each subregion represent averages for several lakes sampled as part of the Western Lake Survey [Landers *et al.*, 1987]. Values not corrected for atmospheric input.

such eolian material should contain readily weatherable calcite, dolomite, and gypsum. At the present time there is no information regarding the flux of wind-blown carbonate to alpine areas in the Colorado Front Range, and it is unknown if eolian inputs would be sufficient to influence calcium levels in surface waters draining LVWS.

In light of the previous discussion it is much more reasonable to explain the excess calcium by the dissolution of trace amounts of calcite present in the local bedrock. Drever and Hurcomb [1986] studied weathering in a temperate glacial environment underlain by igneous and high-grade metamorphic rocks in the northern Cascade Mountains of Washington. Surface waters draining the South Cascade Glacier area contained a high relative abundance of calcium but relatively low levels of sodium and silica. They concluded that the source of calcium was not from the weathering of plagioclase but rather from minor amounts of calcite found in veins and along joints in the local bedrock. Although calcite is present in trace amounts relative to plagioclase in both the Cascades and LVWS, it contributes a significant fraction of the solutes to surface waters. The importance of carbonate weathering in these catchments is the result of two factors. First, and more obvious, is the fact that calcite dissolution rates are typically 6 orders of magnitude faster than rates observed for common aluminosilicate minerals under neutral pH conditions [Plummer *et al.*, 1979; Lasaga, 1984]. Second, high rates of mechanical erosion in alpine areas are sufficient to continually expose fresh bedrock material to incoming precipitation, whereas in lower-elevation sites there is commonly no calcite remaining in near-surface flow paths, and weathering of silicate minerals dominates [Drever *et al.*, 1989].

This result may have implications for the general observation that concentrations of major cations and silica in high-elevation lakes throughout the Rocky Mountains are not consistent with the stoichiometric weathering of common silicate minerals [Stauffer, 1990; Turk and Spahr, 1990]. Figure 4 shows the relative abundance of major cations, silica, and bicarbonate in surface waters draining the Front Range and several other basement uplifts in the Rocky Mountain region. Lakes in the Front Range, as in LVWS, are characterized by high Ca/Na ratios and low relative

levels of silica, suggesting that the weathering of silicate minerals is not the main source of cations in these high-elevation lakes. A similar pattern emerges for lakes in the Park Range just west of Rocky Mountain National Park, the Wind River Range in northwestern Wyoming, and the Beartooth Uplift in southern Montana. All four ranges are cored by Precambrian gneisses and felsic plutonic rocks, yet surface water chemistry is consistent with the weathering of carbonates. Henriksen [1980] made the observation that in areas underlain by granitic rocks, the sum of the nonmarine calcium and magnesium in oligotrophic surface waters unaffected by acid deposition was approximately equivalent to alkalinity, implying that the contribution from feldspar weathering is small [Drever and Hurcomb, 1986].

#### Chemical Denudation Rates

The average cationic denudation rate in LVWS over the 5-year study period is 390 eq/ha/yr. This rate is comparable to a denudation rate of 440 eq/ha/yr calculated for another alpine watershed in the Rocky Mountains [Rochette *et al.*, 1988] and long-term rates in the Adirondack Mountains (500–600 eq/ha/yr) where surface water acidification has occurred [April *et al.*, 1986], suggesting that current weathering rates may not be sufficient to prevent surface water acidification in LVWS. However, predicting the effects of acid deposition on the chemistry surface waters requires not only information regarding present-day rates of weathering but also the effect of an increase in acidity on these rates. The dissolution rates of various feldspar minerals [Chou and Wollast, 1985; Holdren and Speyer, 1985; Mast and Drever, 1987] and biotite [Acker and Bricker, 1989] measured in the laboratory are only weakly dependent on solution pH in the range of most natural waters. In LVWS it is reasonable to assume that rates of silicate mineral weathering would not change significantly if acid levels in precipitation should increase. There is some evidence, however, that increased aluminum concentrations in surface waters might actually cause feldspar dissolution rates to decrease with decreasing pH [Chou and Wollast, 1985; Sverdrup and Warfvinge, 1988].

The effect of acid deposition on the rate of calcite weathering is more difficult to evaluate. Calcite dissolution rate is a complex function of pH and depends on other solute concentrations in addition to solution pH. However, because the absolute rate is so rapid, the limiting factor controlling calcite weathering rates in LVWS is likely the rate at which new material is exposed by physical erosion. Predicting changes in the "weathering" rate of calcite in response to acid deposition will require estimates of calcite exposure rather than changes in the dissolution rate as a function of solution pH.

