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Geochemical and hydrologic controls on the composition of surface water in a high-elevation basin, Sierra Nevada, California

Mark W. Williams¹

Center for Remote Sensing and Environmental Optics, UCSB, Santa Barbara, California 93106

Aaron D. Brown²

Department of Soil and Environmental Sciences, University of California, Riverside

John M. Melack

Department of Biological Sciences, UCSB

Abstract

Hydrologic, mineralogic, and soil data are used to determine the sources and geochemical controls on the composition of surface water in the Emerald Lake watershed (ELW), a high-altitude basin located in the southern Sierra Nevada. The solute composition of stream waters at the ELW can be divided into three periods: snowpack runoff, a transition period in summer as snowpack runoff decreases and little precipitation occurs, and a low-flow period from late summer through winter. Each period has different geochemical controls on the solute composition of surface waters. During snowpack runoff ~50% of stream flow was from direct surface runoff and ~50% of stream flow was return flow from subsurface reservoirs. Hydrologic residence time of subsurface water at maximum snowpack runoff was measured directly with a ⁶LiBr tracer and varied from 9 to 20 h. Three independent measurements show that the acidity in snowpack runoff was neutralized by cation exchange in soils and talus. Discharge from soil reservoirs was the primary source of stream flow during the summer transition period when the composition of stream flow was congruent with the stoichiometry of plagioclase weathering. Processes occurring below the soil zone exerted the dominant geochemical controls on the composition of stream waters during the period of low flow, with preferential weathering of the anorthite component of plagioclase in subsurface rock and further weathering of kaolinite to gibbsite.

The composition of surface waters in montane areas that are underlain by crystalline bedrock has traditionally been interpreted as

being controlled by solutes in chemical equilibria or steady state with bedrock weathering products (Feth et al. 1964; Garrels and MacKenzie 1967; Paces 1972; Miller and Drever 1977; Stoddard 1987). However, there is still much to be learned about the many processes that control the solute content of surface waters in alpine basins. For example, Stauffer (1990), Turk and Spahr (1991), and others have posed a long-standing geochemical enigma: what is the source of the Ca²⁺ that dominates the base cation output of many felsic basins and confounds the predictions of stoichiometric weathering models such as that of Garrels and Mackenzie (1967)?

The solute composition of stream waters depends on the source of the water and the biogeochemical reactions that modify the solute composition of the water as it moves through the catchment (Maule and Stein 1990). If groundwater discharge is the major source of stream flow during storm events in granitic basins, chemical weathering is generally considered to be the major process that neutralizes incoming acidity (Miller and Drever 1977;

¹ Current address: INSTAAR and Dept. of Geography, Campus Box 450, University of Colorado, Boulder 80309-0450.

² Current address: Marine Sciences Institute, UCSB, Santa Barbara, California 93016.

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Drever and Hurcomb 1986; Mast et al. 1990). However, the reaction rates of chemical weathering may be too slow to buffer incoming acidity where small groundwater reservoirs are rapidly flushed by infiltrating meltwater (Bottomley et al. 1986).

In this paper we examine the geochemical and hydrologic processes that control the composition of surface water in the Emerald Lake watershed (ELW), a high-elevation basin in the southern Sierra Nevada. The ELW is representative of granitic headwater basins in the Sierra Nevada, based on statistical analysis of data from the Western Lakes Survey conducted by the Environmental Protection Agency and other sources (Melack and Stoddard 1991). Our primary objective is to determine the sources of solutes in stream flow, with emphasis on the origin of Ca^{2+} , reactive silicate, and HCO_3^- . We determine whether stream waters are in equilibrium with mineral weathering products on both an annual basis and at weekly sampling intervals. We also investigate whether the acidity in atmospheric deposition is neutralized by mineral weathering or other processes, at both annual and weekly time intervals. We use natural and introduced geochemical tracers to infer hydrologic flow paths through the basin and to qualitatively assess the effects such routing has on temporal variation in the chemical composition of surface waters.

Site description

The Emerald Lake basin is a north-facing granitic cirque on the upper Marble Fork of the Kaweah River drainage, in the southern Sierra Nevada of California ($36^{\circ}35'49''\text{N}$, $118^{\circ}40'30''\text{W}$). Basin area is 120 ha; elevation ranges from 2,800 m at the lake outlet to 3,416 m at the summit of Alta Peak. Emerald Lake is a 2.72-ha cirque lake at the bottom of the basin, fed by two main inflows and six intermittent streams, and drained by a single outflow (Fig. 1). The lake and the streams in its watershed are weakly buffered, $\text{Ca}(\text{HCO}_3)_2$ waters (Melack et al. 1989), typical of high-altitude Sierran surface waters (Melack et al. 1985; Melack and Stoddard 1991). Massive rock outcrops cover 33% of the basin area; unconsolidated sand, gravels, and talus cover ~23%. The remaining area is mapped as a

rock-soil complex, which is about half soil and half rock outcrop. Soils are strongly acidic and weakly buffered (Huntington and Akeson 1986). Vegetation covers ~20% of the basin area, of which 3% has scattered trees (Rundel et al. unpubl.).

Bedrock mineralogy—Bedrock in the basin is composed mainly of granite and granodiorite, with some mafic intrusions, aplite dikes, and pegmatite veins (Sisson and Moore 1984; Clow 1987). Granite of the Lodgepole Formation underlies ~75% of the ELW and is composed mainly of An_{24} plagioclase, potash feldspar, and quartz. Dark minerals, mainly biotite and hornblende, range in volume from 2 to 7% of the Lodgepole granite (Clow 1987). Granodiorite of the Castle Creek (An_{24} plagioclase) and Emerald Lake (An_{42} plagioclase) Formations underlies ~15% of the basin; dark minerals comprise ~15% by volume of the granodiorite (Clow 1987). Alaskite and aplite cover ~10% of the basin area and are composed primarily of orthoclase, quartz, and plagioclase; dark minerals comprise from a trace to 5% by volume of these rocks (Clow 1987).

Soil characteristics—Well-drained Cryumbrepts and Cryorthents account for 34% and 17% of the soil area, respectively. Wetter Cryumbrepts found along stream channels account for 37% of the soil area. The estimated average depth of soils, for the 27 ha of soils covering the basin, is ~0.35 m (Brown et al. unpubl.). All soils are derived primarily from weathering of the underlying bedrock. X-ray diffraction of the soil clay fraction collected from soil profiles at soil lysimeter sites found hydroxy-interlayered vermiculite and kaolinite to be the dominant clay minerals in all soil samples (Brown and Lund 1991); gibbsite was also present in all soil samples. Other minerals found in some soil samples included plagioclase, mica, biotite, quartz, and hornblende (Brown and Lund 1991). Cation exchange capacity of soils ranged from 7.8 to 30 meq 100 g^{-1} . Ca and K^+ dominate the exchangeable bases of soils, with weighted averages over the basin of 51 and 45%, respectively. Na constitutes <1% of the exchange bases. Base saturation percentages for the upper 200 mm of soils are typically 26–30% (Brown et al. unpubl.).

The free-water capacity of soils in the basin

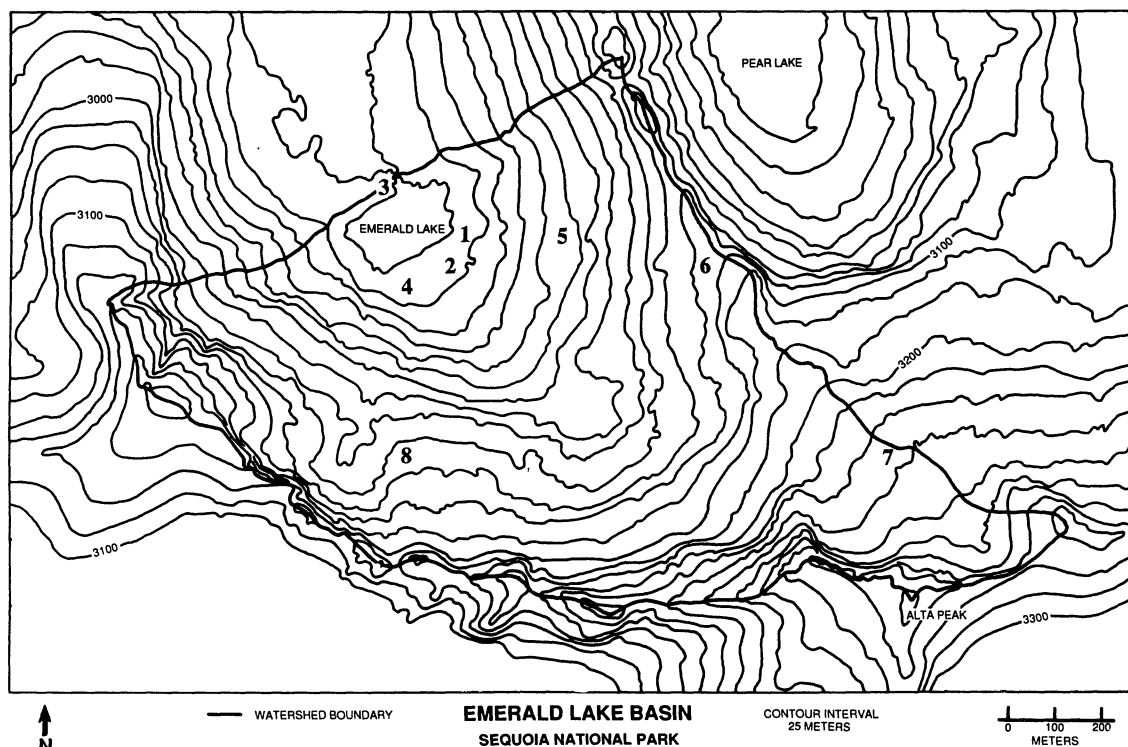


Fig. 1. Topographic map of the Emerald Lake watershed. Location of sites: 1—inflow 1; 2—inflow 2; 3—outflow; 4—inflow 4; 5—bench; 6—ridge; 7—cirque; 8—hole. Discharge was measured and water samples collected immediately above the lake at sites 1, 2, and 4 and immediately below the lake at site 3. Soil lysimeters were located at sites 5 and 6. Snowpit samples were collected in 1986 at sites 2, 6, and 7; in 1987 snowpit and meltwater samples were collected at sites 2, 5, 6, 7, and 8. The LiBr tracer was added near site 8.

is $\sim 29,000 \pm 7,800 \text{ m}^3$, defined as saturated capacity less field capacity and estimated with measured depths and physical properties of the soils. The total free water capacity of the basin is $\sim 48,000 \pm 13,000 \text{ m}^3$ (Brown et al. unpubl.), calculated by combining the free-water capacity of soils with estimates for unconsolidated materials. The heterogeneous distribution of soil water storage (as free water) is governed by the depth and texture of soils and unconsolidated materials, with zones of higher water capacity tending to follow perennial and ephemeral stream channels (Fig. 2). Laboratory measurements of the saturated hydraulic conductivity ranged from 0.1 to 0.01 mm s^{-1} (Brown et al. unpubl.).

