

Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado

David W. Clow and M. Alisa Mast

U.S. Geological Survey, Lakewood, Colorado

Tom D. Bullen

U.S. Geological Survey, Menlo Park, California

John T. Turk

U.S. Geological Survey, Lakewood, Colorado

Abstract. Sr isotopic ratios of atmospheric deposition, surface and subsurface water, and geologic materials were measured in an alpine/subalpine watershed to characterize weathering reactions and identify sources of dissolved Ca in stream water. Previous studies have noted an excess of Ca in stream water above that expected from stoichiometric weathering of the dominant bedrock minerals. Mixing calculations based on $^{87}\text{Sr}/^{86}\text{Sr}$ indicate that on an annual basis, $26 \pm 7\%$ of Ca export in streams is atmospherically derived, $23 \pm 1\%$ is from weathering of plagioclase, and the remainder is from weathering of calcite present in trace amounts in the bedrock. A potential source of error when applying Sr isotopes in catchment studies is determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by mineral weathering, which is complicated by the wide range of mineral isotopic compositions, particularly in older rocks, and the variable rates at which the minerals weather. In this study, base-flow stream chemistry was used to represent the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr derived from mineral weathering because it effectively integrates the potentially variable isotopic composition of Sr released by weathering in the alpine environment.

Introduction

Catchment studies have traditionally used a combination of hydrologic and chemical techniques to identify the important processes controlling surface-water chemistry. Analysis of spatial and temporal trends in major and minor element chemistry has proven to be a powerful tool [Likens *et al.*, 1977; Williams *et al.*, 1993; Campbell *et al.*, 1995], yet many questions cannot be answered with hydrologic and chemical data alone. Mass balance calculations, which are often used to try to identify the important sources of solutes in natural waters [e.g., Garrels and Mackenzie, 1967; Drever, 1988; Mast, 1992], frequently do not yield unique solutions. This occurs when there are multiple potential sources for a given element. Ca, for example, is an important constituent in atmospheric deposition but also is commonly present in plagioclase and carbonate minerals in rocks, and it is impossible to distinguish between the sources of Ca chemically. Several previous studies have established the usefulness of Sr isotopes in differentiating Ca sources [e.g., Aberg and Wickman, 1987; Gosz and Moore, 1989; Jones and Faure, 1978]. The Sr isotopic technique takes advantage of the fact that Sr is geochemically similar to Ca and substitutes for Ca in mineral lattices. Strontium 86 is nonradiogenic, and ^{87}Sr is produced by decay of ^{87}Rb (half-life = 4.8×10^{10} years); Rb is geochemically similar to K and substitutes for K in the mineral lattice. Therefore, in K-bearing minerals such as K-

feldspar and biotite, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increase over time, leading to progressively increasing isotopic separation between individual bedrock minerals. The basic premise in using $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in weathering studies is that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in natural water is a reflection of the contributions made by various minerals as they dissolve. Other processes, including atmospheric deposition, cation exchange, and biological cycling, also can influence the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the water [Graustein and Armstrong, 1983; Miller *et al.*, 1993]. However, unless there have been recent anthropogenic or natural disturbances, annual gains or losses of Sr from cation exchange and biological pools should be minimal.

In the present study the Sr isotopic composition of surface waters was measured to gain insight into hydrogeochemical processes in Loch Vale, an alpine/subalpine watershed in the Rocky Mountains of north-central Colorado. Because the geologic, vegetative, and climatic characteristics of Loch Vale are similar to many basins in the Rocky Mountains [Landers *et al.*, 1987], the methods used and results obtained from this study should have broad applicability throughout the Rocky Mountain region. Our specific objective was to use $^{87}\text{Sr}/^{86}\text{Sr}$ as a tool to characterize the dominant sources of dissolved Ca in surface waters in Loch Vale. Understanding the hydrogeochemical processes controlling Ca in aquatic ecosystems is important because dissolution of Ca-bearing minerals often is a major source of alkalinity in natural waters. It has been commonly assumed that plagioclase weathering is the dominant source of Ca in surface water in granitic terrain because plagioclase is the most common Ca-bearing mineral in granitic rocks. How-

This paper is not subject to U.S. copyright. Published in 1997 by the American Geophysical Union.

Paper number 97WR00856.

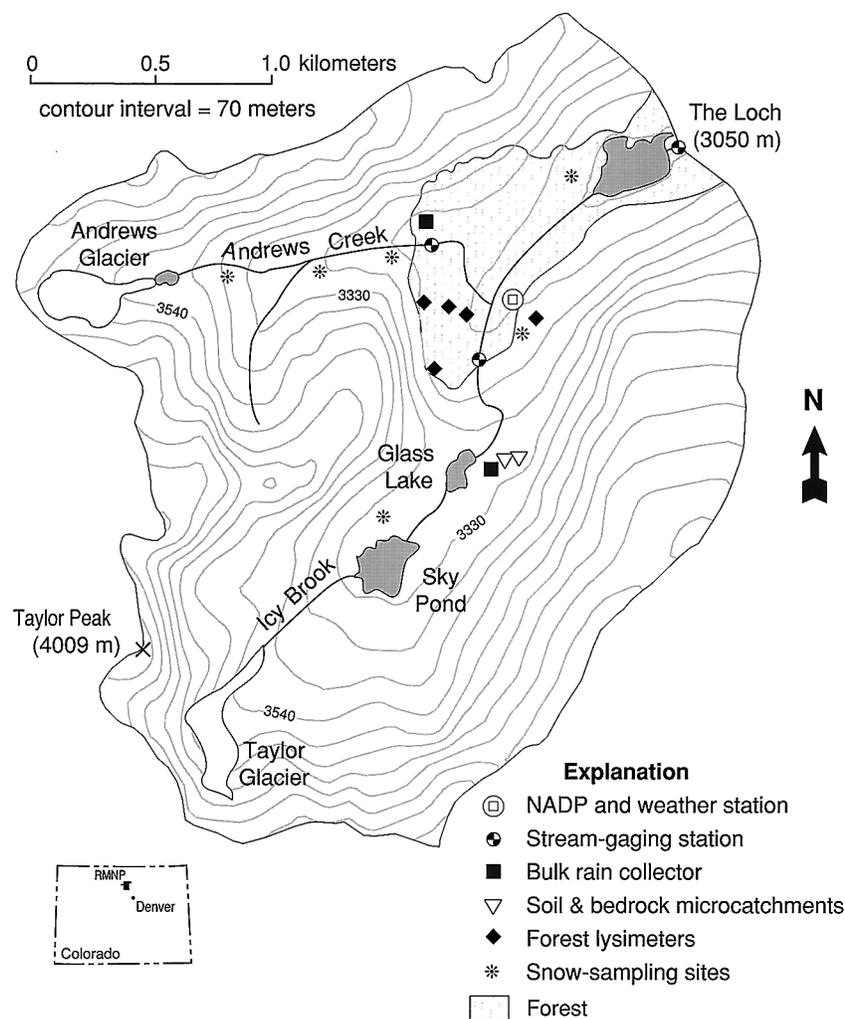


Figure 1. Map showing locations of sampling sites and stream gages in Loch Vale watershed.

ever, in a previous study of solute sources in Loch Vale it was determined that stream water had a much higher Ca/Na ratio than the plagioclase in the bedrock [Mast *et al.*, 1990], and in fact, high Ca/Na ratios are common in surface water throughout the Rocky Mountains [Eilers *et al.*, 1987; Stauffer, 1990; Turk and Spahr, 1991]. Based on element ratios in the rocks and streams in Loch Vale, the most likely source of the excess Ca is carbonate mineral weathering; however, the type and origin of the carbonate are uncertain. Previous work has indicated that weathering of calcite present in trace amounts in the granitic bedrock may be an important source of Ca to surface water [Mast, 1992], but weathering of eolian carbonate dust is also plausible [Litaor, 1987; Turk and Spahr, 1991; Clow and Mast, 1995].

Site Description

The study was conducted in the Loch Vale watershed, located in Rocky Mountain National Park, approximately 80 km northwest of Denver, Colorado. Loch Vale has been a site of ecosystem research by the National Park Service since 1981 [Baron, 1992] and is currently part of the Water, Energy, and Biogeochemical Budgets (WEBB) program of the U.S. Geological Survey [Turk *et al.*, 1993; Lins, 1994]. Loch Vale is a

660-ha alpine/subalpine basin ranging in elevation from 3050 m at the outlet of the Loch (the lowest lake) up to 4009 m at the summit of Taylor Peak (Figure 1). Over 90% of the basin is above tree line; this area is characterized by alpine tundra, bedrock outcrops, and talus slopes. An Engelmann spruce-subalpine fir forest covers the basin below about 3250 m, and several wet-sedge meadows lie next to stream channels. Bedrock consists of Precambrian gneiss (1750 Ma) [Peterman *et al.*, 1968], which underlies 80% of the watershed and crops out mostly above tree line, and Precambrian Silver Plume granite (1450 Ma) [Peterman *et al.*, 1968], which intrudes the gneiss and underlies the lower 20% of the basin. The mineralogy of the two units is similar; primary minerals consist of quartz (28–41%), plagioclase (25–30%), biotite (6–16%), microcline (9–34%), and sillimanite (0–6%) [Cole, 1977]. The plagioclase is not zoned [Cole, 1977] and has a composition of $An_{27\pm 3}$ (2σ), on the basis of microprobe analyses of 27 plagioclase grains in 4 different rocks from Loch Vale [Mast, 1989]. Minor and accessory minerals include ilmenite, magnetite, cordierite, orthopyroxene, zircon, and apatite [Cole, 1977]. Locally, the rocks have undergone secondary alteration, converting biotite to chlorite and plagioclase to sericite. The secondary chlorite is generally visible only under a microscope, except where it

occurs as a coating along fault surfaces. Trace amounts of microcrystalline calcite occur along grain boundaries and hydrothermally altered microfractures in the bedrock [Mast, 1989]. The secondary alteration occurs mainly along faults and fractures that may be related to Laramide faulting and hydrothermal activity [Mast, 1989]. The median weight percentage of calcite in 23 rock samples from Loch Vale was 0.020%, and the range was 0.400–0.003% on the basis of coulometric titration analyses [Mast, 1989].

Since 1992 the U.S. Geological Survey has operated gaging stations on two major tributaries in the basin, Icy Brook (gage altitude = 3180 m) and Andrews Creek (gage altitude = 3215 m), which are the focus of this paper (Figure 1). Icy Brook, which drains an area of 326 ha, originates at the terminus of Taylor Glacier and flows through two alpine lakes, Sky Pond and Glass Lake, before reaching the gage. Andrews Creek drains an area of 183 ha and originates from a small tarn at the base of Andrews Glacier. The two subbasins are almost entirely alpine, and soils cover less than 5% of the basin areas, mostly on the valley floors [Walthall, 1985; Baron et al., 1992]. Extensive talus deposits and debris flows, which were deposited during and after the Neoglacial and Pinedale glaciations [Madole, 1976], mantle the lower parts of sheer bedrock cliffs along the flanks of the valley floor. Soils in the cirque valleys are thin, rocky, poorly sorted materials (Cryorthents and Cryocrepts) formed mostly on Neoglacial till and talus [Madole, 1976; Richmond, 1960; Walthall, 1985], although some of the deposits might be late Pleistocene [Davis, 1988]. The deepest and laterally most continuous soils occur in the forested areas, below the stream gages. Forest soils (Cryoboralfs) are believed to have formed from Pinedale till deposited between 12,000 and 15,000 years ago [Madole, 1976; Birkeland et al., 1987; Davis, 1988] and have horizons that are more well-developed than those in the alpine soils [Baron et al., 1992].

X ray diffraction data for over 50 Loch Vale soils indicate that the dominant mineral assemblage in the clay fraction consists of a mixed-layer smectite-illite mineral, kaolinite, 10-Å mica, chlorite, and trace amounts of quartz and feldspar [Mast, 1989]. A similar mineral assemblage was also reported by Walthall [1985] for Loch Vale soils and by Rochette et al. [1988] for alpine soils in southeastern Wyoming. Of the observed soil minerals, mica, chlorite, feldspar, and quartz are most likely inherited from the local bedrock. Smectite is probably formed from the weathering of biotite and chlorite which, with continued leaching, may eventually be transformed to kaolinite [Walthall, 1985]. This is consistent with a sequence of alteration proposed for mica in soils formed on granite and gneiss in Poland [Stoch and Sikoma, 1976]: mica → mica/smectite → smectite → kaolinite. Allen and Hajeck [1989] also list biotite as a likely precursor for smectite in granitic terrane. This weathering scenario is further supported by the observation that mica and chlorite are much more abundant in the clay and silt fractions of the relatively young alpine soils than in the more highly weathered forest soils [Mast, 1989].

In both subbasins, snowmelt constitutes the major hydrologic event in a given year. Peak flow typically is in late June, and up to 70% of the total discharge occurs between mid-May and late July. Discharge is quite low during the winter (the base-flow period), and at that time is probably derived from perennial seeps and springs. In 1994, annual precipitation to the Loch Vale watershed was 118 cm, slightly above the average for 1984–1992 (100 cm) [NADP/NTN, 1984–1994]. Annual runoff was 89 cm and 68 cm in Andrews Creek and Icy Brook,

respectively. The difference in runoff probably is a result of greater snow input and less evaporation in the Andrews Creek subbasin [Campbell et al., 1995]. A recent water budget indicated that blowing snow contributes a substantial amount of water to the Andrews Creek subbasin [Ingersoll, 1995]. The Andrews subbasin is expected to have lower evaporation rates because there is less open water and the aspect and relief of the valley limit solar heating [Campbell et al., 1995].