#### CONCLUSIONS

Input-output budgets for major chemical species were used to determine the source of solutes in surface waters draining the Loch Vale Watershed. The flux of dissolved solids from LVWS is primarily controlled by interactions between snowmelt and materials derived from the local bedrock. The biomass has a negligible effect on major solute budgets except for ammonium which is reduced by microbial uptake in the lakes. Wet deposition accounts for approxi-

mately 40% of the dissolved load in streams and essentially all of the chloride and sulfate, implying that these ions behave conservatively as they pass through the watershed system. There is a net export of major cations, silica, and bicarbonate from the drainage basin, reflecting the weathering of bedrock materials.

Bedrock in LVWS is Precambrian granite and gneiss containing the minerals quartz, feldspar, biotite, chlorite, and sillimanite. Cathodoluminescence showed that calcite in these crystalline rocks is more widespread than indicated by transmitted-light petrography alone. Mass balance calculations indicate that mineral weathering reactions involve primarily the dissolution of plagioclase, biotite, and calcite. Although calcite is present in trace amounts, it supplies nearly 40% of the cations derived within the basin. The importance of calcite weathering in this watershed is the result of its chemical reactivity and the high rate of physical erosion in this alpine environment. As in LVWS, the concentrations of major cations and silica in many high-elevation lakes throughout the Rocky Mountains are inconsistent with the weathering of common granitic minerals [Turk and Spahr, 1990]. Our results suggest that weathering of carbonate minerals may commonly play an important role in controlling the chemistry of surface waters in alpine drainages underlain by granitic and high-grade metamorphic rocks.

Although LVWS presently shows no evidence of damage resulting from current levels of atmospheric acidity [Baron *et al.*, 1986], surface waters in LVWS should be considered sensitive to possible increases in acid deposition from the atmosphere. The thin, sparse soils of LVWS are characterized as having little capacity to neutralize acid deposition [Walshall, 1985]. The most important process that buffers against acidity in LVWS is the chemical weathering of bedrock minerals. The average cationic denudation rate for LVWS is 390  $\mu\text{eq/L}$ . This value is similar to long-term rates in the Adirondacks where surface water acidification has occurred [April *et al.*, 1986], indicating that current weathering rates may not be sufficient to prevent acidification in LVWS unless present-day rates are accelerated by a decrease in pH. In Loch Vale, changes in the weathering rate will depend largely on the availability of calcite through physical erosion rather than a change in the absolute rate of mineral weathering as a function of solution pH.