Deposition—Snowfall accounted for $\sim 95\%$ of the precipitation input to the basin in 1986 and 1987 (Kattelman and Elder 1991). Water years began on 1 October. The peak accu-

mulation of snow for the 1986 water year was 2,000-mm snow water equivalence, and peak accumulation for 1987 was 670 mm (Elder et al. 1991). The snow-covered area of the basin was $\sim 95\%$ on 15 May 1986 and 55% on the same date in 1987. About 90% of the wet deposition flux to the basin was from the storage and release of snowpack meltwater (1986) or snowpack meltwater plus spring precipitation (1987) (Williams and Melack 1991a). The chemical content of snow was dilute; the volume-weighted mean (VWM) ionic concentrations for each ion did not exceed $8.3 \mu\text{eq liter}^{-1}$ for any sampling date. Spring precipitation in 1986 contributed $<1\%$ of the water and ionic load relative to water and solutes stored in the snowpack at maximum accumulation. In contrast, precipitation quantity and ionic loading from wet deposition during the period of snowpack runoff in 1987 resulted in more ionic

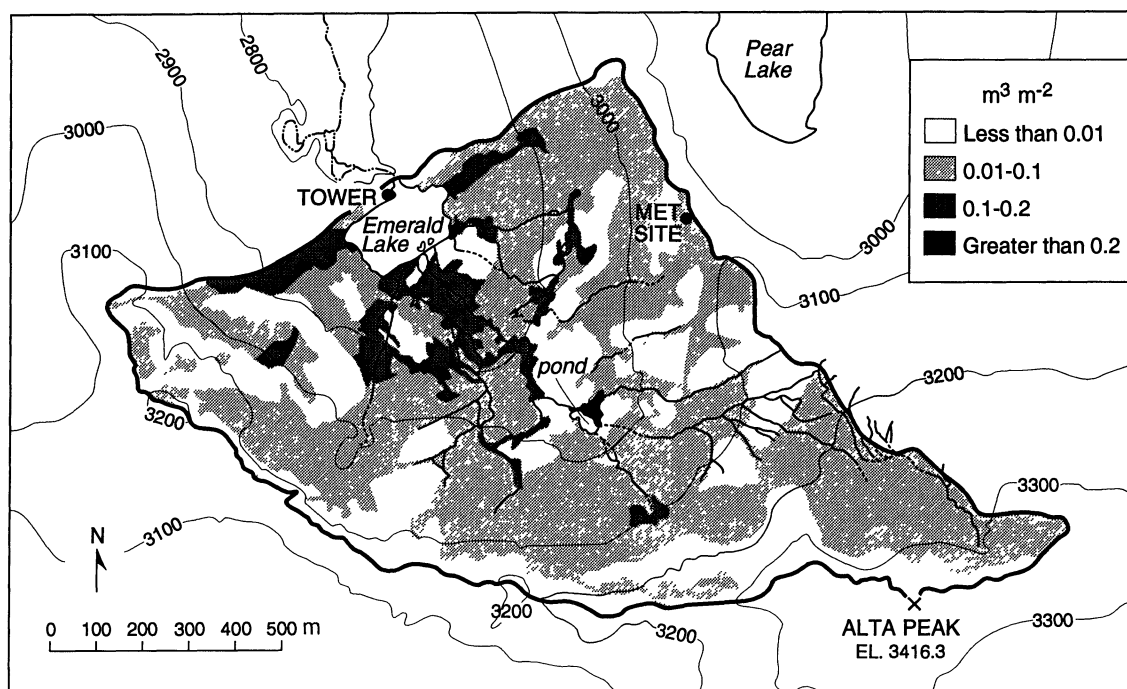


Fig. 2. Map of soil water capacity in the Emerald Lake watershed. The highest amounts of soil water capacity follow perennial and ephemeral stream channels.

loading from spring snowfall and rainfall than from winter snowfall for NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , and Mg^{2+} (Williams and Melack 1991b).

Methods

Stream and soil water—Stage height in the outflow and two main inflows was measured with a Montedero-Whitney pressure transducer and recorded on an Omnidata data logger. Stage-discharge relationships were developed with a salt dilution technique (Kattelman and Elder 1991). Sampling sites for stream water were located immediately above the lake for inflows 1, 2, and 4 and immediately below the lake for the basin outflow (Fig. 1). Water samples were collected from October 1985 through March 1988; samples were collected about weekly from the onset of snowpack runoff to September and about monthly for the remainder of the year, except from November 1986 to April 1987 when inflows 2 and 4 were frozen (Melack et al. unpubl.). Soil lysimeters were installed at five locations in the basin in July 1985; at each site the following measurements were made at depths of ~ 100 and 300 mm: duplicate measurements of the solute com-

position of soil water with membrane-covered porous polyethylene plates under tension, temperature of the soil solution, and moisture content (Brown et al. unpubl.). For this paper we present results from a Lithic Cryobrept located at the ridge site (elevation, 3,100 m) and an Entic Cryobrept located at the bench site (elevation, 2,900 m) (Fig. 1). Sample collection of soil water began in July 1986; the soil solution during the period of snowpack runoff was sampled in 1987.

All water samples were analyzed for major inorganic ions and reactive silicate (Si). Acid-neutralizing capacity (ANC) was determined with the Gran titration method and is considered to equal HCO_3^- . Analytical techniques, detection limits, and measurement precision for the various solutes have been described elsewhere (Melack et al. unpubl.; Brown et al. unpubl.; Williams and Melack 1991a,b). The analytical precision of all solutes was within 6% of mean values, with the exception of Cl^- which was 13.4% and ANC which was $\pm 4 \mu\text{eq liter}^{-1}$ (precision of ANC presented as plus or minus because some measured values were 0 $\mu\text{eq liter}^{-1}$). The detection limit of all solutes

was $<0.5 \mu\text{eq liter}^{-1}$ except for Ca^{2+} which was $1.0 \mu\text{eq liter}^{-1}$. Lake and stream samples collected from August 1986 to April 1988 ($n = 336$) have ionic charge balances within $5 \mu\text{eq liter}^{-1}$ in 81% of the samples and within $10 \mu\text{eq liter}^{-1}$ in 93% of the samples; the mean difference between the sums of cations and anions was $0 \mu\text{eq liter}^{-1}$ (Melack et al. unpubl.).

Mineral weathering—To determine whether the hydrochemical content of stream waters in the ELW was from a combination of wet deposition and groundwater discharge, we followed an approach similar to that of Garrels and Mackenzie (1967). First, we determined whether plagioclase weathering supplied most of the Na^+ and Ca^{2+} in stream waters. Second, we used thermodynamic relationships to determine the weathering products of primary minerals. We then applied a stoichiometric weathering model, similar to that of Garrels and Mackenzie, to the annual input-output balances of the basin for base cations, HCO_3^- , and Si for water years 1986 and 1987. The weathering reactions used for this stoichiometric mass balance were based on the mineralogy of the basin and the weathering products identified by the above analyses. Last, we applied this same stoichiometric mass balance to each individual stream sample from January 1986 to March 1988.

Annual stream loading was calculated by multiplying stream discharge by weekly concentrations for each stream flowing into Emerald Lake, then summing up the weekly loading values for each stream over the water year (Melack et al. unpubl.). Next, the cations in annual wet deposition (Williams and Melack 1991a) were subtracted from those in basin runoff. No adjustment was made for dry deposition for two reasons. Dry deposition was not a significant source of anions during the period of snow accumulation (Williams and Melack 1991b), and dry deposition flux of nitrogen species during summer was much less than nitrogen in annual precipitation (Noppe 1989). Input-output analyses show that NO_3^- , Cl^- , and SO_4^{2-} loadings in stream waters were accounted for by wet deposition (Williams and Melack 1991b). Concentrations of HCO_3^- and Si in wet deposition were analyzed and found to be at or below detection limits.

The same stoichiometric mass balance procedure was applied to each individual stream

sample from January 1986 to March 1988. Adjusting the concentration of base cations in stream waters for wet deposition flux is problematical on a weekly-to-monthly time step. We divided wet deposition flux into three periods: snowpack runoff, rainfall events, and the remainder of the year. A scaling factor to determine the concentration of base cations in snowpack meltwaters in 1986 was developed by dividing the Cl^- concentrations in the basin outflow by the mean Cl^- concentrations of the snowpack. Here we make the assumption that the only source of Cl^- in the basin is from wet deposition and that Cl^- does not undergo mineral weathering or biogeochemical reactions within the basin. Input-output analysis for the time period of snowpack runoff shows that Cl^- did act conservatively in 1987 but that there was retention of Cl^- in the basin in 1986 (Williams and Melack 1991b). To calculate the concentration of base cations in snowpack runoff, the VWM ionic concentration of each base cation measured in the snowpack (14 April, 23 May, and 27 June, from Dozier et al. unpubl.) was multiplied by this scaling factor. The scaling amount for each base cation was decremented daily by dividing the VWM ionic difference between snowpit measurements by the number of days between measurements and subtracting this amount from the previous snowpit sample. For a given sampling day, this daily amount for snowmelt inputs of base cations to stream waters was subtracted from the measured concentration of base cations in stream waters.

Cation concentrations in rainfall were subtracted in a similar fashion, based on the length of the observed Cl^- pulse in stream waters, again assuming Cl^- was a conservative tracer. The remaining wet deposition flux was then distributed evenly over the remaining days in the year. For 1987 the same procedure was followed, with the exception that during the period of snowpack runoff, the mean cation concentrations measured in six snowpack lysimeters (from Williams and Melack 1991b) were used to scale the base cation concentrations in stream waters.

The scaling factor for wet deposition was verified by the following procedure. First, daily flux of wet deposition was calculated as the product of the calculated concentrations from wet deposition multiplied by discharge and by

evapotranspiration amounts reported by Katelmann and Elder (1991). Next, the calculated flux of wet deposition was summed over the water for each ion on a daily time step. Last, the resulting amount was checked against the measured annual flux of wet deposition reported by Williams and Melack (1991a). When the two amounts disagreed by more than an arbitrarily determined 5%, concentrations of base cations in the release of snowpack meltwaters and in precipitation were adjusted until the calculated flux matched that of the measured flux. This adjustment procedure was necessary only during the rain-on-snow events in 1987.

Hydrologic flow paths—We separated the stream hydrograph of the ELW into its baseflow or “pre-event water” and snowpack runoff waters or “event water” with a simple mixing model:

$$Q_p = Q_t \left[\frac{C_t - C_e}{C_p - C_e} \right]$$

where Q is discharge ($\text{m}^3 \text{d}^{-1}$), C is tracer concentration, t is total stream discharge, e is the event (or snowpack meltwater) component, and p the pre-event component. Basic assumptions of this mixing model are that the chemical content of event water is significantly different from that of pre-event water, that event water is characterized by a single value or variations in the value are accounted for, that contributions of soil water are insignificant, and that surface storage contributions are negligible (Sklash and Farvolden 1979; Wels et al. 1990). Pre-event water was the component of surface flow from water stored in soil (vadose) and groundwater reservoirs before snowpack runoff began. Event water was the component of stream flow that was from snowpack meltwater and rain, as defined by Hooper and Shoemaker (1986). Therefore, this mixing model does not consider as baseflow water that infiltrated into groundwater and vadose reservoirs during the period of snowpack runoff, with subsequent discharge to surface flow. We use Si as a tracer because concentrations of Si in rain and snowpack meltwater were always near or below the detection limit ($0.5 \mu\text{mol liter}^{-1}$) and never exceeded $1 \mu\text{mol liter}^{-1}$. Concentrations of Si in rain and snowpack meltwater did not vary throughout the period of interest

and provided a clear separation between event and pre-event waters. Both Hooper and Shoemaker (1986) and Maule and Stein (1990) reported that Si worked as well or better as tracers for hydrograph separation than did stable isotopic tracers such as ^{18}O and deuterium for forested watersheds in eastern North America.