Methods

Samples of bedrock, soil, and dry deposition were collected to characterize the isotopic composition of solid phases in the catchment. Mineral separates of plagioclase, biotite, and potassium feldspar were obtained from crushed samples of unaltered bedrock, and a sample of biotite also was separated from an alpine soil sample. The soil and crushed rock were sieved to a 100- to 200- μm -size fraction, and minerals were separated using a magnetic separator, heavy liquids, and hand picking under a binocular microscope. The purity of the mineral separates was tested by X ray diffraction (XRD) and visual inspection using a binocular microscope. Powdered mineral and whole-rock samples were digested in sealed Teflon vessels using high-purity HF, HNO₃, and HCl (see work by Bullen et al. [1996] for details). Soil samples were collected from the Oe, A, and B horizons in two pits: one in the alpine zone and the other in a forested area. Soils were air dried and sieved to 2 mm, and exchangeable cations were extracted from the <2-mm-size fraction of air-dried soil using 1-M ammonium acetate (NH₄-Ac) [Thomas, 1982]. An eolian dust sample was collected from the dry-side bucket of a wet-dry precipitation collector located at the main weather station during the summer of 1994. Soluble matter in the dust was extracted in deionized water (DI) and analyzed for ⁸⁷Sr/⁸⁶Sr. The mineralogy of the dust was determined by XRD, and the inorganic carbon content was measured by coulometric titration. Mineral and rock digests, cation-exchange solutions, and dry-deposition leachates were filtered through prerinsed 0.45- μm nucleopore filters and acidified with concentrated high-purity nitric acid prior to ⁸⁷Sr/⁸⁶Sr analysis. The isotopic composition of Sr in the digests was measured on a Finnigan MAT 261[®] multicollector mass spectrometer. Isotope ratios have been corrected for natural and analytical stable isotope fractionation to ⁸⁸Sr/⁸⁶Sr = 8.37521 and are precise to within 0.00002 (2 σ). The mass spectrometer used typically yields a value of 0.71024 for the NBS-987 Sr metal standard; Sr concentrations in the rock and minerals are precise to within 1%.

Microcrystalline calcite could not be isolated from the bedrock for ⁸⁷Sr/⁸⁶Sr analysis by standard physical techniques because of its extremely small grain size; therefore two types of leaching experiments, a sequential leach and a single leach, were conducted on crushed rock (<2 mm) in order to extract the calcite from the rock. In the sequential-leach experiments, a 6-g sample of crushed gneiss was leached with six sequential NH₄-Ac treatments; the first three were in 100 mL of 1-M NH₄-Ac at pH 7.0, and the last three were in 100 mL of 0.1-M NH₄-Ac adjusted to pH 5.5, 5.0, and 4.5 with acetic acid. For each treatment the crushed rock and reactant solution were placed in a Teflon bottle and shaken for 1 hour. After each treatment the leachates were centrifuged, solutions were decanted for analysis, and solids were returned to the bottle for the next treatment. In the single-leach experiments, three crushed rock samples (one gneiss and two granites) were split

Table 1. Strontium Isotopic Ratios and Sr and Rb Concentrations of Rocks, Minerals, and Exchangeable Cations From Catchment Soils

	Concentrations		
	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr, ppm	Rb, ppm
<i>Rocks and Minerals</i>			
Whole rock	0.88432	nm	nm
Microcline, * #1	0.85092	187	470
Microcline, #2	0.83059	167	416
Fresh (bedrock) biotite*	4.8339	10	575
Oxidized (soil) biotite	1.9016	23	627
Plagioclase (An_{27})*	0.71956	261	11
Bedrock calcite*	0.73215	858	nm
Dry deposition (soluble fraction)	0.71005	1960	nm
<i>Exchangeable Cations</i>			
Alpine soil, 0–18 cm	0.71861	nm	nm
Alpine soil, 18–33 cm	0.72043	nm	nm
Alpine soil, 33–53 cm	0.72227	nm	nm
Forest soil, 0–10 cm	0.71910	nm	nm
Forest soil, 10–24 cm	0.71898	nm	nm
Forest soil, 24–37 cm	0.71949	nm	nm

The $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration of bedrock calcite were estimated based on leaching experiments described in the text; nm, not measured.

*Minerals and mineral compositions that were used to predict $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by mineral weathering.

into two equal-size subsamples. One subsample was reacted with 100 mL of DI, and the other was reacted with 100 mL of 1-M $\text{NH}_4\text{-Ac}$ solution (pH 7.0). Each subsample was reacted for 1 hour, and the resulting leachates were separated from the solids by centrifugation. Both sets of experiments were conducted at room temperature ($22 \pm 2^\circ\text{C}$). Sr isotopic compositions of leachates were analyzed as previously described. Solutions were analyzed for Ca, Mg, Na, Si, and Sr concentrations by inductively coupled plasma (ICP) and K by atomic absorption spectroscopy. Sr concentrations in all of the input $\text{NH}_4\text{-Ac}$ solutions were below the detection limit of $<0.01 \mu\text{eq L}^{-1}$. Detection limits were $<1 \mu\text{mol L}^{-1}$ for Ca, Mg, Na, K, and Si.

Precipitation, surface-water, and soil-water samples were collected during 1994 to characterize the Sr-isotopic composition of waters in Loch Vale (Figure 1). Stream water samples were collected semiweekly to weekly at the Andrews Creek and Icy Brook gages from early April (prior to snowmelt) through mid-October, when the channel was covered by snow. Samples also were collected at the Icy Brook, Andrews Creek, and the Loch outlet gages in 1991 and 1992, although less frequently than in 1994. Six depth-integrated snowpack samples were collected using an aluminum corer in early April, near peak snow accumulation (approximately 2 m depth). Samples were stored in prerinsed polyethylene bags and melted in polyethylene containers in the laboratory [Campbell et al., 1995]. Bulk rain samples were collected approximately weekly between June 15 and August 30, 1994, at two elevations in the watershed. The polyethylene bulk collector consisted of a funnel connected to a bottle using a piece of looped tubing. Outflow chemistry was monitored at two adjacent alpine microcatchments (Figure 1). Storm runoff was collected at a 30-m² bedrock outcrop during nine summer rain events in 1994 to evaluate the importance of dry deposition in the alpine zone (see Clow and Mast [1995] for details). The second microcatchment, referred to hereafter as the soil microcatchment, consisted of a small pocket of soil surrounded by granitic bedrock,

with an area of 39 m². The soil microcatchment was used for weathering mass balance studies from 1989 through 1995 [Clow, 1992; Drever and Clow, 1995; Clow and Drever, 1996]. Outflow from the soil microcatchment was primarily from subsurface drainage and thus represents alpine soil water. Forest soil water was collected weekly from five pairs of suction lysimeters at depths from 20 to 50 cm in the subalpine forest zone; samples were composited into early (May 25 to June 22) and late (June 23 to September 1) summer samples for $^{87}\text{Sr}/^{86}\text{Sr}$ analyses. Spring and seep water emanating from talus was collected in September 1994 during low-flow conditions. All water samples were analyzed for major-element chemistry, but only results for Sr, Ca, and Na are presented here; a subset of samples were analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$. Samples were filtered through prerinsed 0.45- μm membrane filters and preserved with concentrated high-purity nitric acid. Sr, Ca, and Na concentrations were determined by ICP spectroscopy.

Results

Solid Phases

The rock sample from Loch Vale has a whole rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.88432 (Table 1), which is within the range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reported for other Precambrian granitic rocks in Rocky Mountain National Park [Peterman et al., 1968]. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the bedrock minerals increase in the order plagioclase < microcline < biotite (Table 1). The relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of plagioclase is consistent with the low Rb concentration in the mineral; minerals with low Rb concentrations generate little new ^{87}Sr over time, so their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios tend to remain near the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the rock [Faure, 1986]. The biotite separated from the alpine soil had a substantially lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (1.9016) than the biotite separated from the bedrock (4.8339). Lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and higher Sr concentrations have been reported previously for oxidized biotites compared to their fresh counterparts [Clauer, 1981; Bullen et al., 1997] and may be explained in part by uptake of Sr from soil solutions via exchange reactions. It is also possible that the soil biotite contained some chlorite, because chlorite partially replaces biotite in some of the altered rocks. Chlorite might be expected to have a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio similar to the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the rock (0.7025; [Peterman et al., 1968]) owing to its lack of monovalent alkali sites [Bailey et al., 1996]. It was not possible to separate chlorite from the soil or rocks for Sr analysis because of its intimate association with biotite.

The $^{87}\text{Sr}/^{86}\text{Sr}$ of exchangeable cations extracted from the two soil profiles varied over a relatively narrow range from 0.71861 to 0.72227 (Table 1). These values are consistent with derivation of exchangeable Sr from a mixture of bedrock weathering and atmospheric deposition, although a purely bedrock weathering source cannot be ruled out. Both soil profiles showed a similar trend of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ with depth, although the trend was more pronounced for the alpine soil (Table 1). The water-soluble portion of the eolian dust sample had a relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.71005), similar to ratios reported for Paleozoic marine carbonate minerals which are prevalent in the arid basins to the west [Capo and DePaolo, 1990; Marshall et al., 1991; Dia et al., 1992]. On the basis of XRD analysis, the mineralogy of the dust included plagioclase, quartz, and possibly chlorite, smectite, and kaolinite, all of which are minerals commonly found in Loch Vale soils. The XRD analysis also detected calcite and perhaps gypsum, which are not present in the local soil material. Inorganic carbon

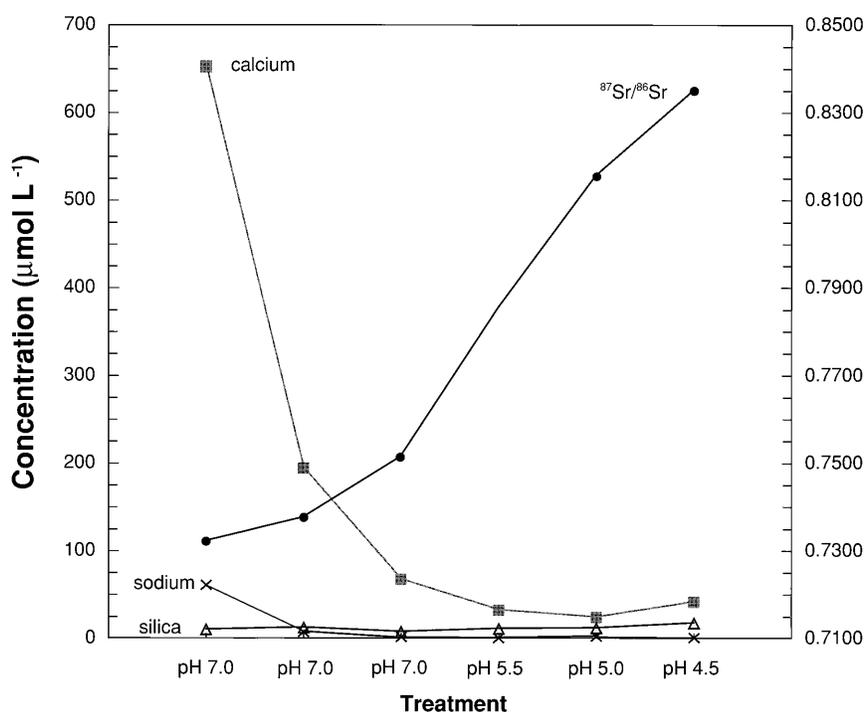


Figure 2. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca, Na, and Si concentrations of sequential ammonium-acetate leaches of crushed gneiss.

analysis indicated that calcite accounted for 1% of the dust by weight.

Ca concentrations in the leachates from the sequential-leaching experiment ranged from 24 to $652 \mu\text{mol L}^{-1}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ ranged from 0.73215 to 0.83501 (Figure 2). Strontium 87/strontium 86 was lowest and Ca concentration was highest in the first leach. Sr concentrations are not shown but were highly correlated with Ca ($r^2 = 0.99$). Sequential leaches yielded progressively higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and lower Ca concentrations, except at the lowest pH, where concentrations of Ca and Si increased slightly. Na and Si concentrations were relatively low in all leachates, ranging from <1 to $60 \mu\text{mol L}^{-1}$ and 7 to $18 \mu\text{mol L}^{-1}$, respectively (Figure 2). In the single-leach experiments, substantially more Ca, Mg, and Sr were released from the crushed rocks in the $\text{NH}_4\text{-Ac}$ solution than in DI, but the amounts of Na and K released were generally similar in the two solutions (Table 2). As in the sequential-leach experiment, Si concentrations in the leachates were low, especially in the DI treatments. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the leachates in the single-leach experiment ranged from 0.73468 to 0.74394.

Precipitation, Surface Water, and Subsurface Water

The range of Sr isotopic ratios measured in Loch Vale waters is illustrated in Figure 3. The least radiogenic samples were rain and snow, which had $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that ranged from 0.70915 to 0.71485, within the range of 0.7077 to 0.7162 reported for precipitation in the literature [Graustein and Armstrong, 1983; Aberg *et al.*, 1989; Miller *et al.*, 1993; Blum *et al.*, 1994; Bailey *et al.*, 1996; Bullen *et al.*, 1996]. Oceanic ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70910 \pm 0.00004$ [Burke *et al.*, 1982]) and terrestrial dust sources (variable $^{87}\text{Sr}/^{86}\text{Sr}$ [Andersson *et al.*, 1990]) were found to be the main controls on the $^{87}\text{Sr}/^{86}\text{Sr}$ of precipitation and aerosols in a study in Scandinavia [Andersson *et al.*, 1990]. The average isotopic ratios of rain (0.71133) and snow (0.71205) in Loch Vale were not statistically different; however, snowpack samples showed a greater range of values than the bulk rain samples (Figure 3). It seems likely that eolian carbonates may strongly influence the chemistry of rain in Loch Vale, driving up Ca and Sr concentrations and regulating Sr ratios within a narrow range. The average isotopic compo-

Table 2. Solute Concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ Ratios of Leachates Obtained From Reacting Crushed Rock with Deionized Water and Ammonium Acetate

Rock Type	Treatment	Ca	Mg	Na	K	Sr	SiO_2	$^{87}\text{Sr}/^{86}\text{Sr}$
Altered gneiss	DI	295	41	28	39	0.16	<1	0.73468
Altered gneiss	$\text{NH}_4\text{-Ac}$	1150	82	17	41	0.86	<1	0.73514
Granite 1	DI	25	4	24	25	0.08	2	0.73850
Granite 1	$\text{NH}_4\text{-Ac}$	490	58	33	82	1.03	43	0.73477
Granite 2	DI	90	21	117	112	0.16	2	0.74190
Granite 2	$\text{NH}_4\text{-Ac}$	543	111	122	140	0.73	31	0.74394

Concentrations of Ca, Mg, Na, K, and Sr are in $\mu\text{eq L}^{-1}$; SiO_2 is in $\mu\text{mol L}^{-1}$. DI, deionized water; $\text{NH}_4\text{-Ac}$, ammonium acetate.