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#### REFERENCES

- Acker, J. C., and O. P. Bricker, pH influence on dissolution rate and cation release from biotite, *Eos Trans AGU*, 70(15), 328, 1989.
- April, R., R. Newton, and L. T. Coles, Chemical weathering in two Adirondack watersheds: Past and present-day rates, *Geol. Soc. Am. Bull.*, 97, 1232–1238, 1986.
- Arthur, M. A., and P. J. Fahy, Mass and nutrient content of decaying boles in an Englemann Spruce-Subalpine Fir forest, Rocky Mountain National Park, Colorado, *Can. J. For.*, 20, 730–737, 1990.
- Baron, J., and O. P. Bricker, Hydrologic and chemical flux in Loch Vale Watershed, Rocky Mountain National Park, in *Chemical Quality of Water and the Hydrologic Cycle*, edited by D. McKnight and R. C. Averett, pp. 141–156, Lewis Publishers, Chelsea, Mich., 1987.
- Baron, J., and A. S. Denning, Hydrologic budget estimates for Loch Vale Watershed, in *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*, edited by J. Baron, Springer-Verlag, New York, in press, 1990.
- Baron, J., S. A. Norton, D. R. Beeson, and R. Herrmann, Sediment diatom and metal stratigraphy from Rocky Mountain lakes with special reference to atmospheric deposition, *Can. J. Fish., Aquat. Sci.*, 43, 1350–1362, 1986.
- Baron, J., S. Spaulding, and B. Olver, Long-term ecological research into the effects of atmospheric deposition in Rocky Mountain National Park, Annual progress report-fiscal year 1986, Water Resour. Div., Natl. Park Serv., Washington, D. C., 1987.
- Charter, K., and R. Swanson, WRENSS hydrologic procedures for rain and snow dominated regions, Personal computer simulation model, Northern Forestry Centre, Edmonton, Alberta, Canada, 1989.
- Chou, L., and R. Wollast, Steady-state kinetics and dissolution mechanisms of albite, *Am. J. Sci.*, 285, 963–993, 1985.
- Clayton, J. L., An estimate of plagioclase weathering rate in the Idaho Batholith based upon geochemical transport rates, in *Rates of Chemical Weathering of Rocks and Minerals*, edited by S. M. Colman and D. P. Dethier, pp. 453–467, Academic, San Diego, Calif., 1986.
- Clayton, J. L., Some observations of the stoichiometry of feldspar hydrolysis in granitic soils, *J. Environ. Qual.*, 17, 153–157, 1988.
- Cole, J. C., Geology of east-central Rocky Mountain National Park and vicinity, with emphasis on the emplacement of the Precambrian Silver Plume Granite in the Longs Peak-St. Vrain Batholith, Ph.D. dissertation, Univ. of Colo., Boulder, 1977.
- Cooper, D. M., E. M. Morris, and C. J. Smith, Precipitation and streamwater chemistry in a subarctic Scottish catchment, *J. Hydrol.*, 93, 221–240, 1987.
- Creasey, J., A. C. Edwards, J. M. Reid, D. A. MacLeod, and M. S. Cresser, The use of catchment studies for assessing chemical weathering rates in two contrasting upland areas in northeast Scotland, in *Rate of Chemical Weathering of Rocks and Minerals*, edited by S. M. Colman and D. P. Dethier, pp. 468–502, Academic, San Diego, Calif., 1986.
- Drever, J. I., and D. R. Hurcomb, Neutralization of atmospheric acidity by chemical weathering in an alpine drainage basin in the North Cascade Mountains, *Geology*, 14, 221–224, 1986.
- Drever, J. I., M. A. Mast, and N. Swoboda-Colberg, Chemical weathering rates in small catchments underlain by silicate rocks, paper presented at the Chapman Conference on Hydrogeochemical Responses of Forested Catchments, AGU, Bar Harbor, Maine, Sept. 18–21, 1989.
- Follet, E., A. C. Mchardy, W. J. Mitchell, and B. F. L. Smith, Chemical dissolution techniques in the study of soil clays, I, *Clay Miner.*, 6, 23–34, 1965.
- Gardner, L. R., Mechanics and kinetics of incongruent feldspar dissolution, *Geology*, 11, 418–421, 1983.
- Garrels, R. M., and F. T. MacKenzie, Origin of the chemical compositions of some springs and lakes, in *Equilibrium Concepts in Natural Water Systems*, *Adv. Chem. Ser.*, vol. 67, edited by R. F. Gould, pp. 222–242, American Chemical Society, Washington, D. C., 1967.
- Giovanoli, R., J. L. Schnoor, L. Sigg, W. Stumm, and J. Zorbrist, Chemical weathering of crystalline rocks in the catchment area of acidic Ticino Lakes, Switzerland, *Clays Clay Miner.*, 36(6), 521–529, 1988.
- Gosz, J. R., D. G. Brookins, and D. I. Moore, Using strontium isotope ratios to estimate inputs to ecosystems, *Bioscience*, 33(1), 23–30, 1983.
- Graustein, W. C., and R. L. Armstrong, The use of strontium-87/strontium-86 ratios to measure atmospheric transport into forested watersheds, *Science*, 219, 289–292, 1983.
- Harte, J., G. P. Lockett, R. A. Schneider, S. Micheals, and C. Blanchard, Acid precipitation and surface water vulnerability on the western slope of the high Colorado Rockies, *Water Air Soil Pollut.*, 25, 313–320, 1985.
- Heit, M., R. Klusek, and J. Baron, Evidence of deposition of anthropogenic pollutants in remote Rocky Mountain lakes, *Water Air Soil Pollut.*, 22, 403–416, 1984.