Hydrologic residence time at maximum discharge was determined experimentally with an applied tracer composed of $^6\text{LiBr}$. Bromide and Li^+ were chosen as tracers because they are known to be relatively unaffected by soil processes. The isotopically enriched ^6Li was used because ^7Li is much more common in surface waters. The experiment was conducted between 4 and 8 June 1987. Discharge and soil saturation were maximal during this 4-d period. The tracer was introduced as a 1-liter solution to a small, ephemeral stream in an area of unconsolidated materials located at the source area of inflow 4, at an elevation of 2,990 m (site 8, Fig. 1). There is no surface discharge from this area; water is discharged through springs and seepage at an elevation of $\sim 2,900$ m. Samples were collected at the gauging site in inflow 4, which is close to the lake at an elevation of $\sim 2,815$ m. The vertical relief between the application site and the collection site was ~ 175 m and the linear distance ~ 350 m, with an average slope of $\sim 30^\circ$. Water samples were collected before the tracer was introduced to determine background concentrations of Br^- and $^6,^7\text{Li}^+$ at the application site and the collection site. Once the tracer was applied, stream water was sampled at the collection site at a decreasing rate: every 30 min for ten 30-min intervals, every hour for ten 1-h intervals, every 1.5 h for ten 1.5-h intervals, then every 2 h for ten 2-h intervals, followed by every 3 h for ten 3-h intervals, and then at 0800, 1400, and 2000 hours for the next 3 d. Every stream sample was analyzed for Br^- with ion chromatography and for $^6,^7\text{Li}^+$ with inductively coupled plasma-mass spectroscopy. Hydrologic residence time was calculated as the elapsed time from application of the tracer to when measurable amounts of tracer were found at the gauging site of inflow 4.

Interactions between snowpack runoff and soils were evaluated with the high concentrations of inorganic ions in rain-on-snow events in spring 1987 for H^+ , Ca^{2+} , NH_4^+ , NO_3^- ,

and SO_4^{2-} . These high concentrations, relative to concentrations in snow, soil, and stream waters, provided natural tracers to determine the extent and type of interactions between snowpack runoff and soils. The solute content of rain, snowpack, and snowpack meltwater are from Williams and Melack (1991b).

A second method of evaluating the importance of interactions between snowpack runoff and soils was the molar ratio of Na : Ca in the soil solution. Selectivity coefficients of soils in the ELW result in soil exchangers preferentially retaining Ca^{2+} over Na^+ . Consequently, Na^+ is leached from soils more readily than Ca^{2+} . This leads to the prediction that if cation exchange is responsible for the neutralization of the H^+ in wet deposition, the molar ratio of Na : Ca in soil solution should increase during snowpack runoff and then decrease toward the end of snowpack runoff.

Results

Stream and soil water—As discharge increased in spring, concentrations of Si, ANC, and base cations decreased (Fig. 3). Solute concentrations then increased to a yearly maximum as discharge decreased in summer. Ca^{2+} concentrations were always greater than concentrations of Na^+ , except for a brief period near maximum snowpack runoff. Maximum concentrations of Ca^{2+} were near $60 \mu\text{eq liter}^{-1}$ and minimum concentrations near $10 \mu\text{eq liter}^{-1}$; maximum and minimum concentrations of Na^+ were ~ 20 and $3 \mu\text{eq liter}^{-1}$. Concentrations of Mg^{2+} and K^+ followed a similar inverse relationship with discharge; concentrations of these ions were generally much lower than concentrations of Ca^{2+} and Na^+ (not shown). ANC generally paralleled concentrations of Ca^{2+} ; maximum concentrations of ANC were $\sim 65 \mu\text{eq liter}^{-1}$ and minimum concentrations were near $10 \mu\text{eq liter}^{-1}$. The decreases in ANC during autumn were associated with rainfall. Concentrations of Si reached an annual maximum during the period of low flow of $\sim 60 \mu\text{mol liter}^{-1}$; minimum concentrations were $\sim 17 \mu\text{mol liter}^{-1}$. Concentrations of the strong acid anions (NO_3^- , SO_4^{2-} , and Cl^-) showed a different pattern. Concentrations of strong acid anions increased to a yearly maximum during the first 30 d of snowpack runoff, followed by a period of dilution (Fig. 4). There was a second peak in anion concentrations

during autumn from rainfall. NO_3^- and Cl^- had larger increases and decreases in concentrations than did SO_4^{2-} .

Solute concentrations in the soil solution differed at times from those of solutes in stream water (Fig. 5). Na^+ concentrations were generally greater than Ca^{2+} in the soil solution. Maximum and minimum concentrations of Na^+ at the bench site were ~ 40 and $12 \mu\text{eq liter}^{-1}$, compared to maximum and minimum concentrations of Ca^{2+} of 24 and $3 \mu\text{eq liter}^{-1}$. Minimum concentrations of Ca^{2+} occurred twice during the year, once during the period of snowpack runoff and again in autumn. ANC at the bench also had two periods of minimum concentration: near $0 \mu\text{eq liter}^{-1}$ during both snowpack runoff and autumn; maximum values near $100 \mu\text{eq liter}^{-1}$ occurred in summer. At the ridge site, ANC at a depth of 100 mm decreased below $0 \mu\text{eq liter}^{-1}$ for several weeks during snowpack runoff and at a depth of 300 mm was close to $0 \mu\text{eq liter}^{-1}$. Concentrations of Si at the bench reached a minimum of $\sim 30 \mu\text{mol liter}^{-1}$ during the period of snowpack runoff and a maximum of $\sim 100 \mu\text{mol liter}^{-1}$ in autumn; Si concentrations at the ridge followed a similar pattern. Concentrations of strong acid anions also increased in the soil solution during the period of snowpack runoff, with concentrations of NO_3^- at the ridge increasing from $0 \mu\text{eq liter}^{-1}$ at the start of snowpack runoff to $\sim 70 \mu\text{eq liter}^{-1}$ at the peak of snowpack runoff in 1987 (Brown et al. unpubl.; Williams and Melack 1991b; Williams et al. 1991).

The soil surface froze at all sites in 1987 and at some sites in 1988, but temperatures under the snowpack increased to 0°C in late winter of both years (Fig. 6). These data indicate that liquid water was probably present in soils at the onset of snowpack runoff. Soil water contents peaked during the period of snowpack runoff and declined in summer (Fig. 6). Soils were saturated during the period of snowpack runoff. Soil moisture recharge occurred in the autumn months after rain events, but soil saturation did not occur until the following spring.

Mineral weathering—The contribution of plagioclase weathering to the solute composition of stream waters was investigated by plotting the molar ratio of Na : Ca in stream waters against the molar ratio of HCO_3^- : Si, following the procedure recommended by Garrels

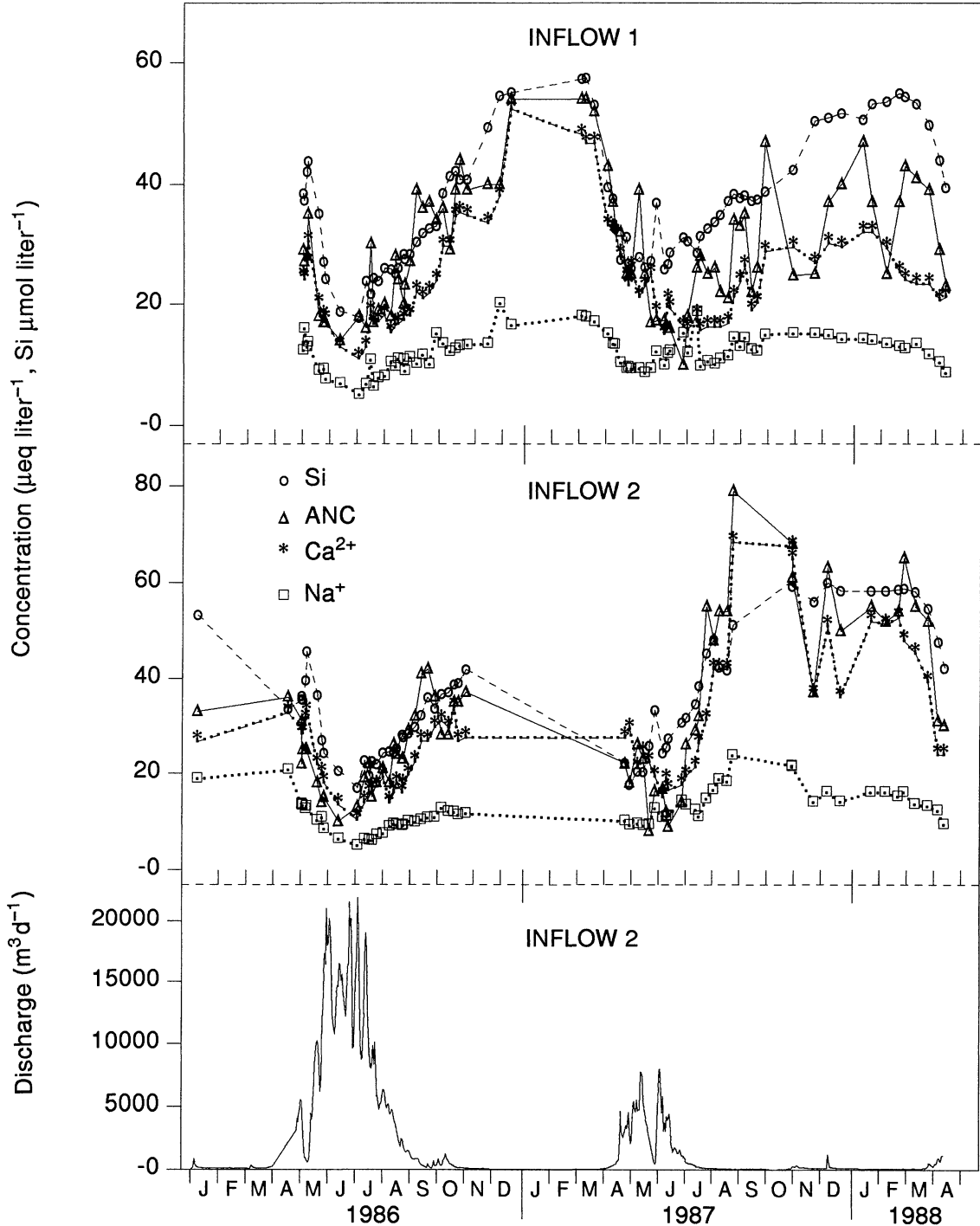


Fig. 3. Concentrations of Si, ANC, Ca^{2+} , and Na^+ in inflows 1 and 2, and discharge from inflow 2.