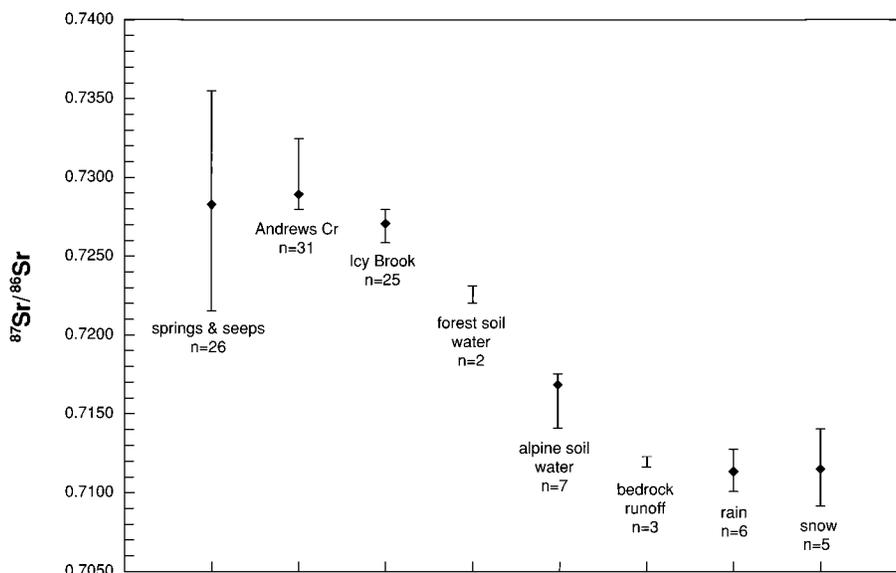


Figure 3. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ of water samples collected in Loch Vale in 1994. Bars represent range of ratios and symbol is the average ratio measured for each water type. Range of values presented for Andrews Creek and Icy Brook also includes samples collected during 1991 and 1992.

sition of runoff from the bedrock microcatchment was 0.71245, only slightly higher than that of bulk rain. This value is also similar to that of the soluble portion of the dust sample (0.7101) but much lower than any of the local bedrock minerals (Table 1), indicating that atmospheric dust was the dominant source of the dissolved Sr in the bedrock runoff.

The Sr isotopic composition of stream water samples ranged from 0.72668 to 0.73247 and was substantially more radiogenic than precipitation (Figure 3). This range of values is characteristic of waters draining Precambrian rocks [Wadleigh *et al.*, 1985; Wickman and Aberg, 1987; Aberg *et al.*, 1989] and reflects the release of radiogenic Sr from the weathering of bedrock

minerals. The $^{87}\text{Sr}/^{86}\text{Sr}$ of stream water is plotted with stream discharge for Andrews Creek during the 1994 snowmelt period in Figure 4; for clarity, discharge for Icy Brook is not shown but it is highly correlated with discharge at Andrews Creek ($r^2 = 0.89$). Strontium 87/strontium 86 exhibited a similar seasonal pattern in both streams; the highest ratios occurred during low-flow periods in early spring and late fall, and the lowest ratios occurred during peak flows in summer. The strong seasonal pattern observed in Loch Vale differs from previous studies, which indicated little temporal variation in stream water $^{87}\text{Sr}/^{86}\text{Sr}$ [Bain and Bacon, 1994; Bullen *et al.*, 1994; Bailey *et al.*, 1996]. The most radiogenic stream water samples

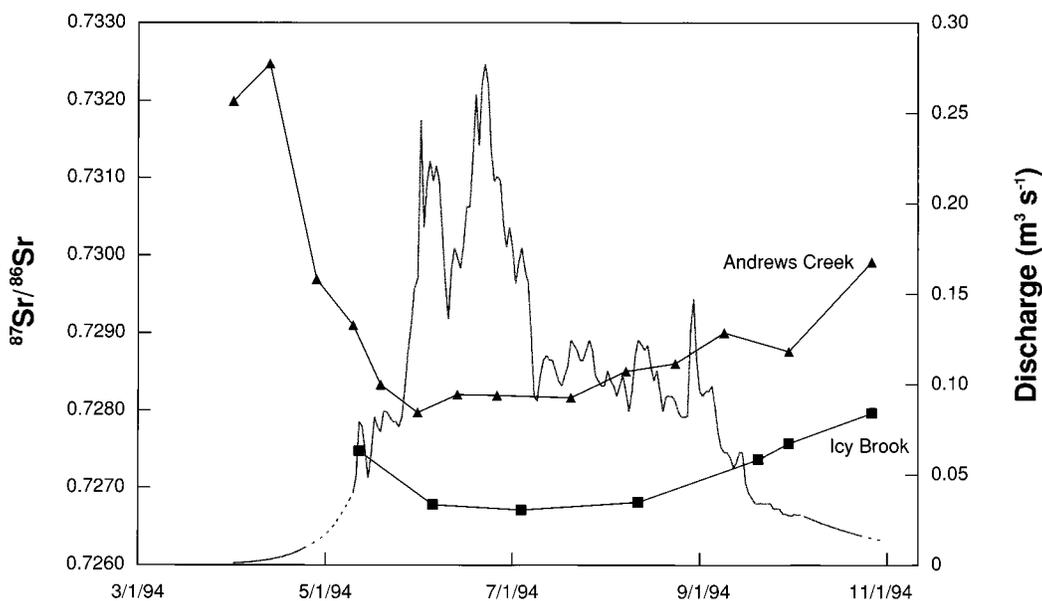


Figure 4. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ of Andrews Creek and Icy Brook stream water and discharge in Andrews Creek during the 1994 snowmelt season. Discharge at the beginning and end of the hydrograph (dashed lines) was estimated using a logarithmic extrapolation of measured flows.

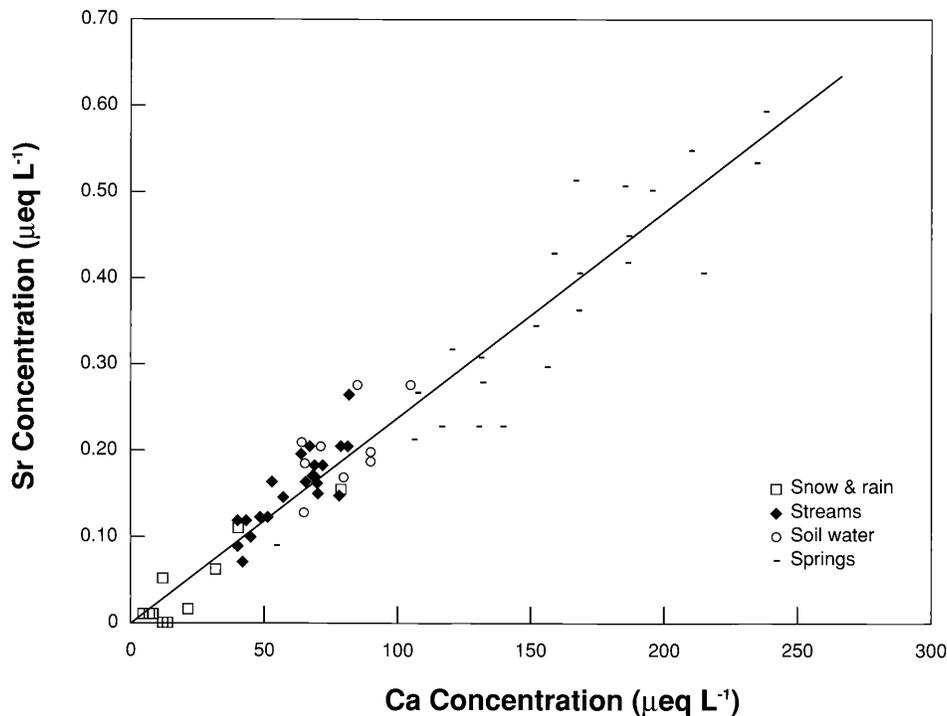


Figure 5. Relation between Ca and Sr concentrations for water samples collected in Loch Vale in 1994.

collected in the present study were from Andrews Creek in early April, before the onset of snowmelt (Figure 4). Because discharge was at its yearly minimum, these $^{87}\text{Sr}/^{86}\text{Sr}$ values probably reflect the chemistry of shallow groundwater, which is thought to dominate stream water inputs during base flow. Stream water base-flow samples were not obtained from Icy Brook because surface flow normally ceases at the Icy Brook gage during the winter. Interestingly, the isotopic composition of Andrews Creek was slightly more radiogenic than Icy Brook during all periods of the hydrologic cycle (Figure 4); $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Loch outlet (not shown) were intermediate between Andrews Creek and Icy Brook in 1991 and 1992.

Soil solutions exhibited Sr-isotopic ratios intermediate between precipitation and stream water (Figure 3), suggesting that soil Sr is derived from a mixture of atmospheric and bedrock sources. It is interesting that soil solutions do not seem to be in equilibrium with the cation-exchange pool (Figure 3, Table 1). At the alpine site, soil water was less radiogenic than the exchange pool, but at the forest site, soil solutions were more radiogenic than the exchange pool. Soil solutions generally showed little variation, despite substantial differences in hydrology during the sampling period. Alpine soil solutions were consistently less radiogenic than the forest soil solutions (Figure 3). Springs and seeps exhibited the widest range of Sr isotopic ratios of the water types sampled in the basin (Figure 3). Most of these samples were collected near the base of large talus slopes, although some were from midslope positions. On the basis of their chemistry, most of the springs are thought to represent shallow subsurface flow in the alpine zone [Campbell *et al.*, 1995; Clow *et al.*, 1995]. The wide range of values in the spring samples emphasizes that a large amount of spatial variability can exist in the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering even in areas of relatively homogeneous bedrock.

Figure 5 shows the range of Sr and Ca concentrations in Loch Vale water samples analyzed for Sr isotopes. Ca and Sr

were highly correlated in all water types ($r^2 = 0.88$ for the entire group of samples), supporting the hypothesis that Sr can be useful for tracing sources of dissolved Ca. Snow was extremely dilute, with most samples having Sr concentrations near the detection limit of $0.01 \mu\text{eq L}^{-1}$. Sr concentrations in bulk rain were slightly higher, averaging $0.06 \mu\text{eq L}^{-1}$. Volume-weighted mean (VWM) Sr concentrations in Andrews Creek and Icy Brook were 0.145 and $0.157 \mu\text{eq L}^{-1}$, respectively. Soil solutions had an average Sr concentration of $0.203 \mu\text{eq L}^{-1}$. Of the water types sampled in Loch Vale, Sr concentrations in the springs and seeps exhibited the largest range and highest values, as they did for $^{87}\text{Sr}/^{86}\text{Sr}$. The average springwater Sr concentration of $0.450 \mu\text{eq L}^{-1}$ was 3 times the VWM concentration of stream water.