- Henriksen, A., Acidification of fresh waters—A large scale titration, in *Ecological Impact of Acid Precipitation*, edited by D. Drablos and A. Tollan, pp. 68–74, SNSF Project, Norw. Inst. for Water Res., Oslo-Ås, 1980.
- Holdren, G. R., Jr., and P. M. Speyer, Stoichiometry of alkali feldspar dissolution at room temperature and various pH values, *Am. J. Sci.*, 285, 994–1026, 1985.
- Jackson, M. L., *Soil Chemical Analysis—Advanced Course*, Department of Soil Science, University of Wisconsin, Madison, 1956.
- Katz, B. G., O. P. Bricker, and M. M. Kennedy, Geochemical mass-balance relationships for selected ions in precipitation and stream waters, Catoctin Mountains, Maryland, *Am. J. Sci.*, 285, 931–962, 1985.
- Kling, G. W., and M. C. Grant, Acid precipitation in the Colorado Front Range: An overview with time predictions for significant effects, *Arct. Alp. Res.*, 16, 321–329, 1984.
- Landers, D. H., et al., Characteristics of lakes in the western United States, vol. I, Population descriptions and physico-chemical relationships, EPA/600/3-86/054a, U.S. Environ. Prot. Agency, Washington, D. C., 1987.
- Lasaga, A. C., Chemical kinetics of water-rock interactions, *J. Geophys. Res.*, 89(B6), 4009–4025, 1984.
- Lewis, W. C., M. C. Grant, and J. F. Saunders, Chemical patterns of bulk atmospheric deposition in the state of Colorado, *Water Resources Res.*, 20(11), 1691–1704, 1984.
- Litaor, M. I., Geochemistry of alpine soils in the Colorado Front Range, with special reference to acid deposition, Ph.D. dissertation, Univ. of Colo., Boulder, 1986.
- Litaor, M. I., The influence of eolian dust on the genesis of alpine soils in the Front Range, Colorado, *Soil Sci. Soc. Am. J.*, 51, 142–147, 1987.
- Lockard, J. M., Laboratory operations, Central Analytical Laboratory, NADP/NTN deposition monitoring, quality assurance report, Ill. State Water Surv., Champaign, 1987.
- Marchand, D. E., Rates and modes of denudation in the White Mountains, eastern California, *Am. J. Sci.*, 270, 109–135, 1971.
- Mast, M. A., A laboratory and field study of chemical weathering with special reference to acid deposition, Ph.D. dissertation, Univ. of Wyoming, Laramie, 1989.
- Mast, M. A., and J. I. Drever, The effect of oxalate on the dissolution rates of oligoclase and tremolite, *Geochim. Cosmochim. Acta*, 51, 2559–2568, 1987.
- Miller, J. P., Solutes in small streams draining single rock types, Sangre de Cristo Range, New Mexico, *U.S. Geol. Surv. Water Supply Pap.*, 1535-F, 1–23, 1961.
- Omernik, J. M., and G. E. Griffith, Total alkalinity of surface waters: A map of the western region, EPA-600/D-85-219, Corvallis Environ. Res. Lab., U.S. Environ. Prot. Agency, Corvallis, Oreg., 1986.
- Paces, T., Rates of weathering and erosion derived from mass balance in small drainage basins, in *Rates of Chemical Weathering of Rocks and Minerals*, edited by S. M. Colman and D. P. Dethier, pp. 531–551, Academic, San Diego, Calif., 1986.
- Plummer, L. N., D. L. Parkhurst, and T. M. L. Wigley, Critical review of the kinetics of calcite dissolution and precipitation, in *Chemical Modeling in Aqueous Systems, Symp. Ser.*, vol. 93, edited by E. A. Jenne, pp. 537–573, American Chemical Society, Washington, D. C., 1979.
- Rochette, E., J. I. Drever, and F. Sanders, Chemical weathering in the West Glacier Lake drainage basin, Snowy Range, Wyoming: Implications for future acid deposition, *Contrib. Geol.*, 26(1), 29–44, 1988.
- Roth, P., C. Blanchard, J. Harte, H. Michaels, and M. El-Ashry, The American west's acid rain test, *Rep. 1*, World Resour. Inst.-Res., Washington, D. C., 1985.
- Stauffer, R. E., On granite weathering and the sensitivity of alpine lakes to acid deposition, *Limnol. Oceanogr.*, in press, 1990.
- Sverdrup, H., and P. Warfvinge, Weathering of primary silicate minerals in the natural soil environment in relation to a chemical weathering model, *Water Air Soil Pollut.*, 38, 387–408, 1988.
- Turk, J. T., and N. E. Spahr, Rocky Mountains: Controls on lake chemistry, in *Acid Deposition and Aquatic Ecosystems: Regional Case Studies*, edited by D. F. Charles, Springer-Verlag, New York, in press, 1990.
- Velbel, A. M., Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge, *Am. J. Sci.*, 285, 904–930, 1985.
- Velbel, M. A., Influence of surface area, surface characteristics, and solution composition on feldspar weathering rates, in *Geochemical Processes at Mineral Surfaces, Symp. Ser.*, vol. 323, edited by J. Davis and K. Hayes, pp. 615–634, American Chemical Society, Washington, D. C., 1986.
- Velbel, M. A., and N. L. Romero, Amphibolite weathering and cation budgets in southern Blue Ridge and Colorado Front Range, USA, paper presented at the 28th International Geological Congress, Washington, D. C., July 9–19, 1989.
- Walthall, P. M., Acidic deposition and the soil environment of Loch Vale Watershed in Rocky Mountain National Park, Ph.D. dissertation, Colo. State Univ., Fort Collins, 1985.
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