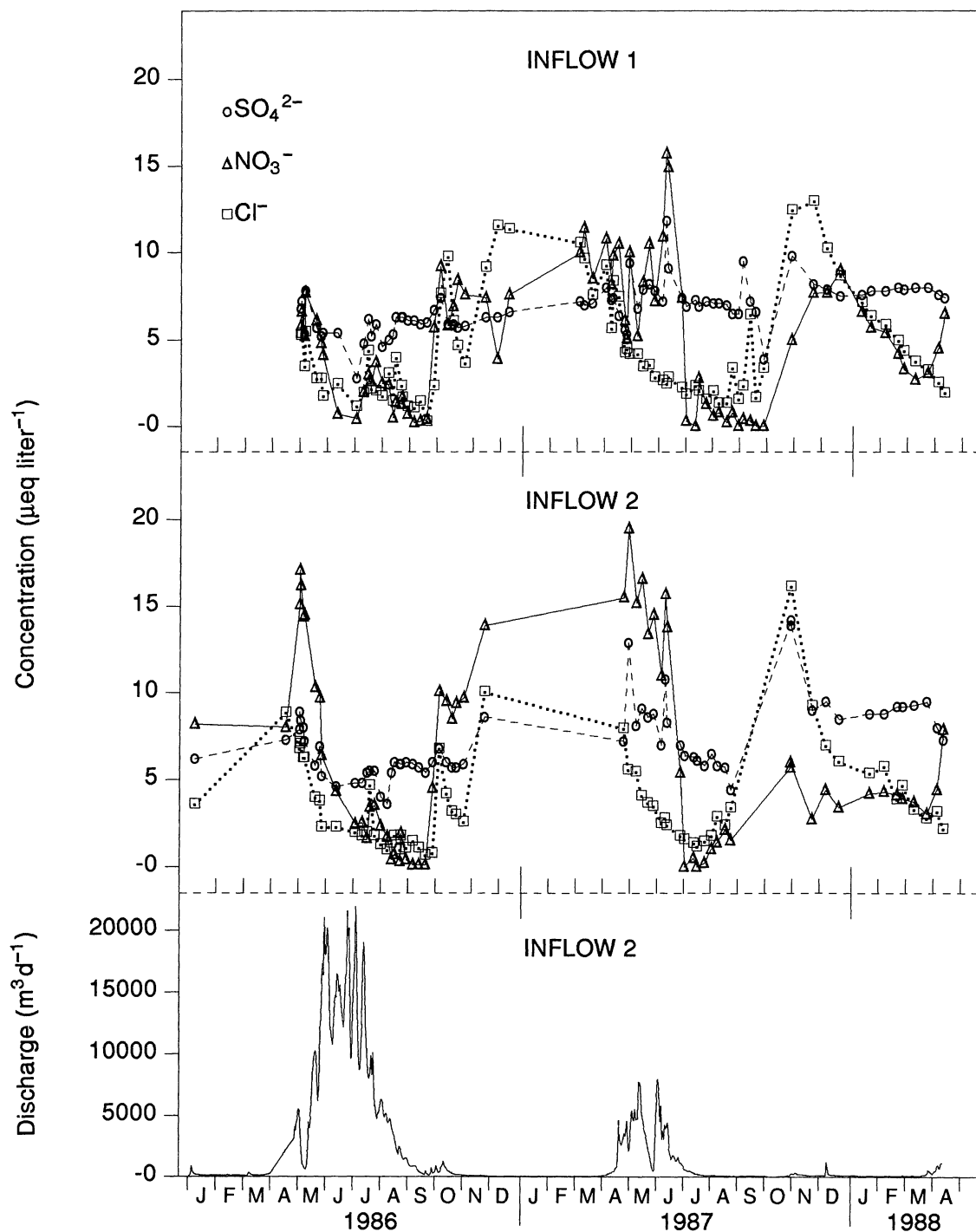


Fig. 4. As Fig. 3, but of concentrations of SO_4^{2-} , NO_3^- , and Cl^- .

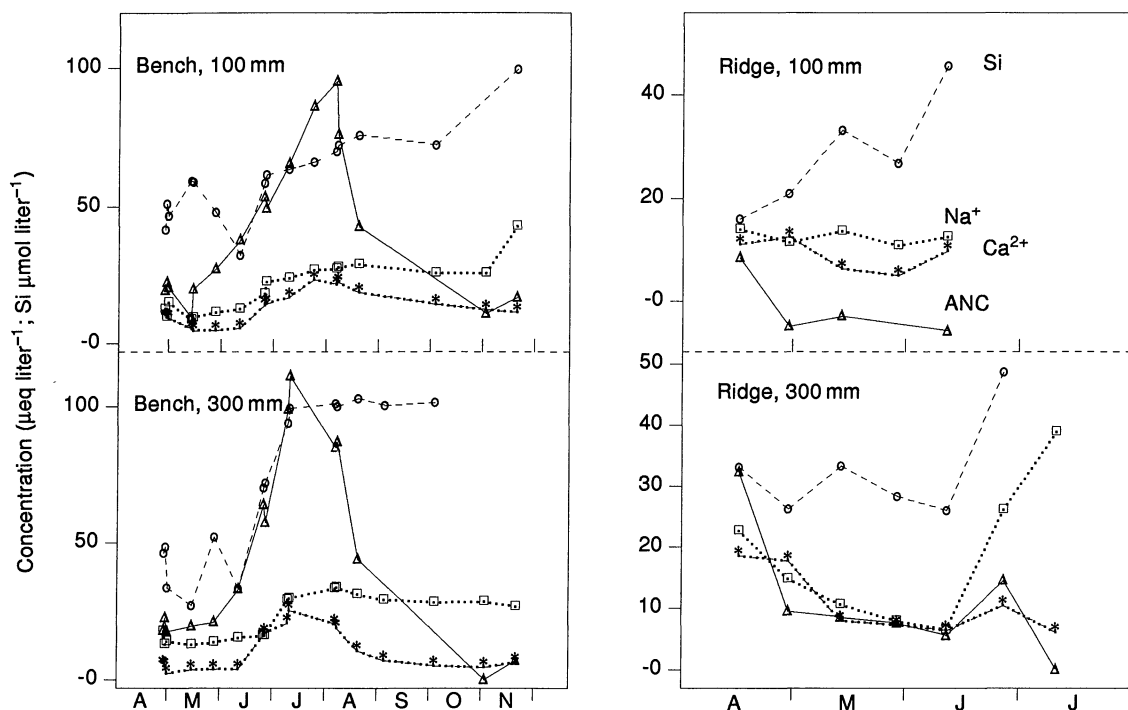


Fig. 5. Concentrations of Na^+ , Ca^{2+} , and ANC in the soil solution at the bench and ridge sites in 1987 at depths of 100 and 300 mm.

(1967) (Fig. 7). If plagioclase is the mineral that releases the most Na^+ and Ca^{2+} , then the molar ratio of $\text{Na} : \text{Ca}$ in stream and soil waters should be similar to that in plagioclase. Similarly, the ratio of $\text{HCO}_3^- : \text{Si}$ should be related to the feldspar composition and to the weathering products. Theoretical curves calculated from various ratios of $\text{Si} : \text{Al}$ in the decomposition products have been redrawn from Garrels (1967) and superimposed on the results from stream and soil samples. Stream and soil water samples from the ELW all plot within the kaolinite and gibbsite fields (Fig. 7). These results complement mineralogical analyses of soils, which showed that kaolinite and gibbsite are important constituents of soils in the ELW (Brown et al. unpubl.).

Mineral stability diagrams based on thermodynamic relationships also show that stream and soil water samples plot in the stability fields of kaolinite and gibbsite. Stability diagrams were plotted with the assumptions that the system was closed with respect to Al and that water temperature was 25°C . Thermodynamic data are from Drever (1982). Replotting the

figures with the actual stream temperatures made no appreciable difference. For the system $\text{Na-Al-Si-H}_2\text{O}$, activities of stream and soil water all plot near the boundary of the kaolinite and gibbsite stability fields (Fig. 7). There was little difference in position when stream water was divided into groups of high flow and low flow (Fig. 7). Stability diagrams plotted for $\text{Ca-Al-Si-H}_2\text{O}$ and $\text{K-Al-Si-H}_2\text{O}$ showed similar results.

The annual loading of solutes in stream waters to Emerald Lake were back-reacted with the appropriate weathering products to produce primary minerals for water years 1986 and 1987. First, all Mg^{2+} and enough Ca^{2+} , Na^+ , K^+ , HCO_3^- , and Si were back-reacted with kaolinite to form hornblende (Table 1). Hornblende was chosen because soil analyses show that hornblende at the ELW is depleted at depth compared to the surface (43% depletion compared to 18% by wt% of total heavy minerals, Weintraub 1986). The hornblende composition is from the ELW area of a detailed mineralogical and geochemical investigation of granitic rocks of the Sierra Nevada batholith

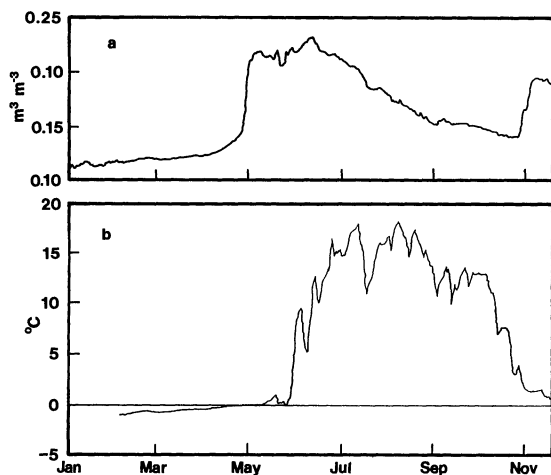


Fig. 6. Time series of soil moisture (a) and soil temperature (b) at the ridge site in 1987.

conducted by Dodge et al. (1968). Then all K^+ and a matching amount of HCO_3^- and Si were back-reacted with kaolinite to make K feldspar.

The solutes Na^+ , Ca^{2+} , HCO_3^- , and Si were then back-reacted with kaolinite to form An_{24} plagioclase. Stoichiometric weathering of plagioclase resulted in large residuals of Ca^{2+} —59% in 1986 and 66% in 1987 (Table 1). The residual of Ca^{2+} was then attributed to the weathering of anorthite (Table 1). The weathering of anorthite lead to a deficiency in HCO_3^- of 28% in 1986 and 22% in 1987. Weathering of kaolinite to gibbsite accounted for about a quarter of the Si in stream waters—28% in 1986 and 22% in 1987.

We next investigated whether concentrations of Ca^{2+} , Si, and HCO_3^- varied on a seasonal basis. The same scaling factor for wet deposition was applied to each stream. The largest amount of adjustment from wet deposition flux was during the period of snowpack runoff. For example, adjusted concentrations of Ca^{2+} in stream waters during snowpack runoff in 1987 were $\sim 8 \mu eq \text{ liter}^{-1}$ less than measured concentrations of Ca^{2+} . This procedure to adjust stream concentrations for inputs of wet deposition ignores spatial differences in the release of solutes from the snowpack (Williams and Melack 1989, 1991b). However, this method partially accounts for temporal differences in wet deposition and is an improvement over traditional methods,

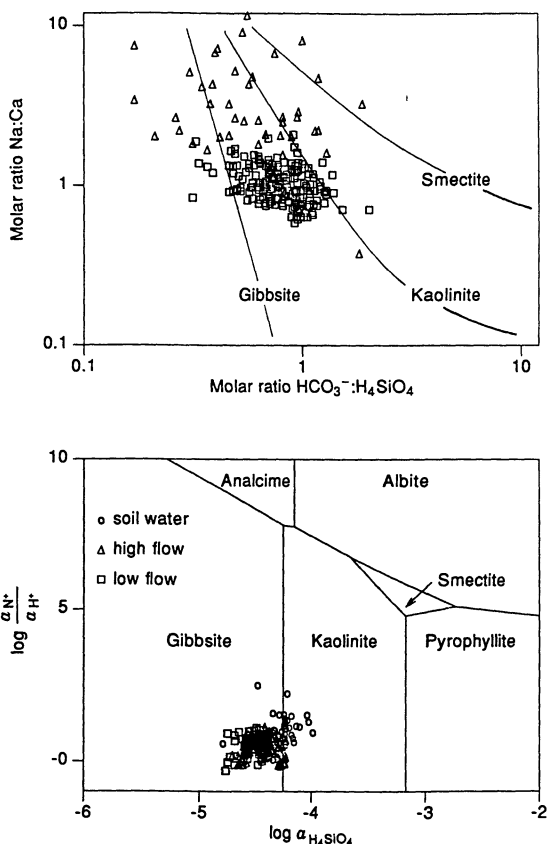


Fig. 7. Upper panel shows the molar ratio of $Na:Ca$ plotted against the molar ratio of $HCO_3^-:Si$ for stream (\square , $n = 199$) and soil (Δ , $n = 56$) waters of the Emerald Lake watershed. Theoretical curves from Garrels (1967) have been drawn for plagioclase weathering to smectite, kaolinite, and gibbsite. In the lower panel, activities of stream and soil water samples are plotted on a mineral stability diagram for the system $Na-Al-Si-H_2O$, at equilibrium and at $25^\circ C$ and 100 kPa pressure (from Drever 1982). Stream samples are further divided into periods of high and low flow.

such as subtracting the annual VWM ionic concentrations in wet deposition (e.g. Stoddard 1987). A quantitative analysis of errors is difficult to assign to this type of exercise. However, this procedure provides a qualitative assessment of the importance of temporal variations in weathering and geochemical processes in the basin. We addressed the issue of the spatial distribution of weathering products by using our weathering model on the solute content of stream water from three adjacent subbasins (inflows 1, 2, and 4); results were similar for each subbasin and for both 1986

Table 1. Source minerals for annual basin discharge (10^3 moles), 1986 and 1987.