Discussion

Separation of Atmospheric and Weathering Sources of Sr

The ultimate sources of Sr (and by implication Ca) to undisturbed alpine/subalpine watersheds are atmospheric deposition, which includes wet and dry deposition, and weathering of local bedrock minerals. Although adequate methods exist for estimating wet-deposition fluxes to watersheds, measurement of the dry-deposition flux of Ca, which occurs mainly through gravitational settling of particulates transported by wind, has remained problematic [Fennelly, 1976; Gatz *et al.*, 1986; Edgerton *et al.*, 1991; Clow and Mast, 1995]. Sampling of seasonal snowpacks provides a means for measuring bulk atmospheric inputs (wet plus dry) during the winter, but there is no universally accepted method for directly measuring bulk or dry deposition inputs during the summer. Several researchers have used Sr isotopes to evaluate the relative inputs of atmospheric deposition and weathering to forested ecosystems [Gosz *et al.*, 1983; Graustein and Armstrong, 1983; Gosz and Moore, 1989]. The technique involves measuring the Sr-

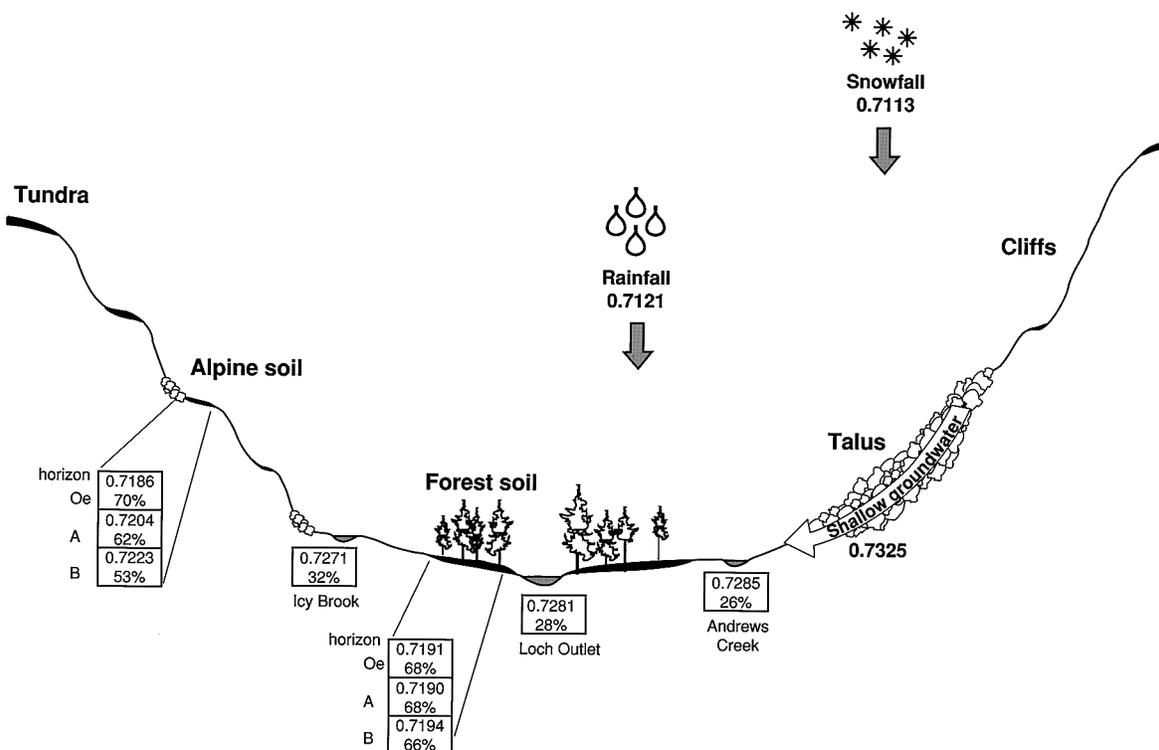


Figure 6. Schematic of Loch Vale watershed showing the Sr-isotope ratios of various watershed compartments. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and atmospheric-deposition contribution (ADC) in percent to the streams and soils are shown in boxes. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the streams were calculated as annual volume-weighted means.

isotopic ratios of a mixture, such as stream water or biomass, and its components (i.e., Sr sources), and solving a simple mixing equation. It is assumed that Sr behaves as an analog for Ca. For a two-component mixture the following equation applies:

$$(^{87}\text{Sr}/^{86}\text{Sr})_m = x(^{87}\text{Sr}/^{86}\text{Sr})_a + (1 - x)(^{87}\text{Sr}/^{86}\text{Sr})_b \quad (1)$$

where the subscripts refer to a mixture and its components. If $^{87}\text{Sr}/^{86}\text{Sr}$ values of the components differ by less than 10%, $^{87}\text{Sr}/^{86}\text{Sr}$ can be replaced by $^{87}\text{Sr}/^{86}\text{Sr}$ with little loss of accuracy [Bullen *et al.*, 1997]. However, this is not the case for system components in Loch Vale; $^{87}\text{Sr}/^{86}\text{Sr}$ can be calculated from $^{87}\text{Sr}/^{86}\text{Sr}$ as shown in the appendix. Equation (1) can easily be solved for x , which is the fraction of Sr derived from component a . In this study, stream water was taken as the mixture because it is the main Sr (and Ca) output from the ecosystem. Atmospheric deposition was taken as component a , and mineral weathering was taken as component b . Volume-weighted mean $^{87}\text{Sr}/^{86}\text{Sr}$ values were used for the stream water (Figure 6), and a median $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was used for atmospheric deposition (0.7118) because it did not vary seasonally. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for weathering was assumed equal to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of stream water at base flow (i.e., Andrews Creek at the gage in early April 1994).

Selection of a weathering end-member deserves special attention because it is difficult to define. In some studies, the whole rock Sr-isotope ratio has been used [Graustein and Armstrong, 1983]; however, this method is problematic because it does not take into account the variable weathering rates of individual minerals in the bedrock. The problem is accentuated in terranes with old rocks, such as Loch Vale, because the

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the individual minerals diverge over time. Another approach that has been used is to assume that the weathering end-member is equal to the Sr-isotope ratio of a leachate obtained by reacting local geologic materials with an acidic solution [e.g., Miller *et al.*, 1993]. The validity of this approach is uncertain given the variability in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained in the leaching experiments in the present study. Both approaches are complicated by the large range in $^{87}\text{Sr}/^{86}\text{Sr}$ of bedrock that can occur because of spatial variability in the mineralogical proportions in the bedrock.

In the present study the Sr-isotopic ratio of the stream at base flow was used to represent the Sr signature of chemical weathering. Hydrograph separations using $\delta^{18}\text{O}$ indicate that the dominant source of water and solutes in the stream at base flow is drainage of water from the shallow groundwater reservoir present in the young moraine and talus deposits that occur along the alpine valley floor and its flanks [Mast *et al.*, 1995]. Although the main geochemical process contributing cations to water in the groundwater reservoir is undoubtedly chemical weathering, it is likely that atmospheric deposition also makes a small contribution. The $^{87}\text{Sr}/^{86}\text{Sr}$ of base flow was adjusted for wet-deposition inputs using the VWM concentration of Sr in wet deposition and assuming a precipitation $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7118. The adjustment amounted to 0.0020 units, yielding an estimate of 0.7345 for the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by mineral weathering, compared to the base-flow Sr ratio of 0.7325. Unfortunately, it was not possible to quantify the effect of dry-deposition inputs on base-flow chemistry because dry-deposition fluxes were not known *a priori*. The lack of adjustment for dry-deposition inputs should cause our estimate of the $^{87}\text{Sr}/^{86}\text{Sr}$ of mineral weathering to be slightly below the

true chemical weathering Sr-isotope ratio. For example, if the effect of dry deposition on base flow chemistry is equivalent to that of wet deposition, the estimated $^{87}\text{Sr}/^{86}\text{Sr}$ of mineral weathering would be 0.7369.

The main benefit of using base flow to represent the chemical-weathering end-member is that the stream effectively integrates the potentially variable isotopic signature of weathering from the geologic materials in the catchment above the gage. The variability in the $^{87}\text{Sr}/^{86}\text{Sr}$ of mineral weathering, which is evidenced in Loch Vale by the range in the springwater Sr-isotope ratios, may result from localized zones of hydrothermal alteration, variations in the mineral percentages in the rocks, or differences in weathering regimes. One potential problem in using base-flow chemistry as a surrogate for mineral weathering is that in some instances, the Sr released by weathering might change depending on hydrologic conditions. During snowmelt for example, the water table typically rises into soils that are unsaturated much of the year. If the mineralogy of those soils is substantially different from that of the bedrock, as might be the case if the soils are extensively weathered or contain autochthonous materials, then the Sr released by weathering might be different during snowmelt than during low-flow periods. The complication of a variable weathering signature is more likely to be a problem in older or warmer terrains, or areas that have undergone continental rather than alpine glaciation. In Loch Vale, soils in the alpine zone have a mineralogy very similar to the bedrock [Clow, 1992], but forest soils are depleted in biotite and chlorite owing to longer and more intense weathering [Mast, 1989]. This suggests that while it may be reasonable to use one value (base flow) as a surrogate for weathering in the alpine zone, it may be less appropriate at lower elevations, where a variable weathering signature is possible depending on the hydrologic season.

Assuming a value of 0.7345 for the mineral-weathering end-member and 0.7118 for atmospheric deposition, the mixing calculations indicate that the atmospheric-deposition contribution (i.e., the percent of the annual flux of Sr in the stream, referred to hereafter as ADC) of Sr to Andrews Creek was 26% (Figure 6). The ADC calculated for Icy Brook was somewhat higher (32%), and at the Loch outlet the estimated ADC was intermediate between those of the two streams (28%). The estimates of the ADC are sensitive to the value used for the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by mineral weathering. For example, if a value of 0.7369 is used instead of 0.7345 as the $^{87}\text{Sr}/^{86}\text{Sr}$ of mineral weathering, the estimated ADC to the streams would be 7% higher than those indicated in Figure 6. Conversely, if the $^{87}\text{Sr}/^{86}\text{Sr}$ of mineral weathering is actually 0.7325, then the ADC would be 7% lower than indicated. The indeterminate nature of the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by mineral weathering precludes definitive statements about the relative contributions of atmospheric deposition and mineral weathering to Sr in stream water. However, the uncertainty analysis allows reasonable limits to be set on the ADC to stream water in Loch Vale; results indicate that atmospheric deposition probably accounts for between one fifth and one third of the annual stream Sr flux.

There are at least two possible explanations for the lower $^{87}\text{Sr}/^{86}\text{Sr}$ and concomitant higher estimated ADC for Icy Brook compared to Andrews Creek. The lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher ADC might be due to greater atmospheric deposition of eolian carbonate dust. This is supported by higher Ca/Na ratios in Icy Brook than in Andrews Creek (1.8 compared to 1.6 on a molar basis). The higher Ca/Na ratios in Icy Brook cannot be

explained by additional bedrock-calcite weathering because that would tend to increase the $^{87}\text{Sr}/^{86}\text{Sr}$ of the stream rather than lower it. Deposition of eolian carbonate dust might be enhanced in the Icy Brook drainage because of the prevalence of gently sloping terrain in the valley bottoms and on the ridge tops. Those areas contain shallow pockets of vegetated soil that might be relatively effective at trapping eolian dust.

Another possible explanation for the higher ADC estimated for Icy Brook is that it could be an artifact of using the same weathering signature for both subbasins, which might be inappropriate. If the Sr released by weathering in the Icy Brook drainage has a lower average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than in the Andrews Creek drainage, then the atmospheric contribution calculated for Icy would be overestimated. As noted above, spatial variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering could be caused by minor differences in the primary mineralogy of the bedrock, the amount of hydrothermal alteration products, or the importance of physical weathering. Possible differences in mineralogy or alteration are difficult to evaluate. Although there are no obvious differences in the percentage of gneiss and granite or in the degree of alteration between the Andrews and Icy subbasins, any differences may be too subtle to quantify. There are, however, quantifiable differences in topography. Approximately 30% of the Icy drainage has slopes of less than 25° , but in the Andrews subbasin, only 20% of the area has a slope of less than 25° . Most of the difference in slope distribution may be attributed to the wider valley bottom in the Icy drainage than the Andrews drainage. Because physical weathering is particularly active on very steep slopes in the alpine zone, the Andrews subbasin may have a higher average physical weathering rate than the Icy subbasin. This has important implications pertaining to the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering in the two subbasins. It has been postulated that the Sr released from recently exposed rock surfaces by physical weathering might have a substantially higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than the Sr released from rocks that have been exposed for longer periods of time [White *et al.*, 1992; Blum *et al.*, 1994; Blum and Erel, 1995; White *et al.*, 1996; Bullen *et al.*, 1997]. The proposed mechanism is related to incipient weathering of biotite and perhaps K-feldspar. In the first stage of biotite weathering, Fe^{+2} is oxidized to Fe^{+3} , and in order to maintain charge balance, interlayer cations are exchanged for cations in solution [Rebertus *et al.*, 1986; Acker and Bricker, 1992]. The interlayer cations are predominantly K, but also include ^{87}Sr produced by decay of ^{87}Rb . Small amounts of unradiogenic Sr might occupy octahedral sites in biotite due to substitution of Sr for Mg during crystallization; because this Sr would be relatively unradiogenic, the leaching of ^{87}Sr from interlayer sites could lead to a decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ of biotite over time. Sr may also be taken up from soil solutions via exchange reactions; since soil solution Sr has a much lower $^{87}\text{Sr}/^{86}\text{Sr}$ than fresh biotite (Table 1, Figure 3), it also could contribute to the decline in $^{87}\text{Sr}/^{86}\text{Sr}$ as weathering proceeds. This is supported by observations of decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ and increasing Sr concentrations in biotites from progressively weathered soils [Clauer, 1981; Bullen *et al.*, 1997]. Evidence that this process occurs in Loch Vale is provided by the higher Sr concentration and lower Sr-isotope ratio in the biotite obtained from the soil compared to the biotite separated from the bedrock (Table 1). K-feldspar could provide another transient source of radiogenic Sr. Bullen *et al.* [1996] have proposed that K-feldspar might release Sr held in defect sites in the crystal lattice, which might tend to dissolve preferentially because they are locations

Table 3. Estimated Annual Atmospheric Deposition Input Fluxes of Ca at the Loch Vale Watershed for the Period 1992 Through 1995

	Atmospheric Deposition Contribution, %		
	21	28	35
Atmospheric deposition (ADC × stream export)	1.87	2.49	3.11
Minus winter wet	-0.35	-0.35	-0.35
Minus winter dry (bulk - wet)	-0.58	-0.58	-0.58
Minus summer wet	<u>-0.97</u>	<u>-0.97</u>	<u>-0.97</u>
Equals summer dry	-0.03	0.59	1.21

The atmospheric deposition contribution is the estimated percent of the annual Sr (or Ca) flux in streamwater at the Loch outlet that is derived from atmospheric deposition. Units are $\text{kg ha}^{-1} \text{yr}^{-1}$. Mean annual stream exports of Ca were $8.89 \text{ kg ha}^{-1} \text{yr}^{-1}$. Sources: stream exports from J. Baron, National Biological Service, written communication, 1996; wet deposition inputs from *National Atmospheric Deposition Network/National Trends Network* [1984–1995].

of high free energy [Wollast, 1967; Goosens et al., 1989; Gautier et al., 1994]. The Sr losses from biotite and microcline are rapid relative to the Sr loss from and weathering of plagioclase. Thus the $^{87}\text{Sr}/^{86}\text{Sr}$ in the residuum will decrease over time. This is supported by studies in the Sierra Nevada [Blum et al., 1994] and Wind River mountains [Blum and Erel, 1995], in which inverse correlations were noted between the age of glacial till and the $^{87}\text{Sr}/^{86}\text{Sr}$ of exchangeable cations in till soils. Similar trends were identified in a soil chronosequence in the Sierran foothills [White et al., 1992].