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Si
Water Year 1986						
Annual basin export	21.95	4.07	21.95	4.34	50.84	65.43
Annual wet deposition	2.1	0.6	4.9	2.8	0.0	0.0
Mineral weathering prod.	19.85	3.47	17.05	1.54	50.84	65.43
subtract kaolinite to hornblende*	2.90	3.47	0.49	0.24	13.47	8.30
subtract kaolinite to K feldspar†	0.0	0.00	0.00	1.30	1.30	2.61
subtract kaolinite to plagioclase‡	5.24	0.00	16.56	0.00	27.02	33.12
subtract kaolinite to anorthite§	11.71	0.00	0.00	0.00	23.41	0.00
End result	0.00	0.00	0.00	0.00	-14.36	21.41
Water Year 1987						
Annual basin export	11.95	2.20	10.73	4.15	23.86	28.36
Annual wet deposition	3.30	1.10	4.10	1.2	0.0	0.0
Mineral weathering prod.	8.65	1.10	6.63	2.95	23.86	28.36
subtract kaolinite to hornblende	0.92	1.10	0.15	0.08	4.27	2.63
subtract kaolinite to K feldspar	0.0	0.00	0.00	2.87	2.87	5.75
subtract kaolinite to plagioclase	2.05	0.00	6.48	0.00	10.56	5.75
subtract kaolinite to anorthite	5.68	0.00	0.00	0.00	11.36	0.00
End result	0.00	0.00	0.00	0.00	-5.21	7.03

* Kaolinite to hornblende: $7\text{Al}_2\text{Si}_2\text{O}_5(\text{OH},\text{F},\text{Cl})_4 + 18.4\text{Ca}^{2+} + 22.0\text{Mg}^{2+} + 3.1\text{Na}^+ + 1.5\text{K}^+ + 85.4\text{HCO}_3^- + 52.0\text{Si} \rightarrow 10\text{Ca}_{1.84}\text{Mg}_{2.20}\text{Na}_{0.31}\text{K}_{0.15}\text{Al}_{1.56}\text{Si}_{16.76}(\text{OH},\text{F},\text{Cl})_{1.95} + 85.4\text{CO}_2 + 48.6\text{H}_2\text{O}$.

† Kaolinite to K feldspar: $7\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 14\text{K}^+ + 14\text{HCO}_3^- + 28\text{SiO}_2 \rightarrow 14\text{KAISi}_3\text{O}_8 + 14\text{CO}_2 + 21\text{H}_2\text{O}$.

‡ Kaolinite to plagioclase: $5\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6.1\text{Na}^+ + 1.9\text{Ca}^{2+} + 10\text{HCO}_3^- + 12.3\text{Si} \rightarrow 8.1\text{Na}_{0.76}\text{Ca}_{0.24}\text{Al}_{1.24}\text{Si}_{12.76}\text{O}_8 + 10\text{CO}_2 + 15\text{H}_2\text{O}$.

§ Kaolinite to anorthite: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 + 3\text{H}_2\text{O} + 2\text{CO}_2$.

and 1987. We restrict our presentation of results to inflow 2 from March 1987 to March 1988 in the interests of brevity and clarity.

The relative contributions of the calculated products of mineral weathering to the measured concentrations of Ca^{2+} in stream waters varied through the year. The maximum contribution of plagioclase weathering in the Ca^{2+} in stream waters was $\sim 70\%$ and occurred in late June and July as discharge decreased (Fig. 8). The contribution of plagioclase weathering to concentrations of Ca^{2+} in stream waters then declined to $\sim 25\%$ through autumn and into winter. During the period of spring runoff, the amount of plagioclase weathering decreased rapidly and, at minimum amounts, supplied $\sim 10\%$ of the measured Ca^{2+} . The contribution of anorthite weathering was inversely related to that of plagioclase weathering. Anorthite weathering contributed $\sim 20\%$ of measured Ca^{2+} in July; contributions of anorthite weathering then increased steadily to $\sim 60\%$ in autumn and winter. The stoichiometry shows a peak of anorthite weathering during the period of snowpack runoff, reaching an annual maximum of 80% at this time. About 10–20% of the Ca^{2+} in stream waters was from the weathering of hornblende. The seasonal differences

in the calculated contributions of plagioclase and anorthite weathering to measured Ca^{2+} in stream waters suggest that either hydrologic flow paths or the relative importance of differing biogeochemical processes change during the year.

The relative contributions of mineral weathering to the measured concentrations of Si in stream waters also varied through the year (Fig. 8). As with Ca^{2+} , the maximum contribution of plagioclase weathering to measured Si occurred in July. At this time, the weathering of plagioclase to kaolinite accounted for as much as 80% of Si measured in stream waters. Contributions of plagioclase weathering to measured Si then decreased with time. The weathering of kaolinite to gibbsite was inversely related to that of plagioclase weathering: highest during the winter period of snow cover over the basin and lowest in summer. The weathering stoichiometry shows a rapid increase and annual maximum in the weathering of kaolinite to gibbsite during the period of snowpack runoff. The kaolinite to K feldspar reaction accounted for only 5–10% of the silicate production at periods of low flow. However at periods of high flow in 1987, K feldspar accounted for as much as 80% of the silicate

production, based on back-reacting kaolinite with all the K^+ in stream water to form K feldspar. Note that during the period of snowpack runoff, these stoichiometric reactions yield $>100\%$ of the Si measured in stream waters. Sources of cations in addition to mineral weathering are indicated by both the high percentage of K feldspar weathering and the stoichiometric yield of $>100\%$ of measured Si. Back-reacting kaolinite to hornblende accounted for only a small fraction of the silicate in stream waters for any time of the year. As with Ca^{2+} , the seasonal differences in the calculated contributions of plagioclase and kaolinite weathering to measured Si in stream waters suggest that either hydrologic flow paths or biogeochemical processes change during the year.

Measured alkalinity was consistent with the products of mineral weathering during the period of low flow, but not during snowpack runoff or rain. The HCO_3^- concentrations calculated from the weathering of hornblende, K feldspar, plagioclase, and anorthite were subtracted from the measured HCO_3^- in stream samples. The resulting residual was then plotted as a time series (Fig. 8). If mineral weathering can account for the measured alkalinity, the residual for HCO_3^- should be $0 \pm 4 \mu\text{eq liter}^{-1}$ (indicated by dashed lines in Fig. 8). The HCO_3^- residual was near $0 \mu\text{eq liter}^{-1}$ in stream waters during summer and into winter. In contrast, there was a pronounced deficit of HCO_3^- during the period of snowpack runoff and again during the period of low flow that was coincident with rain. The temporal variations in the residual HCO_3^- indicate that geochemical controls and hydrologic flow paths change through the year.

Hydrologic flow paths—The mixing model indicates there was little difference in the pre-event and snowpack runoff contributions to stream flow in 1986 and 1987. The pre-event component of runoff for inflow 2 was calculated with values of $C_p = 58 \mu\text{mol liter}^{-1}$ and $C_e = 0 \mu\text{mol liter}^{-1}$. The C_p value is representative of Si concentrations in inflow 2 during the period of low flow (Fig. 3). At peak flow, in both 1986 and 1987, the mixing model calculated pre-event water to be $\sim 30\%$ of total flow (Fig. 9). Over the entire period of snowpack runoff for inflow 2, the mixing model

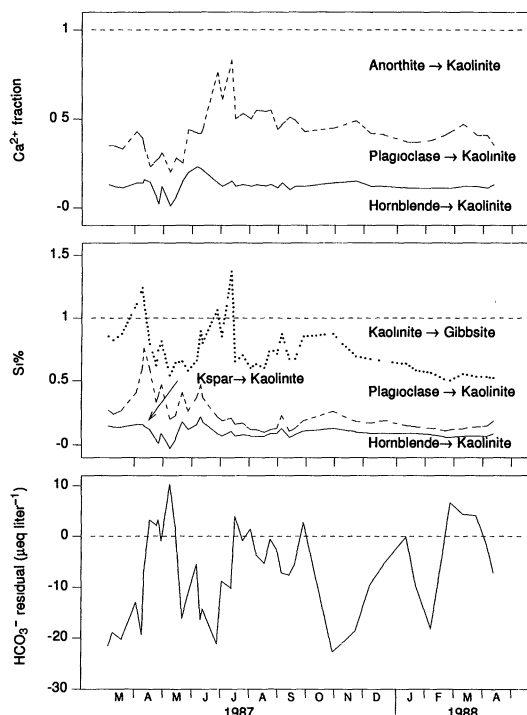


Fig. 8. Time series ($n = 44$) of the fraction of Ca^{2+} and Si produced by mineral weathering reactions and the HCO_3^- residual from mineral weathering for inflow 1. Dashed lines for Ca^{2+} and Si indicate a fraction of 1; dashed line for the HCO_3^- residual indicates a residual of $0 \pm 4 \mu\text{eq liter}^{-1}$, where $4 \mu\text{eq liter}^{-1}$ is the analytical error for HCO_3^- .

calculates that pre-event water contributed $\sim 41\%$ of total discharge in 1986 and 44% in 1987. Other inflows had similar values.

However, the assumption that a single value can represent pre-event water does not work at the ELW. We calculated the mean residence time of groundwater in the ELW for 1986 by dividing the volume of groundwater discharge (Q_{GW}) by the size of the groundwater reservoir (V_{GW}). Kattelman (1989) has calculated V_{GW} for the ELW as $120,000 \pm 60,000 \text{ m}^3$. For the period 10 April to 30 August 1986, the mixing model calculated that Q_{GW} supplied $\sim 1.124 \times 10^6 \text{ m}^3$ of the $2.284 \times 10^6 \text{ m}^3$ of the water discharged in the outflow. The groundwater reservoir was flushed from 6 to 19 times during this period, using the minimum ($60,000 \text{ m}^3$) and maximum ($180,000 \text{ m}^3$) values for V_{GW} . The mean hydrologic residence time for this period of 143 d was in the range of 7–23 d.

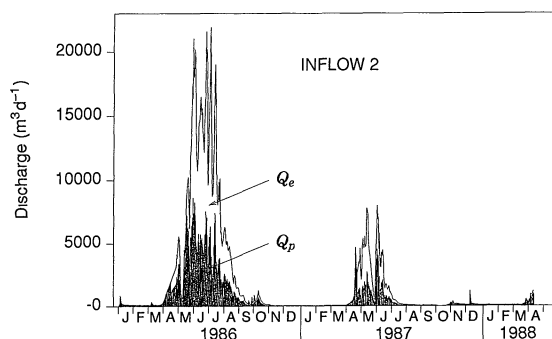


Fig. 9. Hydrograph separation of inflow 2 into contributions from pre-event water (Q_e) and snowpack runoff (Q_p).

Clearly, this flushing rate is incompatible with the assumption of the mixing model that measured Si in surface waters during snowpack runoff represents pre-event waters.

The tracer experiment with LiBr shows that the residence time of groundwater at maximum discharge in 1987 was ~ 12 h at this site. The Br^- tracer was first detected 9 h after injection and the last measurable amount was observed 10 h later (Fig. 10). The peak occurred 12 h after injection and ~ 1 h after discharge measured in inflow 4 reached its annual maximum. The well-defined temporal response curve for Br^- suggests that Br^- was conserved. In contrast, the results for $^6\text{Li}^+$ ion intensity and the $^6\text{Li}^+ : ^7\text{Li}^+$ both increased to a maximum which was temporally coincident with that of Br^- . However neither the ion intensity of $^6\text{Li}^+$ nor $^6\text{Li}^+ : ^7\text{Li}^+$ returned to within 1 SD of background levels at the end of the experiment. The temporal response of ^6Li suggests that this ion was not conserved.