The cation-exchange pools of the soils sampled on the basin floor have Sr with relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Table 1) compared to stream water (Figure 3). Sr-source calculations made for the cation-exchange pools in the forest and alpine soils using a $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7345 for the mineral weathering end-member are shown in Figure 6. Substituting mineral-weathering end-member values of 0.7369 and 0.7325 shift the estimated atmospheric-deposition contributions by +3% and -3%, respectively. These results suggest that roughly one half to three fourths of the Sr in the cation-exchange pools at the two soil-sampling sites has an atmospheric-deposition source. If the Sr released by weathering in the soils has a lower $^{87}\text{Sr}/^{86}\text{Sr}$ than that assumed, as could be the case if soils are depleted in radiogenic minerals such as biotite, then the atmospheric-deposition contribution would be overestimated. The increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with depth in the alpine and forest soils probably reflects the way bedrock mineral-weathering sources of Sr mix with atmospheric-deposition sources; because atmospheric deposition falls on the soil surface, that is where its influence tends to be greatest. Alternatively, the upper soil horizons might be more altered by weathering than the deeper soils. Nutrient cycling and physical disturbances may partially obscure the pattern of $^{87}\text{Sr}/^{86}\text{Sr}$ with depth in the forest soils [Graustein and Armstrong, 1983; Gosz and Moore, 1989].

Using the results of the Sr-source calculations for the streams and making the assumption that Sr can be used as an analogue for Ca, annual wet and dry atmospheric-deposition fluxes of Ca were calculated for Loch Vale. Annual atmospheric deposition of Ca was calculated by multiplying annual stream exports of Ca times the fraction of Sr (and by implica-

tion Ca) in stream water derived from atmospheric deposition (Figure 6). Winter bulk deposition of Ca was calculated on the basis of the Ca concentration and water content of the snowpack at maximum accumulation (early April). Winter and summer wet deposition were calculated from the wet-deposition chemistry and precipitation amounts measured at the wet-deposition collector in Loch Vale [*National Atmospheric Deposition Program/National Trends Network Coordination Office (NADP/NTN)*, 1984–1994]. Winter dry deposition was computed as the difference between winter bulk and winter wet deposition. Summer dry deposition was calculated by difference as shown below and in Table 3:

$$\begin{aligned} & \text{total atmospheric deposition} \\ & - (\text{winter wet deposition} + \text{winter dry deposition} \\ & + \text{summer wet deposition}) = \text{summer dry deposition} \end{aligned}$$

Average annual fluxes of Ca in wet deposition were estimated to be $1.32 \text{ kg ha}^{-1} \text{yr}^{-1}$ for the period 1992 through 1995, compared to mean annual stream exports of $8.89 \text{ kg ha}^{-1} \text{yr}^{-1}$ (Table 3). Winter wet-deposition inputs were substantially lower than summer wet-deposition inputs because concentrations in snow are much lower than those in rain. The higher concentrations in rain might be because rain is more efficient than snow at scavenging Ca aerosols from the atmosphere [Likens et al., 1977]. Average winter dry deposition was estimated to be $0.58 \text{ kg ha}^{-1} \text{yr}^{-1}$. The effect of uncertainty in the atmospheric deposition-contribution estimates was tested by varying the ADC from 21 to 35%. Summer dry deposition and total annual atmospheric deposition flux estimates were highly dependent on the choice of ADC. Essentially zero summer dry deposition was predicted when the ADC was set to 21%. Estimated fluxes of summer and winter dry deposition were approximately equal when an ADC of 28% was used, and when ADC was assumed to be 35%, summer dry-deposition fluxes were calculated to be about twice that of winter dry deposition fluxes.

Unfortunately, these calculations did not provide a precise estimate of summertime dry deposition of Ca. However, it is possible to place reasonable bounds on summer dry deposition on the basis of certain observations. First, it can be noted that in the Rocky Mountains and surrounding basins, wind erosion is likely to be more important in the summer than in the winter because much more soil is exposed (there is less snow cover), and soil conditions are generally drier. Thus it seems unlikely that transport and deposition of eolian dust in the summer would be zero; it should perhaps be at least as important as it is in the winter. Second, the ratio of VWM Ca concentrations in wet and bulk deposition samples collected in Loch Vale are similar during the summer and winter. During a 6-week period in the summer of 1994, VWM Ca concentrations in wet and bulk deposition were 8.5 and $23.0 \mu\text{eq L}^{-1}$, respectively [NADP/NTN, 1984–1994; Clow and Mast, 1995]. From 1992 through 1995, the VWM Ca concentrations in wet deposition and the snowpack at maximum accumulation were 2.9 and $7.7 \mu\text{eq L}^{-1}$ [NADP/NTN, 1984–1994]. Although these data are from different time periods, they suggest that summertime dry-deposition fluxes of Ca are at least comparable to winter dry-deposition fluxes in Loch Vale and may be higher. These observations also indicate that an ADC of 21% is too low because a summer dry-deposition Ca flux of near zero is predicted using that value (Table 3), which is unlikely. ADC values

of 28% and 35% give dry-deposition flux estimates that are more consistent with observed differences in VWM concentrations of Ca in wet and bulk deposition.

The $^{87}\text{Sr}/^{86}\text{Sr}$ Ratio of Bedrock Calcite

The processes considered most likely to affect the solute concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of leachates in the two laboratory experiments include carbonate mineral dissolution, silicate mineral dissolution, and cation exchange. In the sequential-leach experiments, the evolution of solute and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the leachates argues for a change in the relative importance of these processes during the course of the experiment (Figure 2). It appears that initially, carbonate dissolution was the dominant source of solutes, but it became less important in subsequent treatments, perhaps because less carbonate was available for reaction. This is supported by the initially high, but rapidly declining, Ca concentrations and Ca/Na ratios in the leachates. Dissolution of 101 μmol of calcite is required to account for the amount of Ca released to solution. This compares to a total calcite content of 240 μmol in the 6-g sample of crushed rock based on 0.4% calcite by weight (measured on a separate subsample by coulometric titration). These data indicate that not all of the calcite in the rock dissolved, but this is reasonable because some calcite was probably present inside mineral grains that did not contact the reacting solutions. Throughout the experiment, Ca/Si and Ca/Na ratios were much higher than would be expected from stoichiometric dissolution of the dominant silicate minerals. The relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in solutions from later treatments indicate release of Sr from biotite and perhaps microcline, which were the only minerals present having $^{87}\text{Sr}/^{86}\text{Sr}$ ratios radiogenic enough to explain the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the more acidic leachates. Exchange and mineral dissolution are both plausible mechanisms for release of Sr from biotite and microcline, although exchange is perhaps more likely from biotite than from microcline because mica has a more open mineral structure. Low Na concentrations in most of the leachates indicate that cation exchange from and dissolution of plagioclase were of minor importance. A modest increase in mineral dissolution rates in the most acidic solution is indicated by a small increase in Ca and Si concentrations in the final leachate (Figure 2).

The single-leach experiments were done in order to further evaluate the relative importance of carbonate dissolution and cation exchange in influencing the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the leachates. It is important to characterize the effect of cation exchange relative to carbonate dissolution because small amounts of exchangeable Sr from biotite could have a major influence on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the leachates. Prior to the experiment, it seemed likely that cation-exchange reactions would be minimal in DI but might be more important in the $\text{NH}_4\text{-Ac}$ solutions because of the strong exchange characteristics of $\text{NH}_4\text{-Ac}$ [Thomas, 1982]. Surprisingly, results indicated that there was little difference in the contributions from cation exchange in the two treatments based on the similarity of Na and K concentrations in the DI and $\text{NH}_4\text{-Ac}$ leachates (Table 2). One possible explanation is that there might have been a limited number of exchange sites occupied by Na and K at the mineral surfaces, and the acidity in DI might have been sufficient to remove most of the exchangeable Na and K that was readily available. A small amount of acidity in DI could be derived from dissolved atmospheric CO_2 , which would form carbonic acid. An important implication is that the additional Ca and Sr released in the $\text{NH}_4\text{-Ac}$ treatments probably was

mostly due to carbonate mineral dissolution rather than cation exchange. Mg concentrations were somewhat higher in the $\text{NH}_4\text{-Ac}$ leachates compared to the DI leachates, but the source of the Mg is uncertain. It is interesting that the granite-2 leachates had the highest K concentrations and the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. These data might indicate that biotite or microcline had a relatively large influence on those leachates.

To summarize, it appears that in the first treatment of the sequential-leach experiment and in the $\text{NH}_4\text{-Ac}$ treatments of the single-leach experiment, carbonate mineral dissolution was the dominant process controlling solute release. This suggests that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of those leachates, which ranged from 0.73215 to 0.74394, reflect that of bedrock carbonate. The ratio obtained from the altered gneiss (0.73215, Figure 2) probably provides the best estimate of the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering of bedrock carbonate because the altered gneiss has the highest carbonate content of the rocks in the watershed [Mast, 1989]. This value is reasonable given that the Sr in the bedrock carbonate probably was derived from a mixture of mineral sources during the Laramide orogeny, approximately 65 million years ago. Those mineral sources include the plagioclase, biotite, and microcline present in the local bedrock units, whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratios had evolved by that time to values similar to those of the present. It should be noted that if some of the Sr in the leachates was released by biotite or microcline via cation exchange, then the estimate of the $^{87}\text{Sr}/^{86}\text{Sr}$ of bedrock carbonate provided by the leaching experiments would be too high.

Relative Mineral Weathering Rates

Determination of the types and relative rates of mineral-weathering reactions operating in a watershed is fundamental to identifying the sources of solutes in surface water and groundwater. Traditionally, the mass balance technique has been used to attempt to identify and quantify weathering reactions [e.g., Garrels and Mackenzie, 1967]. Unfortunately, when there are multiple possible sources of a given element, as is common for Ca, it is difficult to obtain a unique result. Blum *et al.* [1994] used Sr isotopes to further constrain the results of mass balance calculations done on stream waters in granitic terrane in the Sierra Nevada. Using the Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the minerals in conjunction with weathering rates estimated by mass-balance, they attempted to predict the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering and compare it to the $^{87}\text{Sr}/^{86}\text{Sr}$ measured in the streams. The equation may be written as

$$\begin{aligned} & (^{87}\text{Sr}/^{\text{total}}\text{Sr})_m \\ &= [R_a C_a (^{87}\text{Sr}/^{\text{total}}\text{Sr})_a + \dots + R_n C_n (^{87}\text{Sr}/^{\text{total}}\text{Sr})_n] / C_m \quad (2) \end{aligned}$$

where C is the Sr concentration in a mineral and R is its relative weathering rate estimated from the mass balance. The subscript m refers to the mixture of solutes obtained from mineral weathering, and the other subscripts refer to the components (minerals). It is assumed that mineral weathering is the main source of solutes in the mixture. Close similarity between predicted and measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios does not prove that the estimated mineral-weathering rates are correct, but it does indicate whether they are reasonable.

Relative mineral-weathering rates were calculated by mass balance using weathering reactions listed in Table 4, which were identified by Mast [1992] and Clow [1992], on the basis of petrography, microprobe, and X ray diffraction analyses of

Table 4. Weathering Reactions Used in Mass Balance Calculations

	Reaction
Biotite to mixed-layer smectite-illite	$1.15(\text{K}_{0.98}\text{Mg}_{1.00}\text{Fe}_{1.33}\text{Ti}_{0.18}\text{Al}_{0.33})(\text{Al}_{1.35}\text{Si}_{2.65})\text{O}_{10}(\text{OH})_2 + 0.10\text{Ca}^{+2} + 0.49\text{H}_4\text{SiO}_4 + 1.21\text{O}_2 + 2.13\text{CO}_2 + (0.73 + n)\text{H}_2\text{O} \rightarrow (\text{K}_{0.32}\text{Fe}_{0.25}\text{Ca}_{0.10}\text{Mg}_{0.39}\text{Al}_{1.93}\text{Si}_{3.54})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O} + 0.76\text{Mg}^{+2} + 0.81\text{K}^+ + 1.28\text{FeO}(\text{OH})_6 + 2.13\text{HCO}_3^- + 0.21\text{TiO}_2$
Chlorite to mixed-layer smectite-illite	$1.39(\text{Mg}_{1.81}\text{Fe}_{2.72}\text{Al}_{1.39})(\text{Al}_{1.23}\text{Si}_{2.77})\text{O}_{10}(\text{OH})_8 + 0.10\text{Ca}^{+2} + 0.32\text{K}^+ + 0.31\text{H}_4\text{SiO}_4 + 1.78\text{O}_2 + 3.74\text{CO}_2 + n\text{H}_2\text{O} \rightarrow (\text{K}_{0.32}\text{Fe}_{0.25}\text{Ca}_{0.10}\text{Mg}_{0.39}\text{Al}_{1.93}\text{Si}_{3.54})\text{O}_{10}(\text{OH}) \cdot n\text{H}_2\text{O} + 2.13\text{Mg}^{+2} + 3.53\text{FeO}(\text{OH})_8 + 3.74\text{HCO}_3^-$
Oligoclase to kaolinite	$\text{Ca}_{0.27}\text{Na}_{0.73}\text{Al}_{1.27}\text{Si}_{2.73}\text{O}_8 + 1.27\text{CO}_2 + 4.82\text{H}_2\text{O} \rightarrow 0.64\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 0.27\text{Ca}^{+2} + 0.73\text{Na}^+ + 1.46\text{H}_4\text{SiO}_4 + 1.27\text{HCO}_3^-$
Microcline to kaolinite	$2\text{KAlSi}_3\text{O}_8 + 2\text{CO}_2 + 11\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 4\text{H}_4\text{SiO}_4 + 2\text{HCO}_3^-$
Calcite dissolution	$\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}^{+2} + 2\text{HCO}_3^-$

soils and rocks. The calculations were based on the solute ratios in Andrews Creek at base flow. Only a brief description of the mass balance calculations is provided here; for details see work by Mast *et al.* [1990], Mast [1992], Clow [1992], and Clow and Drever [1996]. VWM precipitation concentrations were subtracted from stream water concentrations to obtain the net solute flux attributable to weathering. All of the Na in the net solute flux was assigned to weathering of plagioclase (An₂₇) to kaolinite. This also accounted for some of the Ca; remaining Ca was assigned to calcite dissolution. Mg and K were attributed to weathering of biotite to a mixed-layer smectite clay containing approximately 30% illite layers. Any remaining K was assigned to weathering of microcline to kaolinite. As previously noted, chlorite partially replaces biotite in some of the altered rocks, and the mineral phase referred to here as biotite probably included some chlorite. In a laboratory dissolution experiment on a biotite separated from an alpine soil in Loch Vale (*pH* 5.6, 20°C [see Clow 1992]), the stoichiometry of solute release was consistent with dissolution of biotite and chlorite in a 2:1 ratio. However, nonstoichiometric dissolution of biotite could also explain the solute ratios in the leachates [Acker and Bricker, 1992], and unfortunately it is not possible to determine which of these processes was dominant. In the mass balance it was assumed that biotite and chlorite weathered in a 2:1 ratio, although in the discussion below, the chloritized biotite is referred to simply as biotite. The soil-derived biotite listed in Table 1 probably contained some chlorite, which is presumably reflected in its Sr isotopic ratio and concentration. Chlorite should have a relatively low Sr-isotope ratio, so if it was present in either of the biotites listed in Table 1, it would have the effect of lowering the measured ⁸⁷Sr/⁸⁶Sr ratio below that of pure biotite.

The mass balance calculations indicate that plagioclase weathering accounted for 42% of the weathering flux in the Andrews Creek subbasin at base flow, calcite accounted for 38%, biotite accounted for 18%, and microcline accounted for 2% (expressed as moles of each type of mineral weathered divided by the total moles of all minerals weathered; Table 5). Equation (2) was used to predict the ⁸⁷Sr/⁸⁶Sr of Sr released by weathering of plagioclase, bedrock calcite, bedrock biotite, and microcline in the proportions estimated from the mass balance calculations. Initially, the ⁸⁷Sr/⁸⁶Sr ratios and concentrations of the bedrock minerals listed in Table 1 were used in the calculations. Subsequently, the ⁸⁷Sr/⁸⁶Sr ratios of the plagioclase, bedrock calcite, and biotite were varied to test how uncertainty in mineral Sr ratios would affect the predicted ⁸⁷Sr/⁸⁶Sr. The ⁸⁷Sr/⁸⁶Sr of plagioclase was varied from the initial rock ⁸⁷Sr/⁸⁶Sr ratio of 0.7025 to 0.725; higher ratios are unlikely for a mineral containing few monovalent alkali sites, such as plagioclase

[Bailey *et al.*, 1996]. The ⁸⁷Sr/⁸⁶Sr of bedrock calcite was varied from 0.731 to 0.736, spanning the range of values considered most likely based on the results from the leaching experiments (Figure 2). The ⁸⁷Sr/⁸⁶Sr of biotite was varied from 1 to 5 to include the measured values of fresh and oxidized biotites (Table 1), as well as values that might be expected from a biotite/chlorite mixture.

Using the measured ⁸⁷Sr/⁸⁶Sr ratios and Sr concentrations, the estimated ⁸⁷Sr/⁸⁶Sr of Sr released by weathering was 0.7419 (Table 5), which is somewhat higher than the value estimated from the base-flow stream chemistry (0.7325). Plausible variations in the plagioclase and bedrock calcite ⁸⁷Sr/⁸⁶Sr ratios cannot account for the difference between bedrock-weathering ⁸⁷Sr/⁸⁶Sr estimates (Figure 7a and b). In contrast, variability in the ⁸⁷Sr/⁸⁶Sr of biotite could cause large differences in the ⁸⁷Sr/⁸⁶Sr of Sr released by weathering (Figure 7c). The ⁸⁷Sr/⁸⁶Sr of Sr released from biotite may vary depending on landscape position. Despite the immaturity of soils in the alpine valley bottoms, biotite from those soils probably release Sr that is substantially less radiogenic than biotite in areas of higher relief, which presumably have been exposed to weathering for a shorter period of time. The biotite-derived Sr in the stream may represent a mixture of Sr from biotites in various terrains.

The ⁸⁷Sr/⁸⁶Sr signature of weathering was predicted using two Sr-concentration scenarios for biotite. A constant Sr-concentration model is shown to allow comparisons with Figure 7a and b. A variable Sr-concentration model is also shown because in this study the oxidized biotite has a substantially higher Sr concentration than fresh biotite, which is consistent with trends in Sr concentrations in weathered biotites noted in previous work [Clauer, 1981; Bullen *et al.*, 1997]. In the variable

Table 5. Relative Mineral Weathering Rates and ⁸⁷Sr/⁸⁶Sr Ratios Predicted for Weathering of Geologic Materials in the Loch Vale Watershed

	Andrews Creek, Base Flow	
	Relative Weathering Rate	
Plagioclase		0.42
Calcite		0.38
Biotite		0.18
Microcline		0.02
	⁸⁷ Sr/ ⁸⁶ Sr Ratio	
Measured		0.7325
Predicted		
If biotite ⁸⁷ Sr/ ⁸⁶ Sr = 1.0000		0.7329
If biotite ⁸⁷ Sr/ ⁸⁶ Sr = 1.9016		0.7398
If biotite ⁸⁷ Sr/ ⁸⁶ Sr = 4.8339		0.7419

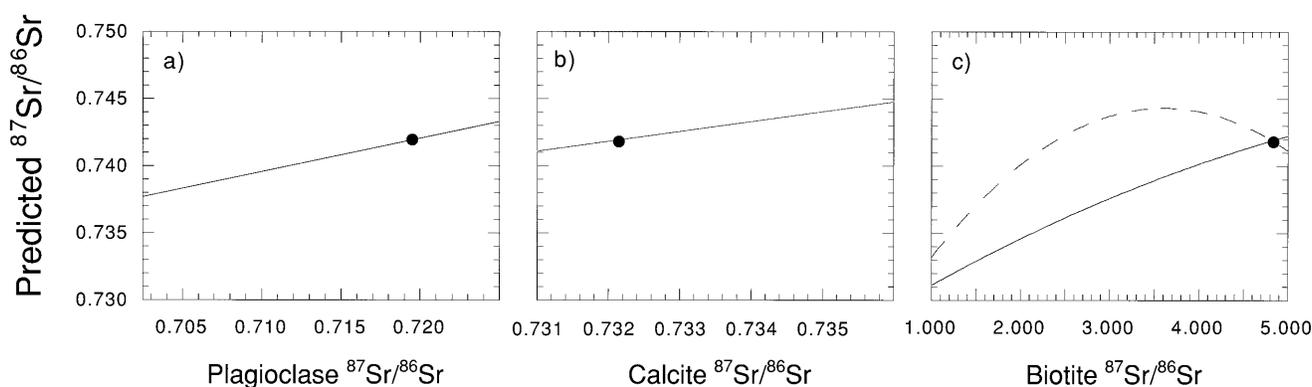


Figure 7. Variation in predicted $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering relative to possible variations in (a) the $^{87}\text{Sr}/^{86}\text{Sr}$ of plagioclase, (b) the $^{87}\text{Sr}/^{86}\text{Sr}$ of calcite, and (c) the $^{87}\text{Sr}/^{86}\text{Sr}$ of biotite. In Figure 7c the solid line represents the $^{87}\text{Sr}/^{86}\text{Sr}$ predicted for weathering when the Sr concentration of biotite is assumed constant at 10 ppm. The dashed line represents the $^{87}\text{Sr}/^{86}\text{Sr}$ predicted when the Sr concentration of biotite is assumed to follow an inverse linear relation to the $^{87}\text{Sr}/^{86}\text{Sr}$ of biotite.

Sr-concentration model, biotite concentrations were estimated by regressing the Sr concentration against the $^{87}\text{Sr}/^{86}\text{Sr}$ of biotite using the data in Table 1. Results indicate that as biotite Sr ratios increase, the predicted $^{87}\text{Sr}/^{86}\text{Sr}$ of weathering at first increases more rapidly in the variable Sr-concentration model than in the constant Sr-concentration model. However, above a certain biotite Sr ratio, the $^{87}\text{Sr}/^{86}\text{Sr}$ signature of weathering predicted by the variable Sr-concentration model begins to decline. This decline occurs because of the decrease in modeled Sr concentrations.

Uncertainty in the Sr concentrations of bedrock calcite could also cause some error in the estimated $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering. If the Sr concentration calculated for bedrock calcite from the sequential-leaching experiment is an underestimate (858 ppm, Table 1), then the predicted $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr from weathering will be too high. For example, if the Sr concentration in bedrock calcite is assumed to be equal to that in the soluble portion of atmospheric deposition (1960 ppm, Table 1), the predicted $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering would be 0.7372 rather than 0.7419.

The exposure of fresh bedrock surfaces through physical weathering appears to have two important geochemical implications for the Loch Vale watershed, and perhaps for the Rocky Mountains in general: (1) replenishment of the supply of bedrock calcite available for weathering and (2) renewal of the supply of fresh (unoxidized) biotite. Bedrock calcite weathering has a large effect on the solute concentrations of the reacting waters, in terms of elevating the Sr and Ca concentrations. Active physical weathering, causing exposure of fresh rocks containing trace amounts of calcite, might explain the dependence of Ca/Na ratio with elevation in Rocky Mountain lakes; *Stauffer* [1990] noted that of the lakes sampled in the Western Lake Survey in 1985, those from recently glaciated alpine terrain generally had higher Ca/Na ratios than those in less recently glaciated subalpine areas. In Loch Vale, the effect of bedrock calcite weathering on the Sr isotopic composition of reacting waters is to decrease the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio somewhat from the ratio expected from silicate weathering alone (~ 0.748 ; calculated using equation (2) with carbonate weathering excluded) towards that of bedrock calcite (~ 0.732). Oxidation of fresh biotite in the bedrock has a relatively small effect on solute concentrations, releasing minor amounts of Sr; however, it could have an important effect on the $^{87}\text{Sr}/^{86}\text{Sr}$

ratio of reacting waters because it is so radiogenic. It seems likely that exposure of fresh biotite through physical weathering would cause the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by chemical weathering to be higher in areas of active physical weathering, such as cliffs and talus areas, than in areas where physical weathering is less important, as on the valley floor.

Contrary to the results in this study, the $^{87}\text{Sr}/^{86}\text{Sr}$ values predicted for weathering of Sierran rocks were below the values measured in the streams [*Blum et al.*, 1994]. *Blum et al.* [1994] attributed the underestimation of the stream $^{87}\text{Sr}/^{86}\text{Sr}$ to an underestimation of the biotite weathering rate. They proposed that Mg was preferentially retained in biotite during weathering, and thus weathering rates based on Mg fluxes underestimated the true biotite weathering rate [*Blum et al.*, 1994]. Dividing the absolute weathering rates by the modal abundance of the minerals in the rock provides one measure of the relative weathering rates of minerals and allows comparisons between localities. In the Sierran study the mass balance results indicated a biotite:plagioclase weathering ratio of 0.1 to 0.5; however, calculations based on Sr isotopes suggested that biotite weathered 4 to 6 times faster than plagioclase [*Blum et al.*, 1994]. Mass balance calculations in the present study indicate a biotite:plagioclase weathering ratio of 0.8 for Andrews Creek and 0.7 for the entire Loch Vale watershed. In the present study, if the biotite weathering rate has been underestimated, then the $^{87}\text{Sr}/^{86}\text{Sr}$ released by weathering would be even higher than the values predicted using equation (2), which seems unlikely.

Partitioning of Ca Sources

As previously noted, the ultimate sources of Ca to alpine/subalpine basins in the Rocky Mountains are weathering of local bedrock minerals and atmospheric deposition. In Loch Vale the bedrock minerals that contribute Ca through weathering are plagioclase and interstitial calcite. Major ion chemistry in wet and bulk precipitation and runoff from the bedrock microcatchment suggest that calcite dust is the main source of Ca in atmospheric deposition [*Clow and Mast*, 1995]. This hypothesis is supported by the similarity between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in precipitation, bedrock runoff, and likely dust sources to the west [*Capo and DePaolo*, 1990; *Marshall et al.*, 1991; *Dia et al.*, 1992].