The hydrologic residence time of water in soils and talus was estimated at hours to days during maximum snowpack runoff based on two additional methods. First, hydrologic residence time was estimated as the amount of free water in the basin divided by the amount of discharge from the basin. The calculated free-water capacity of soil and talus at the ELW was estimated at $\sim 48,000 \pm 13,000 \text{ m}^3$. Peak daily discharge from the basin was $36,000 \text{ m}^3$ in May 1986 and $\sim 17,000 \text{ m}^3$ in May 1987. Therefore, water storage in soils and talus could turn over almost daily in 1986 and every other day in 1987, assuming all snowpack runoff flowed through soils and talus. The second

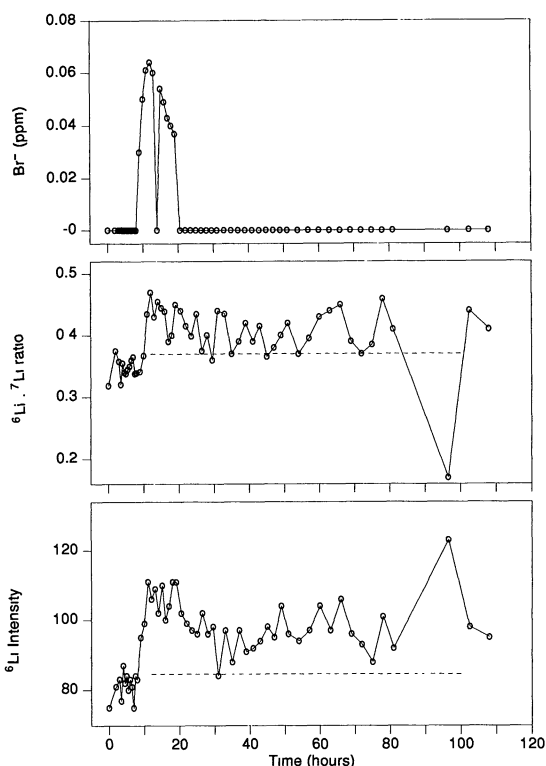


Fig. 10. Time series of Br^- concentrations, $^6\text{Li}^+ : ^7\text{Li}^+$ ratio, and ^6Li intensity from inflow 4 after a salt of $^6\text{LiBr}$ was applied to an ephemeral stream during the period of snowpack runoff in the recharge area of inflow 4. Dashed lines are the average background ion intensity ($^6\text{Li}^+$) or ratio ($^6\text{Li}^+ : ^7\text{Li}^+$) plus 1 SD.

method of determining hydrologic residence time was to calculate the saturated hydraulic conductivity (K_w) of each soil type in the ELW, then multiply K_w by soil depth. During spring runoff, soils are saturated (Fig. 6) and water movement through the soil can be described by K_w . Given average soil depths of 0.5–1 m in the basin and saturated conditions, water would pass through the soil profile in a matter of minutes to hours and then be available for surface runoff.

Two independent methods show that interactions between snowpack runoff and soils were an important determinant of the solute composition of surface waters during the period of snowpack runoff. First, rainfall with relatively high ionic concentrations percolated through the snowpack and into snowpack lysimeters with little change (Table 2). Ionic concentrations in meltwater were similar to concentra-

tions in rainfall and 10-fold or greater than bulk snowpack concentrations. Infiltration of meltwater into the soil solution is demonstrated by the concentrations of H^+ and NO_3^- , which were similar in meltwater and in the soil solution (Table 2). The much lower concentrations in the soil solution of SO_4^{2-} , NH_4^+ , and Ca^{2+} , relative to meltwater (Table 2), indicate that soil processes modified the composition of infiltrating water. All soil lysimeters showed a similar pattern of Ca^{2+} and SO_4^{2-} retention and NH_4^+ uptake; however the amount of biogeochemical modifications of infiltrating meltwater varied with depth and soil type. ANC of the soil solution was $<0 \mu\text{eq liter}^{-1}$ at this time (Fig. 5). The decrease in ANC $<0 \mu\text{eq liter}^{-1}$ can only be caused by acidification; dilution can result in ANC concentrations decreasing to $0 \mu\text{eq liter}^{-1}$ but not below it. Furthermore, an analysis of time-series data by Brown et al. (unpubl.) shows that this depression of ANC in soil water was correlated with NO_3^- concentrations in meltwater and not with concentrations of SO_4^{2-} in meltwater or DOC in soil water.

Second, the molar ratio of Na : Ca in the soil solution increased during the period of snowpack runoff. The Na : Ca molar ratio increased by 230% at depths of both 100 and 300 mm at the bench site during snowpack runoff (Fig. 11). The Na : Ca ratio at the bench site then decreased back to presnowmelt levels toward the end of snowpack runoff. The retention of Ca^{2+} by soil exchangers is consistent with the removal of Ca^{2+} from infiltrating meltwater (Table 2).

If cation exchange in soils had an effect on the solute composition of surface waters, the molar ratio of Na : Ca in stream waters should have increased during the period of snowpack runoff, provided that exchange in snowpack runoff for base cations on soil exchange sites was important at the scale of the basin and that discharge from soil reservoirs was an important component of stream flow. The molar ratio of Na : Ca in all three streams increased by a factor of 230% during the period of snowpack runoff (Fig. 11). The large increase in the Na : Ca ratio of stream waters during the period of snowpack runoff was comparable to that in soil reservoirs and indicates that cation exchange was important at the scale of the basin. The ratio of Na : Ca then decreased back

Table 2. Concentrations of selected ions in rainfall, snowpack, meltwater, and soil water ($\mu\text{eq liter}^{-1}$), 27 May 1987. Snowpack and meltwater samples are from the cirque site; soil water samples are from the ridge site, at a depth of 100 mm.

	H^+	Ca^{2+}	NH_4^+	NO_3^-	SO_4^{2-}
Rainfall	9.1	23.5	133.1	95.5	74.1
Snowpack	2.3	0.7	7.3	4.5	2.8
Meltwater	12.9	31.1	66.4	72.9	71.6
Soil water	9.4	2.6	12.5	71.7	6.1

to presnowmelt levels, as did the Na : Ca ratio in the soil solution. During autumn the Na : Ca ratio in soils and stream became progressively out of phase. The Na : Ca ratio at this time reached an annual maximum in the soil solution and an annual minimum in stream waters (Fig. 11). Discharge from soil reservoirs does not appear to be an important source of stream flow during autumn and winter months.

Discussion

Mineral weathering—One reason our stoichiometric mass balance may not have worked as well as that of Garrels and Mackenzie (1967) for spring waters of the Sierra Nevada is that the wrong weathering reactions were used. A plausible weathering reaction at the ELW is the weathering of biotite to hydroxy-interlayered vermiculite, and then further weathering of vermiculite to kaolinite. However, a stoichiometric mass balance using these reactions produced a much greater deficit of HCO_3^- and a greater proportion of kaolinite weathering to gibbsite. Furthermore, Clow (1987) reported that waters of the ELW are undersaturated with respect to vermiculite.

Our results suggest that processes other than the stoichiometric weathering of plagioclase contribute to the solute composition of stream waters in the Sierra Nevada on both an annual basis and on the basis of individual stream samples. The stoichiometric excess of Si and Ca^{2+} indicates that mineral weathering of plagioclase was not sufficient to account for the Si and Ca^{2+} in surface waters. The stoichiometric deficit of HCO_3^- indicates that there must be sources of alkalinity in addition to mineral weathering.

Other investigators have also reported a stoichiometric excess of Ca^{2+} and Si in stream waters of the Sierra Nevada. Stoddard (1987)

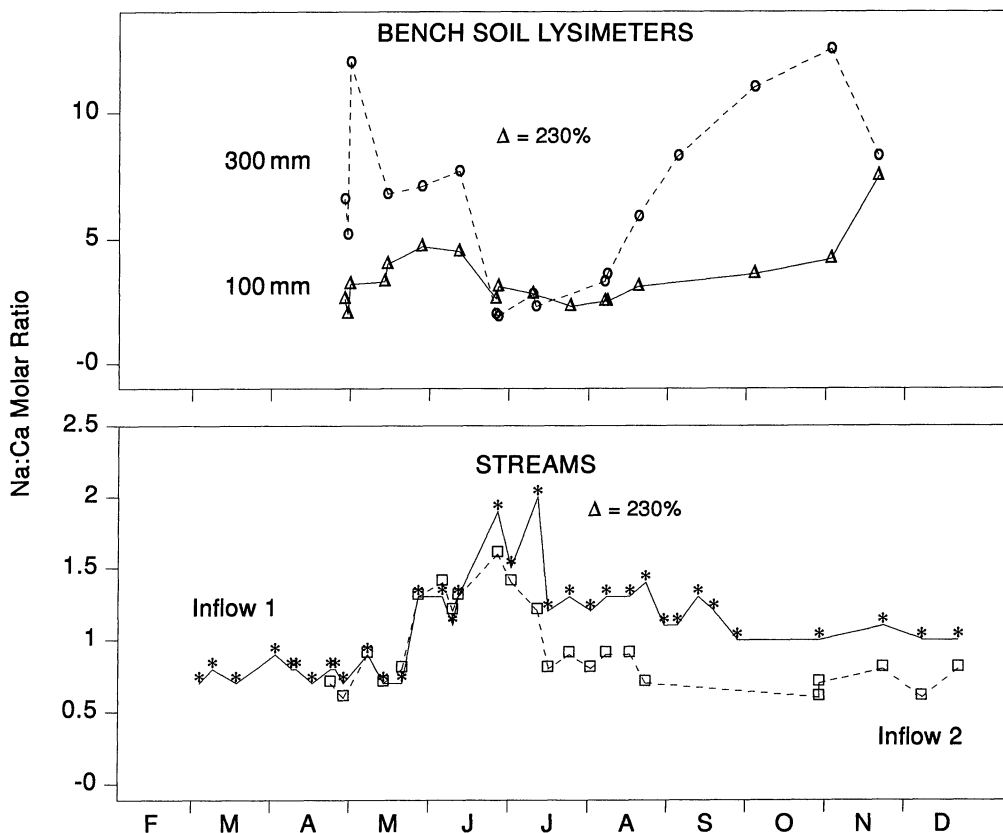


Fig. 11. Time series from 1987 of the molar ratios of Na:Ca from soil lysimeters at the bench site and for inflows 1 and 2.

applied a similar weathering model to surface waters of the Gem Lake basin (3,595 m) in the eastern Sierra Nevada. He reported that this approach worked very well with water collected during low-flow periods, with less-satisfying results during periods of high flow. Water collected during snowpack runoff at Gem Lake resulted in a Ca^{2+} excess of 41%, similar to our results for annual values. Brown and Lund (1988) reported that the stoichiometry of waters entering Eastern Brook Lake (3,155 m), also in the eastern Sierra Nevada, was also not in agreement with the Garrels and Mackenzie (1967) model due to an excess of Ca^{2+} . Clow (1987) has studied mineral weathering in the ELW. He reported good agreement between ephemeral spring water collected in August 1985 and a weathering stoichiometry similar to the one we used. However, for stream water he too reported an excess of Ca^{2+} and Si at the ELW.

Preferential weathering of the anorthite

component of plagioclase may be one source of Ca^{2+} . Headden (1903) first suggested the differential release of Ca^{2+} after reacting alkali feldspars with water rich in CO_2 and finding a low Na:Ca ratio in the solution. The preferential loss of Ca^{2+} from felsic rock follows the classical reactivity series proposed by Goldich (1938): $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. Clayton (1988) reported evidence for the preferential weathering of anorthite for three watersheds in Idaho. The basins he studied had bedrock similar to the ELW, with an An_{19} plagioclase. He was able to account for all Si in annual stream flow by back-reacting kaolinite with orthoclase and an An_{46} plagioclase. Furthermore, Clayton (1986) observed that plagioclase feldspars in the Idaho batholith are commonly zoned and the more calcic core is often preferentially weathered, leading to an enrichment of Na^+ relative to Ca^{2+} in the C horizons of soil compared to rock samples.

Preferential weathering of anorthite was in-

vestigated for stream waters of the ELW. First, all of the Mg^{2+} and K^+ in annual stream loading was back-reacted with kaolinite to form hornblende and K feldspar. Next, the remaining Na^+ and Ca^{2+} in annual stream flux was attributed to end-member weathering of plagioclase. Last, the resulting proportions of albite and anorthite were combined to form a composite plagioclase. The calculated plagioclase composition, from the annual stream fluxes of Na^+ and Ca^{2+} , was An_{54} in 1986 and An_{50} in 1987. This similarity in calculated plagioclase composition, from two years with very different hydrologic and deposition fluxes, is a strong indicator that preferential weathering of anorthite was an important source of Ca^{2+} in stream waters of the ELW.

Weathering of calcite (CaCO_3) is a possible source of the stoichiometric excess of Ca^{2+} . Garrels and Mackenzie (1967) invoked such a mechanism to attain stoichiometric congruency in deeper circulating water of the Sierra Nevada. Preferential weathering of calcite, which was found only in trace amounts was shown by Drever and Hurcomb (1986) to account for the majority of Ca^{2+} and ANC in stream waters of an alpine basin in the North Cascade Mountains that was underlain by igneous and high-grade metamorphic rock. Mast et al. (1990) presented evidence that preferential weathering of calcite was the major source of Ca^{2+} and ANC at the Loch Vale watershed in Colorado. If weathering of calcite was the primary source of Ca^{2+} at the ELW, two criteria as set forth by Drever and Hurcomb (1986) must be met. First, ANC must be present to balance the concentrations of Ca^{2+} ; second, the Si to Ca^{2+} ratio must be much lower than that in plagioclase. The first criterion was not met at the ELW, as there was often an overabundance of Ca^{2+} in stream samples with respect to ANC (Fig. 8 and Table 1). The second criterion was also not met. The molar ratio of Si : Ca in annual stream flux was 3.29 in 1986 and 3.27 in 1987. The annual molar ratio of Si : Ca is lower than the ratio of 6.3 from stoichiometric weathering of plagioclase weathering, but still much higher than the expected ratio of <1.0 from preferential weathering of CaCO_3 (Mast et al. 1990). Furthermore, mineralogical investigations to date at the ELW have failed to find calcite crystals in rock fractures (D. Clow pers. comm.). Therefore we are led to conclude that differ-

ential weathering of calcite was not a significant source of Ca^{2+} in surface waters at the ELW. Additional mineralogical work to investigate the presence or absence of plagioclase zoning and calcite crystals would provide insight to this problem.

Silicate concentrations in stream waters of the ELW undergo an annual cycle that is inconsistent with stoichiometric weathering of plagioclase. During the period of low flow, kaolinite appears to undergo further weathering to gibbsite, yielding additional silicic acid but no base cations (Fig. 8). The kaolinite to gibbsite reaction appears to be saturated on an Si concentration of $\sim 60 \mu\text{mol liter}^{-1}$; maximum concentrations of Si in stream waters during the period of low flow were $\sim 60 \mu\text{mol liter}^{-1}$ for all streams from January 1986 to March 1988 (Fig. 3). Stauffer (1990) has shown that the predicted equilibrium Si concentration is $\sim 59 \mu\text{mol liter}^{-1}$ at 25°C for kaolinite weathering to gibbsite, depending on the crystalline state of equilibrium $\text{Al}(\text{OH})_3$ and the source of the free energy data used for the computation. The consistency of maximum concentrations of Si at $\sim 60 \mu\text{mol liter}^{-1}$ suggests that stream waters in the ELW are in steady state with weathering products during the period of low flow.

During the period of snowpack runoff, the release of silicic acid from clay minerals and (or) the dissolution of amorphous phases may explain the high proportion of weathering from kaolinite to gibbsite that is indicated by our weathering stoichiometry (Fig. 8). The insensitivity of Si concentrations to changes in discharge is well documented (Cleaves et al. 1970; Edwards and Liss 1973) but not thoroughly understood (Kennedy 1971). Dissolution of silica minerals is unlikely to be sufficiently rapid to account for the relative constancy of measured Si concentrations during individual storm events. At the ELW, the hydrologic residence time of water during snowpack runoff is on the order of hours to days. Mineral weathering of silica is commonly on the order of months to years (Schnoor and Stumm 1986) and is not sufficiently rapid to account for the high proportion of kaolinite to gibbsite weathering during snowpack runoff indicated by our stoichiometric weathering model (Fig. 8). Therefore, the Si content of stream waters does not appear to be in equilibrium with weathering products of granitic rocks during this pe-

riod. Dissolution of solid phases, biological activity, and especially sorption reactions may be important regulators of Si concentrations (Gaudet and Melack 1981). For example, precipitation and weathering of imogolite and proto-imogolite may be an important source and sink for Si in the ELW (e.g. Ugolini and Dahlgren 1991). Imogolite was not detected by X-ray diffraction; however it is a difficult mineral to detect without a scanning electron microscope.

Mineral weathering does not appear to be the primary process neutralizing the acidity in snowpack runoff. Williams and Melack (1991*b*) reported that 80–90% of the H^+ in snowpack runoff and >99% of the NH_4^+ was consumed before reaching Emerald Lake. Neutralization of these acidic cations seems to be the result of processes with kinetic rates that are rapid relative to silicate weathering. Uptake and retention of a portion of the NO_3^- in meltwater appears to be one source of alkalinity (Williams and Melack 1991*b*). SO_4^{2-} adsorption in soils accounts for some or all of the SO_4^{2-} removal from infiltrating meltwater (Williams *et al.* 1991).

Cation exchange appears to be the major process neutralizing acidity in snowpack runoff. Kinetic rates are consistent with exchange reactions buffering the acidity in snowpack runoff and are not compatible with the reaction times for silicate weathering. The time to completion of exchange reactions is generally on the order of seconds to minutes (Sparks 1989), vs. months to years for silicate weathering. The relatively rapid reaction rates of cation exchange are compatible with a residence time of water in subsurface reservoirs during snowpack runoff of hours to days.

Several additional results also indicate that cation exchange and not mineral weathering was the primary source of buffering for snowpack runoff. The increase of 230% in the molar ratio of Na:Ca in soil and stream waters during snowpack runoff is consistent with soil exchangers replacing the H^+ in infiltrating meltwater with Na^+ . Cation exchange can also explain the stoichiometric excess of Si during the period of snowpack runoff in 1987 (Fig. 8). Replacement of the H^+ in infiltrating meltwater with base cations would result in more base cations in stream waters than are produced by mineral weathering. When base cations were

used to reconstruct the sources of Si measured in stream waters, >100% of the Si measured was produced by the model. Furthermore, mobilization of K^+ by cation exchange may be one explanation for the large percentage of K feldspar weathering indicated by our weathering model during snowpack runoff in 1987. Moreover, cation exchange appears to be important in talus and glacial till. The nonconservative behavior of Li^+ with respect to Br^- in the LiBr tracer experiment is consistent with retention and release of Li^+ by cation exchange (Fig. 10). The selectivity coefficient of Li^+ is generally comparable to that of Na^+ (Bohn *et al.* 1979). Retention and release of Li^+ by soil exchangers may be the reason that Li^+ concentrations varied over time (Fig. 10) and did not return to background levels by the end of the experiment.

The relative importance of mineral weathering and cation exchange as sources of alkalinity can be evaluated by comparing modeled alkalinity to measured alkalinity. Samples from the soil solution showed that acidification occurred at the ridge site during snowpack runoff (Table 2). Acidification from strong acid anions at the basin scale has been evaluated by Almer *et al.* (1978), Henriksen (1980), and others in surface waters of Scandinavia by comparing measured alkalinity to the sum of Ca^{2+} and Mg^{2+} . Their rationale was based on the reasoning that hydrolysis reactions describing the stoichiometric weathering of granitic materials yield HCO_3^- in equal proportion to the sum of base cations liberated ($C_b = Ca^{2+} + Mg^{2+} + Na^+ + K^+$, as equivalents), and that the sum of Ca^{2+} plus Mg^{2+} was much greater than the sum of Na^+ plus K^+ . We investigated the presence of acidification at the ELW by a variation of this procedure that is suitable for the dilute waters typical of the Sierra Nevada. We used the sum of base cations, rather than the sum of Ca^{2+} and Mg^{2+} . We then adjusted C_b for wet deposition flux by the same procedure as for the stoichiometric mass balance. The ratio of adjusted C_b to HCO_3^- should yield a slope of 1 if no acidification has occurred or if mineral weathering has neutralized the acidity. Acidification will cause the ratio of adjusted C_b to measured HCO_3^- to be >1, due to either a decrease in HCO_3^- through titration or an increase in C_b as a result of cation leaching. Dilution will not cause the slope to change,

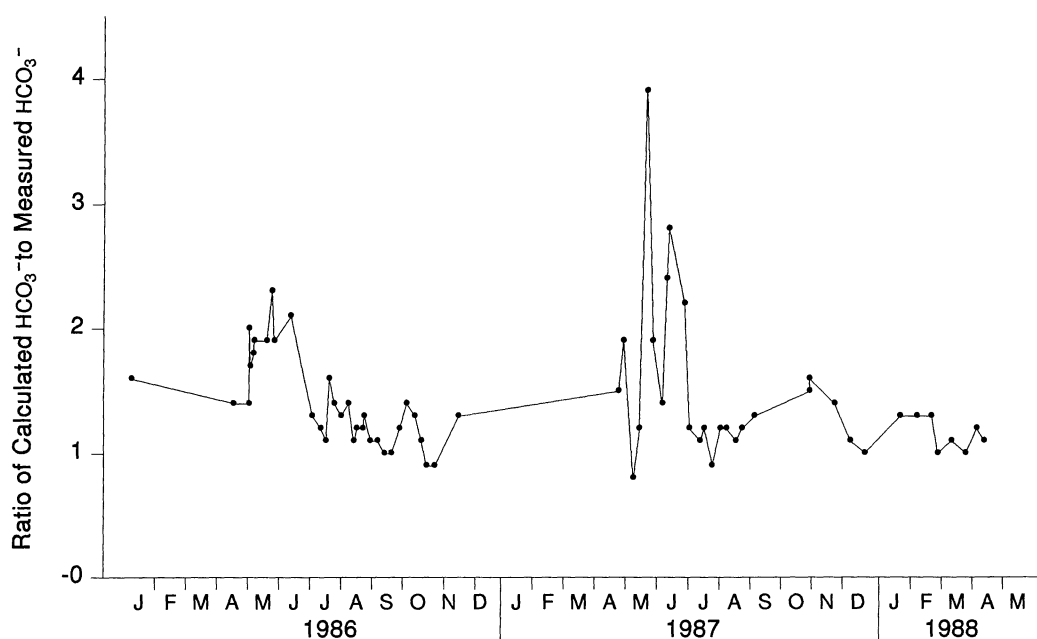


Fig. 12. Ratio of calculated to measured HCO_3^- for inflow 2 plotted as a time series. Calculated HCO_3^- is the sum of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , in equivalent units, after correction for atmospheric deposition.

since all solutes are diluted by equal amounts after adjusting for inputs of wet deposition.