It is possible to partition Ca among the three main mineral

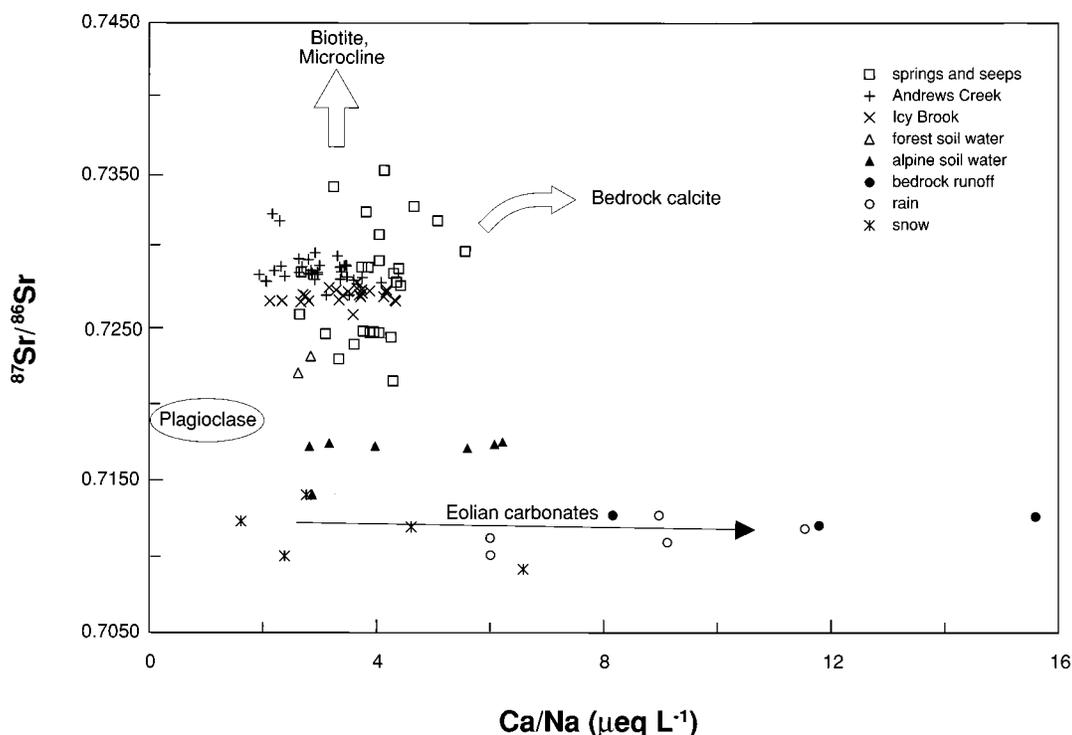


Figure 8. Relation between $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Na ratios ($\mu\text{eq L}^{-1}$) for different water types sampled in Loch Vale.

sources (eolian calcite, bedrock calcite, and plagioclase) on the basis of the results from the mass balance and isotopic mixing calculations reported in previous sections of this paper. Isotopic mixing calculations indicated that atmospheric deposition accounts for between one third and one fifth of the Sr and Ca in Andrews Creek, with a “best-estimate” value of 26%. Based on the mineral mass balance, plagioclase weathering contributes $23 \pm 1\%$ of the Ca in the stream. The plagioclase contribution is relatively well constrained because the weathering reaction is well defined and the plagioclase composition varies little within Loch Vale. The remainder of the Ca in stream water is derived from weathering of bedrock calcite, which accounts for between 43 and 59% of the total Ca flux, with a “best-estimate” value of 49%.

Evolution of $^{87}\text{Sr}/^{86}\text{Sr}$ in Surface Water

The chemistry of stream water is the result of a combination of processes that occur in the atmospheric, terrestrial, and aquatic environments. As water moves along a given flow path, beginning with deposition from the atmosphere, the relative importance of the various processes changes. The effect of several important processes on the chemical and isotopic composition of water in Loch Vale is illustrated in Figure 8, in which the chemistry of water samples of various types are plotted according to $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Na ratios. Because precipitation represents the beginning of the hydrologic cycle, it makes a useful chemical reference point for describing the effects of geochemical processes on natural waters. Precipitation that reacts with eolian carbonate dust will tend to have increasing Ca/Na ratios, and relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Plagioclase weathering will tend to decrease the Ca/Na ratio and increase the $^{87}\text{Sr}/^{86}\text{Sr}$ of rain and snow. Weathering of bedrock calcite will tend to increase the Ca/Na ratio, and the

$^{87}\text{Sr}/^{86}\text{Sr}$ of reacting waters should tend toward a value of about 0.732. Biotite and microcline weathering will elevate the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio but will have a negligible effect on the Ca/Na ratios because they do not contain appreciable Ca or Na.

Snow samples have relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ and moderate Ca/Na ratios; rain has similar Sr ratios, but higher Ca/Na ratios (Figure 8). Additionally, the Sr ratio of precipitation is much lower than that of any of the local bedrock minerals. These data suggest that most of the Ca in precipitation is derived from airborne carbonate dust. The higher Ca/Na ratios in rain compared to snow indicate that carbonate particulates have an even more important influence on the chemistry of rain than on that of snow. Carbonate dust also appears to be a dominant control on the chemistry of runoff from bedrock; Ca/Na ratios are high, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are within the range expected for eolian carbonates. The importance of carbonate dust dissolution at the bedrock microcatchment is reasonable given the very short residence time of water in this environment (<15 min). Only highly reactive minerals such as calcite would dissolve appreciably during the short periods when rain wets the rocks and the particulates on the rock surface. Soil solutions in the alpine zone also appear to be strongly influenced by atmospherically deposited carbonates given the relatively low Sr-isotope ratios in soil water. However, the influence of silicate weathering is evident in the somewhat higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and lower Ca/Na ratios of soil water compared to rain and bedrock runoff. Forest soil solutions are more strongly influenced by silicate weathering than the alpine soil solutions, as indicated by higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower Ca/Na ratios. This may reflect a more intense weathering environment due to higher average temperatures and greater concentrations of organic acids in the forest soils. Spring and seep water samples, which

were collected from the talus environment, display a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Na ratios; $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the spring and seep samples generally are higher than in precipitation, bedrock runoff, or soil solutions. Although dissolution of eolian carbonates undoubtedly make a contribution, especially to spring and seep samples with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios towards the low end of the range, it is clear that talus-zone waters are dominated by weathering of bedrock minerals. Weathering in the talus environment probably mostly takes place in the unconsolidated silt, sand, and gravel below the bouldery surface of the talus deposits. It is likely that the finer-grained materials in the talus deposits and the poorly developed soils in the valley bottoms contribute substantial water and weathering-derived solutes to the stream, especially during base flow. This is supported by the similarity of spring and stream water solute and isotope ratios (Figure 8). Stream water samples tend to plot near the middle of the range of the spring and seep samples. It is interesting that the variation in Ca/Na ratios in the stream tends to be much greater than the variation in the stream water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Most of the variation in Ca/Na ratios is attributable to changes in Ca concentrations over a given hydrologic season. These results suggest that although the fluxes of Ca derived from various pools (i.e., cation exchange, flushing of soil water, and mineral weathering reactions) vary seasonally, changes in the relative importance of individual mineral weathering reactions are small.

Conclusions

Partitioning sources of Sr (and Ca) into atmospheric deposition and bedrock mineral weathering using Sr-isotope mixing calculations is possible, but it is complicated by the choice of an appropriate value for the bedrock-weathering end-member. In this study the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the stream at base flow was used to represent the bedrock-weathering end-member because most of the solutes in the stream are believed to be derived from mineral weathering at that time. An important benefit of using base-flow stream chemistry to represent the weathering end member is that the stream effectively integrates the Sr signature from potentially variable bedrock sources. Using a Sr-isotope mixing equation, it was estimated that atmospheric deposition accounted for between one fifth and one third of the annual Sr inputs to the streams.

Estimating the fraction of Ca derived from specific minerals is theoretically possible if the relative mineral-weathering rates of the important minerals are known. However, calculating relative mineral-weathering rates by geochemical mass balance for many natural systems is problematic because there are often multiple mineral sources of Ca. This is the case in Loch Vale, where there are three mineral sources of Ca (i.e., eolian calcite, bedrock calcite, and plagioclase) that weather and contribute appreciable Ca to stream water. Similar problems may be encountered when attempting to use Sr-isotope mixing equations to calculate relative weathering rates. Solving the inverse problem (i.e., predicting the $^{87}\text{Sr}/^{86}\text{Sr}$ released by weathering on the basis of mineral-weathering rates measured in the laboratory or the field) can be useful in terms of validating a conceptual weathering model. Values predicted for the $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr released by weathering in the Andrews Creek drainage are consistent with the $^{87}\text{Sr}/^{86}\text{Sr}$ measured in Andrews Creek at base flow, suggesting that the mass balance weathering model provides reasonable estimates of relative mineral-weathering rates. The predicted $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr re-

leased by weathering is sensitive to the value used for the $^{87}\text{Sr}/^{86}\text{Sr}$ of biotite, which appears to depend in part on the amount of time the mineral has been exposed to weathering. Weathering of fresh bedrock, which contains relatively radiogenic biotite, may yield Sr with a higher average $^{87}\text{Sr}/^{86}\text{Sr}$ than weathering of alpine soil, which contains less radiogenic biotite.

Sources of Ca in stream water were quantified by combining the results from the chemical mass balance model with results from the Sr-isotope mixing calculations. The mass balance model results indicate that $23 \pm 1\%$ of the annual flux of Ca in Andrews Creek was derived from weathering of plagioclase; Sr-isotope mixing calculations suggest that about $26 \pm 7\%$ was derived from weathering of eolian carbonate dust. Subtracting those contributions from the total Ca flux in stream water provides an estimate of 41 to 59% for the contribution from dissolution of calcite in the bedrock. The major uncertainty in the calculations was in the $^{87}\text{Sr}/^{86}\text{Sr}$ of the mineral-weathering end-member, which affected the estimated contribution of Ca from atmospheric deposition. Despite the uncertainty, these results confirm the importance of bedrock weathering in controlling the Ca flux in the stream and indicate that weathering of calcite present in trace amounts in the bedrock was a major contributor of Ca to the aquatic ecosystem.

Appendix: $^{87}\text{Sr}/^{\text{total}}\text{Sr}$ Calculations

To calculate $^{87}\text{Sr}/^{\text{total}}\text{Sr}$ from $^{87}\text{Sr}/^{86}\text{Sr}$, begin with

$$^{\text{total}}\text{Sr} = {}^{84}\text{Sr} + {}^{86}\text{Sr} + {}^{87}\text{Sr} + {}^{88}\text{Sr}$$

Multiply the right side times $^{86}\text{Sr}/^{86}\text{Sr}$:

$$^{\text{total}}\text{Sr} = {}^{86}\text{Sr}({}^{84}\text{Sr}/^{86}\text{Sr} + 1 + {}^{87}\text{Sr}/^{86}\text{Sr} + {}^{88}\text{Sr}/^{86}\text{Sr})$$

Rearrange:

$$^{\text{total}}\text{Sr}/({}^{84}\text{Sr}/^{86}\text{Sr} + 1 + {}^{87}\text{Sr}/^{86}\text{Sr} + {}^{88}\text{Sr}/^{86}\text{Sr}) = {}^{86}\text{Sr}$$

Multiply both sides times ($^{87}\text{Sr}/^{86}\text{Sr}$):

$$({}^{87}\text{Sr}/^{86}\text{Sr})[{}^{\text{total}}\text{Sr}/({}^{84}\text{Sr}/^{86}\text{Sr} + 1 + {}^{87}\text{Sr}/^{86}\text{Sr} + {}^{88}\text{Sr}/^{86}\text{Sr})] = {}^{87}\text{Sr}$$

Divide both sides by $^{\text{total}}\text{Sr}$:

$$({}^{87}\text{Sr}/^{86}\text{Sr})/({}^{84}\text{Sr}/^{86}\text{Sr} + 1 + {}^{87}\text{Sr}/^{86}\text{Sr} + {}^{88}\text{Sr}/^{86}\text{Sr}) = {}^{87}\text{Sr}/^{\text{total}}\text{Sr}$$

${}^{84}\text{Sr}/^{86}\text{Sr}$ and ${}^{88}\text{Sr}/^{86}\text{Sr}$ are constants because they are nonradiogenic; $^{87}\text{Sr}/^{86}\text{Sr}$ is the measured Sr isotope ratio of the mineral.

Acknowledgments. Thanks are due to the reviewers, Alex Blum, Karen Rice, Bryce Winter, Tom Johnson, and Joel Blum, whose comments substantially improved the quality of the manuscript. We would also like to thank Alex Blum for performing the X ray diffraction analysis on the dry-deposition sample. Jill Baron provided the chemistry and flow data for the Loch outlet. This work was funded by the U.S. Geological Survey, Water Resources Division, as part of the Water, Energy, and Biogeochemical Budgets program.

References

- Aberg, F., and F. E. Wickman, Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ in water from streams discharging into the Bothnian Bay, Baltic Sea, *Nord. Hydrol.*, 18, 33–42, 1987.
- Aberg, G., G. Jacks, and P. J. Hamilton, Weathering rates and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios: An isotopic approach, *J. Hydrol.*, 109, 65–78, 1989.
- Acker, J. G., and O. P. Bricker, The influence of pH on biotite disso-

- lution and alteration kinetics at low temperature, *Geochim. Cosmochim. Acta*, 56(8), 3073–3092, 1992.
- Allen, B. L., and B. F. Hajek, Mineral occurrence in soil environments, in *Minerals in Soil Environments*, edited by J. B. Dixon and S. B. Weed, pp. 228–231, Soil Sci. Soc. of Am., Madison, Wis., 1989.
- Andersson, P., R. Lofvendahl, and G. Aberg, Major element chemistry, $\delta^{2}\text{H}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ in a snow profile across central Scandinavia, *Atmos. Environ.*, 24A(10), 2601–2608, 1990.
- Bailey, S. W., J. W. Hornbeck, C. T. Driscoll, and H. E. Gaudette, Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes, *Water Resour. Res.*, 32(3), 707–719, 1996.
- Bain, D. C., and J. R. Bacon, Strontium isotopes as indicators of mineral weathering in catchments, *Catena*, 22, 201–214, 1994.
- Baron, J., Introduction, in *Biogeochemistry of an Alpine Ecosystem*, edited by J. Baron, pp. 108–141, Springer-Verlag, New York, 1992.
- Baron, J., P. M. Walthall, M. A. Mast, and M. A. Arthur, Soils, in *Biogeochemistry of an Alpine Ecosystem*, edited by J. Baron, pp. 108–141, Springer-Verlag, New York, 1992.
- Birkeland, P. W., R. M. Burke, and R. R. Shroba, Holocene alpine soils in gneissic cirque deposits, Colorado Front Range, in *Soil Chronosequences in the Western United States*, U.S. Geol. Surv. Bull. 1590, pp. E1–E21, 1987.
- Blum, J. D., and Y. Erel, A silicate weathering mechanism linking increases in marine $^{87}\text{Sr}/^{86}\text{Sr}$ with global glaciation, *Nature*, 373, 415–418, 1995.
- Blum, J. D., Y. Erel, and K. Brown, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Sierra Nevada stream waters: Implications for relative mineral weathering rates, *Geochim. Cosmochim. Acta*, 58, 5019–5025, 1994.
- Bullen, T. D., J. B. Shanley, and S. Clark, Sr and Pb isotopes as surrogate tracers of water flowpaths in a forested catchment, *Eos Trans. AGU*, 75(16), Spring Meet. Suppl., 144, 1994.
- Bullen, T. D., D. P. Krabbenhoft, and C. Kendall, Kinetic and mineralogic controls on the evolution of groundwater chemistry and $^{87}\text{Sr}/^{86}\text{Sr}$ in a sandy silicate aquifer, northern Wisconsin, USA, *Geochim. Cosmochim. Acta*, 60(10), 1807–1821, 1996.
- Bullen, T. D., A. F. White, A. E. Blum, J. W. Harden, and M. S. Schulz, Chemical weathering of a soil chronosequence on granitoid alluvium, II. Mineralogic and isotopic constraints on the behavior of Sr, *Geochim. Cosmochim. Acta*, 61(2), 291–306, 1997.
- Burke, W. H., R. E. Denison, E. A. Hetherington, R. B. Koepnick, N. F. Nelson, and J. B. Otto, Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time, *Geology*, 10, 516–519, 1982.
- Campbell, D. H., D. W. Clow, G. P. Ingersoll, M. A. Mast, N. E. Spahr, and J. T. Turk, Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains, *Water Resour. Res.*, 31(11), 2811–2821, 1995.
- Capo, R. C., and D. J. DePaolo, Seawater strontium isotopic variations from 2.5 million years ago to the present, *Science*, 249, 51–55, 1990.
- Clauer, N., Strontium and argon isotopes in naturally weathered biotites, muscovites and feldspars, *Chem. Geol.*, 31, 325–334, 1981.
- Clow, D. W., Weathering rates from field and laboratory experiments on naturally weathered soils, Ph.D. dissertation, 116 pp., Univ. of Wyo., Laramie, 1992.
- Clow, D. W., and J. I. Drever, Weathering rates as a function of flow through an alpine soil, *Chem. Geol.*, 132, 131–141, 1996.
- Clow, D. W., and M. A. Mast, Composition of precipitation, bulk deposition, and runoff at a granitic bedrock catchment in the Loch Vale Watershed, Colorado, USA, in *Biogeochemistry of Seasonally Snow-Covered Catchments*, edited by K. A. Tonnessen et al., pp. 235–242, Int. Assoc. of Hydrol. Sci., Boulder, Colo., 1995.
- Clow, D. W., M. A. Mast, D. H. Campbell, T. D. Bullen, and C. Kendall, Initial characterization of talus hydrology and biogeochemistry in an alpine/subalpine basin, Rocky Mountains, USA, *Eos Trans. AGU*, 76(46), Fall Meet. Suppl., 209, 1995.
- 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, 344 pp., Univ. of Colo., Boulder, 1977.
- Davis, P. T., Holocene glacier fluctuations in the American Cordillera, *Quat. Sci. Rev.*, 7, 129–157, 1988.
- Dia, A. N., A. S. Cohen, R. K. O'Nions, and N. J. Shackleton, Seawater Sr isotope variation over the past 300 kyr and influence of global climate cycles, *Nature*, 356, 786–788, 1992.
- Drever, J. I., *Geochemistry of Natural Waters*, 437 pp., Prentice-Hall, Englewood Cliffs, N. J., 1988.
- Drever, J. I., and D. W. Clow, Weathering rates in catchments, in *Chemical Weathering Rates of Silicate Minerals, Rev. in Mineral.*, vol. 31, edited by S. Brantley and A. White, pp. 463–483, Mineral. Soc. of Am., Washington, D. C., 1995.
- Edgerton, E. S., T. F. Lavery, and H. S. Prentice, National dry deposition network third annual report (1989), EPA/600/3-91/018, Environ. Prot. Agency, Washington, D. C., 1991.
- Eilers, J. M., et al., Western lake survey, phase 1, Characteristics of lakes in the western United States, vol. 2, Data compendium for selected physical and chemical variables, EPA-600/3-86/054b, U.S. Environ. Prot. Agency, Washington, D. C., 1987.
- Faure, G., *Principles of Isotope Geology*, 589 pp., John Wiley, New York, 1986.
- Fennelly, P. F., The origin and influence of airborne particulates, *Am. Sci.*, 64, 46–56, 1976.
- Garrels, R. M., and F. T. Mackenzie, Origin of the compositions of some springs and lakes, in *Equilibrium Concepts in Natural Water Systems*, *Adv. Chem. Ser.*, vol. 67, edited by W. Stumm, pp. 222–242, Am. Chem. Soc., Washington, D. C., 1967.
- Gatz, D. F., W. R. Barnard, and G. J. Stensl, The role of alkaline materials in precipitation chemistry: A brief review of the issues, *Water Air Soil Pollut.*, 30, 245–251, 1986.
- Gautier, J. M., E. H. Oelkers, and J. Schott, Experimental study of K-feldspar dissolution rates as a function of chemical affinity at 150°C and pH 9, *Geochim. Cosmochim. Acta*, 58, 4549–4560, 1994.
- Goossens, D. A., J. G. Philippaerts, R. Gijbels, A. P. Pijpers, S. Van Tendeloo, and E. Althaus, A SIMS, XPS, SEM, TEM, and FTIR study of feldspar surfaces after reacting with acid solutions, in *6th International Symposium on Water-Rock Interaction*, edited by D. L. Miles, pp. 271–274, A. A. Balkema, Rotterdam, 1989.
- Gosz, J. R., and D. I. Moore, Strontium isotope studies of atmospheric inputs to forested watersheds in New Mexico, *Biogeochemistry*, 8, 115–134, 1989.
- Gosz, J. R., D. G. Brookins, and D. I. Moore, Using strontium isotope ratios to estimate inputs to ecosystems, *Bioscience*, 33, 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.
- Ingersoll, G. I., Estimating snowmelt contribution to the seasonal water balance in a small alpine watershed, Master's thesis, 137 pp., Univ. of Colo., Boulder, 1995.
- Jones, L. M., and G. Faure, A study of strontium isotopes in lakes and surficial deposits of the ice-free valleys, southern Victoria Land, Antarctica, *Chem. Geol.*, 22, 107–120, 1978.
- Landers, D. H., J. M. Eilers, D. F. Brakke, W. S. Overton, P. E. Kellar, M. E. Silverstein, R. D. Schonbrod, R. E. Crowe, R. A. Linthurst, J. M. Omernik, S. A. Teague, and E. P. Meier, Western lake survey, phase 2, Characteristics of lakes in western United States, vol. 1, Population descriptions and physico-chemical relationships, EPA-600/3-86/054a, U.S. Environ. Prot. Agency, Washington, D. C., 1987.
- Likens, G. E., F. H. Bormann, R. S. Pierce, J. S. Eaton, and N. M. Johnson, *Biogeochemistry of a Forested Ecosystem*, 135 pp., Springer-Verlag, New York, 1977.
- Lins, H. F., Recent directions taken in water, energy, and biogeochemical budgets research, *Eos Trans. AGU*, 75(38), 433, 438–439, 1994.
- Litaor, 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.
- Madole, R. F., Glacial geology of the Front Range, Colorado, in *Quaternary Stratigraphy of North America*, edited by W. C. Mahaney, pp. 297–318, Van Nostrand Reinhold, New York, 1976.
- Marshall, B. D., Z. E. Peterman, K. Futa, and J. S. Stuckless, Strontium isotopes in carbonate deposits at Crater Flat, Nevada, in *High Level Radioactive Waste Management*, pp. 1423–1428, Am. Nucl. Soc., LaGrange Park, Ill., 1991.
- Mast, M. A., A laboratory and field study of chemical weathering with special reference to acid deposition, Ph.D. dissertation, 174 pp., Univ. of Wyoming, Laramie, 1989.
- Mast, M. A., Geochemical characteristics, in *Biogeochemistry of an Alpine Ecosystem*, edited by J. Baron, pp. 93–107, Springer-Verlag, New York, 1992.
- Mast, M. A., J. I. Drever, and J. Baron, Chemical weathering in the Loch Vale watershed, Rocky Mountain National Park, Colorado, *Water Resour. Res.*, 26(12), 2971–2978, 1990.
- Mast, M. A., C. Kendall, D. H. Campbell, D. W. Clow, and J. Back, Determination of hydrologic pathways in an alpine-subalpine basin using isotopic and chemical tracers, in *Biogeochemistry of Seasonally*

- Snow-Covered Catchments*, edited by K. Tonnessen et al., pp. 263–270, Int. Assoc. of Hydrol. Sci., Boulder, Colo., 1995.
- Miller, E. K., J. E. Blum, and A. J. Friedland, Determination of soil exchangeable-cation loss and weathering rates using Sr isotopes, *Nature*, 362, 438–441, 1993.
- National Atmospheric Deposition Program/National Trends Network Coordination Office, *Annual Data Summary, Precipitation Chemistry in the United States*, Nat. Resour. Ecol. Lab., Colo. State Univ., Fort Collins, 1984–1994.
- Peterman, Z. E., C. E. Hedge, and W. A. Braddock, Age of Precambrian events in the Northwestern Front Range, Colorado, *J. Geophys. Res.*, 73(6), 2277–2296, 1968.
- Rebertus, R. A., S. B. Weed, and S. W. Buol, Transformations of biotite to kaolinite during saprolite-soil weathering, *Soil Sci. Soc. Am. J.*, 50, 810–819, 1986.
- Richmond, G. M., Glaciation of the east slope of Rocky Mountain National Park, Colorado, in *Geoecology of the Colorado Front Range: A study of Alpine and Subalpine Environments*, edited by J. D. Ives, pp. 24–34, Westview Press, Boulder, Colo., 1960.
- Rochette, E. A., J. I. Drever, and F. S. Sers, Chemical weathering in the West Glacier Lake drainage basin, Snowy Range, Wyoming: Implications for future acid deposition, *Contrib. Geol.*, 26(1), 29–44, 1988.
- Stauffer, R. E., Granite weathering and the sensitivity of alpine lakes to acid deposition, *Limnol. Oceanogr.*, 35(5), 1112–1134, 1990.
- Stoch, L., and W. Sikoma, Transformations of micas in the process of kaolinization of granites and gneisses, *Clays Clay Mineral.*, 24, 156–162, 1976.
- Thomas, G. W., Exchangeable cations, in *Methods of Soil Analysis, part 2, Chemical and Microbiological Properties, Agron. Monogr.*, vol. 9, edited by A. L. Page et al., pp. 159–165, Am. Soc. of Agron., Madison, Wis., 1982.
- Turk, J. T., and N. Spahr, Rocky Mountains, in *Acidic Deposition and Aquatic Ecosystems*, edited by D. F. Charles, pp. 471–499, Springer-Verlag, New York, 1991.
- Turk, J. T., N. E. Spahr, and D. H. Campbell, Planning document of water, energy, and biogeochemical-budget (WEBB) research project, Loch Vale watershed, Rocky Mountain National Park, Colorado, *U.S. Geol. Surv. Open File Rep. 92-628*, 1993.
- Wadleigh, M. A., J. Veizer, and C. Brooks, Strontium and its isotopes in Canadian Rivers: Fluxes and global implications, *Geochim. Cosmochim. Acta*, 49, 1727–1736, 1985.
- Walthall, P. M., Acidic deposition and the soil environment of Loch Vale watershed in Rocky Mountain National Park, Ph.D. Dissertation, 148 pp., Colo. State Univ., Fort Collins, 1985.
- White, A. F., A. E. Blum, T. D. Bullen, M. L. Peterson, M. S. Shultz, and J. W. Harden, A three million year weathering record for a soil chronosequence developed in granitic alluvium, Merced, California, in *7th International Symposium on Water-Rock Interaction*, edited by Y. K. Kharaka and A. S. Maest, pp. 607–610, A. A. Balkema, Rotterdam, 1992.
- White, A. F., A. E. Blum, M. S. Schulz, T. D. Bullen, J. W. Harden, and M. L. Peterson, Chemical weathering rates of a soil chronosequence on granitic alluvium, I, Quantification of mineralogical and surface area changes and calculation of primary silicate reaction rates, *Geochim. Cosmochim. Acta*, 60(14), 2533–2550, 1996.
- Wickman, F. E., and G. Aberg, Variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in lake waters from central Sweden, *Nord. Hydrol.*, 18, 21–32, 1987.
- Williams, M. W., A. D. Brown, and J. M. Melack, Geochemical and hydrologic controls on the composition of surface water in a high-elevation basin, Sierra Nevada, California, *Limnol. Oceanogr.*, 38(4), 775–797, 1993.
- Wollast, R., Kinetics of the alteration of K-feldspar in buffered solutions at low temperature, *Geochim. Cosmochim. Acta*, 31, 635–648, 1967.
-
- T. D. Bullen, D. W. Clow, M. A. Mast, and J. T. Turk, USGS/WRD, MS 415, Federal Center, Box 25046, Lakewood, CO 80225-0046.

(Received October 17, 1996; revised March 7, 1997;
accepted March 19, 1997.)