A time series of the ratio of calculated to measured HCO_3^- shows an annual maximum during snowpack runoff of this ratio of 2–3.5 and an annual minimum during the low-flow period of ~ 1.0 (Fig. 12). The 2–3-fold increase in the ratio of calculated to measured HCO_3^- strongly indicates that episodic acidification occurred during the period of snowpack runoff. Furthermore, the higher peak in 1987 compared to 1986 is consistent with increased cation leaching from acidic rain-on-snow events that occurred in 1987 but not in 1986. The ratio was further analyzed by separating stream samples into periods of high and low flow. For each period, calculated alkalinity was then regressed on measured alkalinity. At periods of low flow, $C_b = 3.4 + 1.11 \text{ HCO}_3^-$, with an r^2 of 0.76 ($n = 149$). The y -intercept of 3.4 and slope of 1.11 at low flow were not significantly different from a y -intercept of 0 and a slope of 1 at the 98% confidence level. At periods of high flow, $C_b = 21.8 + 0.56 \text{ HCO}_3^-$, with an r^2 of 0.21 ($n = 49$). The y -intercept of 21.8 was significantly different from 0 and the slope of 0.56 was significantly different from 1 at the 98% confidence level.

The ratio of calculated to measured HCO_3^- shows that episodic acidification does occur at the ELW during snowpack runoff. These results are consistent with those of Melack et al. (1988) and Williams and Melack (1991b), who reported that episodic acidification of streams at the ELW is from the strong acid anions stored and released from the seasonal snowpack. Furthermore, episodic acidification is consistent with decreases in ANC to $<0 \mu\text{eq liter}^{-1}$ measured in the soil solution at the ridge (Fig. 5). In contrast, the same ratio shows that mineral weathering was the source of alkalinity during the period of low flow from about July to the following March.

Hydrologic flow paths—Knowledge of the hydrologic pathways of rain and snowpack runoff is essential to determine the hydrochemical response of stream waters to wet deposition. Previous work on hydrographic separation has shown that much of stream flow is composed of pre-event or baseflow rather than rain or snowpack runoff (e.g. Bottomley et al. 1984/1985, 1986; Hooper and Shoemaker 1986). However, much of this research on hydrographic separation of stream waters has been conducted in forested sites in eastern North America, which generally have large de-

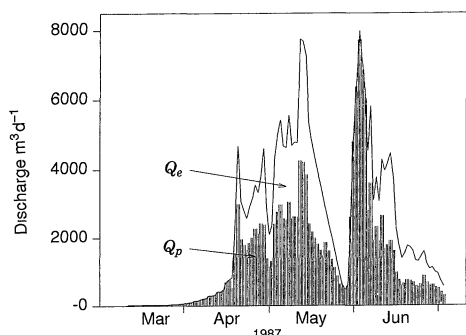


Fig. 13. Hydrograph separation of inflow 2 into contributions from soil discharge (Q_p) and surface runoff (Q_e).

posits of glacial till and relatively large water storage capacity compared to high-elevation basins in the western U.S.

Little is known on hydrologic pathways in alpine areas of western North America. In general, stream and lake waters in alpine basins in western North America have been considered to be a mixture of groundwater and relatively dilute snowpack runoff (Miller and Drever 1977; Loranger and Brakke 1988). Infiltration of meltwater into soil and groundwater reservoirs and the resulting biogeochemical interactions in alpine basins have generally been ignored (e.g. Drever and Hurcomb 1986). Pre-event water at the ELW contributes only a small fraction of stream flow during the period of snowpack runoff. The use of a single C_p for hydrograph separation of stream flow during runoff generally underestimates the contribution of groundwater to stream flow in basins with small groundwater reservoirs (Wels *et al.* 1990). Our results suggest that much snowpack runoff in the ELW infiltrates soils and unconsolidated materials, undergoes reactions with soil water and soil exchangers, and then is discharged to stream flow.

We re-evaluated the contribution of subsurface water to stream flow by allowing C_p to vary over time, the "piecewise linear" method of hydrographic flow separation developed by Hooper and Shoemaker (1986). We made the assumption that the Si content of the soil solution and groundwater were the same (e.g. Wels *et al.* 1990). The concentrations of Si used for C_p were calculated by averaging all Si measurements in the soil solution (Fig. 5) for a particular day; this value of C_p was used in the mixing model until the next date of Si measurements in the soil solution. The time-frame

represented by Si measurements of the soil water component of the hydrograph was therefore shortened from seasonal to daily. One confounding factor is that our previous analysis of Si has shown that it does not act conservatively in the ELW. What effect the apparent nonconservative behavior of Si has on the mixing model is impossible to quantify.

The hydrograph for snowmelt runoff in 1987 shows two melt episodes, one starting in mid-April and the second starting in early June (Fig. 13). Our new hydrograph shows that subsurface discharge in 1987 accounted for ~62% of total flow in inflow 2; surface runoff accounted for ~38% of flow. Subsurface contributions to stream flow were near 100% at the beginning of each melt episode. The contributions of subsurface water to stream waters then decreased and the relative contributions of surface runoff to stream flow increased. Much of the subsurface contribution to stream flow was new water that had infiltrated into subsurface reservoirs. Caine (1989) reported similar results for an alpine basin in Colorado; up to 50% of snowpack runoff was routed through surficial deposits in the Martinelli catchment of the Green Lakes Valley.

These results combined with our previous analysis suggest that the first fraction of snowpack meltwater during a melt episode infiltrates soils and talus. Soils and talus then become saturated and discharge water to streams as saturated overland flow. The volume of snowpack runoff then exceeds the infiltration capacity of soils and an increasingly larger percentage of snowpack runoff flows toward streams as Hortonian overland flow. The congruency between changes in the Na:Ca molar ratio of soils and stream water is consistent with return flow from soils supplying much of stream discharge. The location of zones of higher water capacity along stream channels (Fig. 2) also suggests that much snowpack runoff finds its way into soil and talus before becoming stream flow. Maule and Stein (1990) reported that snowpack meltwater infiltrating into and traveling through soils supplied a large percentage of stream flow in the Lac Laflamme watershed of Quebec, Canada. They too reported that soil water contributions to stream flow were high at the beginning of melt episodes and decreased with time. Processes with rapid kinetics that occur in subsurface reservoirs may therefore be the primary controls

on the composition of surface waters in alpine basins during the period of snowpack runoff.

The primary source of stream flow following the period of snowpack runoff may be return flow from soil reservoirs. All snowpack melt-water at this time infiltrates soils and talus and gains the chemical signature of soil water within several meters of melting snowpacks (Clow 1987). Both the Na:Ca ratio (Fig. 11) and Si content of soils (Fig. 5) were similar to that in stream waters (Fig. 3) during summer. Furthermore, levels of soil moisture at this time began to decrease (Fig. 6), indicating that the soil column was losing water. The composition of stream flow at this time was congruent with the stoichiometry of plagioclase weathering (Fig. 8). The congruency of stream waters with the stoichiometry of plagioclase weathering suggests that the H^+ retained in the soil column from exchange reactions resulted in more intense mineral weathering.

Geochemical controls on the composition of stream waters during the period of low flow from autumn through the following winter were by processes occurring below the soil zone. Three measurements indicate that the soil solution lost hydrologic contact with stream flow at this time. The molar ratio of Na:Ca at this time reached an annual maximum in soils but an annual minimum in stream flow (Fig. 11). Second, concentrations of Si in soils ($\sim 100 \mu\text{mol liter}^{-1}$, Fig. 5) were much higher than in stream waters ($\sim 60 \mu\text{mol liter}^{-1}$, Fig. 3). Last, levels of soil moisture became too low to measure, because of either low water content or freezing of water (Fig. 6). Stream waters at this time were in stoichiometric equilibrium with mineral weathering products (Fig. 12). Kaolinite appeared to undergo further weathering to gibbsite until stream waters were saturated with Si at a concentration of $\sim 60 \mu\text{mol liter}^{-1}$. Alkalinity in surface waters was produced from mineral weathering. Preferential weathering of the anorthite component of plagioclase occurred in subsurface rock at this time; stoichiometric weathering of plagioclase contributed only a small portion of the Ca^{2+} and Si in stream waters (Fig. 8).

Conclusions

Mineral weathering and wet deposition were the primary sources of solutes in stream flow on an annual basis. However, our weathering model shows that these sources accounted for

only 75% of the annual alkalinity in stream flow. The excess alkalinity can be accounted for when nitrogen reactions and losses of NH_4^+ and NO_3^- are considered. Here we assume that each mole of NH_4^+ retained in the basin is converted to NO_3^- plus 2 moles of H^+ and that each mole of NO_3^- retained in the basin is converted to organic nitrogen plus 1 mole of OH^- . There is a final residual in estimated alkalinity of 1,745 moles fewer than measured alkalinity in stream flow or $\sim 2\%$ of the estimated alkalinity produced from weathering for the two study years. Our weathering analysis also shows that preferential weathering of the anorthite component of plagioclase accounted for $\sim 60\%$ of the annual export of Ca^{2+} from the basin in stream waters. The large excess of Si after accounting for weathering processes of granitic bedrock is consistent with results from other alpine basins underlain by crystalline bedrock (e.g. Mast et al. 1990) and underscores the need to improve our understanding of the sources and sinks of Si in granitic basins. Additional research on the weathering reactions and mineralogical content of the ELW would provide additional insight into geochemical controls of surface waters, particularly the potential importance of calcite and imogolite weathering.

A combination of changes in hydrologic routing, relative contributions of water from different hydrologic reservoirs, and residence time within these reservoirs caused temporal variations in the geochemical controls on the solute composition of surface waters. Stoichiometric weathering products of surface waters at the ELW were not consistent over time and can be divided into three distinct periods: snowpack runoff, a transition period during summer as snowpack runoff decreases and little precipitation occurs, and a low-flow period from late summer through winter. Each period was characterized by different geochemical controls on the solute composition of surface waters.

About half of snowpack runoff became stream flow as Hortonian overland flow and the other half infiltrated soils and talus before becoming stream flow after discharge from subsurface reservoirs. Applied tracers and two additional measurements show that hydrologic residence time in subsurface reservoirs was on the order of hours to days during snowpack runoff. Stream waters were not in chemical

equilibrium or steady state with the products of mineral weathering at this time. Soil processes with relatively fast kinetics, particularly cation exchange, modified the composition of infiltrating snowpack meltwater. Three independent analyses all indicate that cation exchange occurred during snowpack runoff. First, a tracer experiment conducted with LiBr demonstrated that snowpack runoff infiltrated unconsolidated materials, underwent interactions with the soil solution and soil exchangers, and that discharge from the soils and talus then contributed to stream flow. Second, the increase in the molar ratio of Na : Ca in both soil water and stream waters was consistent with the selectivity coefficients of soil exchangers. Third, modeled vs. measured concentrations of HCO_3^- indicate that during the period of snowpack runoff more cations were present than were produced by mineral weathering.

Discharge from soil reservoirs appears to be the primary source of stream flow during the summer transition period. Hydrologic residence time of water in soils is on the order of months and mineral weathering reactions seem to reach completion. No overland flow reaches stream channels during this time period and surface water collected only tens of meters below melting snowfields has the chemical signature of soil water (Clow 1987). Baseflow supplies an unknown but increasingly important amount of stream flow at this time.

Processes below the soil zone exerted the dominant geochemical controls on the composition of stream waters during the period of low flow. Soils during this period lost hydrologic contact with stream flow. The residence time of water discharged from groundwater reservoirs during the period of low flow is on the order of months to years (Kattelmann 1989). Mineral weathering processes reach completion and renew the base cations lost from the basin by exchange reactions.

The ELW and other granitic basins in the Sierra Nevada are sensitive to possible increases in acid deposition from the atmosphere. Episodic acidification occurs at present deposition levels. Furthermore, the susceptibility of catchments to acidification increases as the hydrologic residence time decreases during snowpack runoff (Bottomley et al. 1986; Wels et al. 1990). Water held in storage before snowpack runoff provides only a small fraction of stream

flow during runoff, in contrast to montane areas of eastern North America. At the ELW, the hydrologic residence time of hours to days during snowpack runoff increases the potential for acidification from atmospheric deposition. Incoming acidity is neutralized primarily by cation exchange; weathering of silicate minerals supplies alkalinity to the basin on an annual basis.

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