Geochemistry and Source Waters of Rock Glacier Outflow, Colorado Front Range

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ABSTRACT

We characterize the seasonal variation in the geochemical and isotopic content of the outflow of the Green Lake 5 rock glacier (RG5), located in the Green Lakes Valley of the Colorado Front Range, USA. Between June and August, the geochemical content of rock glacier outflow does not appear to differ substantially from that of other surface waters in the Green Lakes Valley. Thus, for this alpine ecosystem at this time of year there does not appear to be large differences in water quality among rock glacier outflow, glacier and blockslope discharge, and discharge from small alpine catchments. However, in September concentrations of Mg^{2+} in the outflow of the rock glacier increased to more than $900\,\mu eq\,L^{-1}$ compared to values of less than $40\,\mu eq\,L^{-1}$ at all the other sites, concentrations of Ca^{2+} were greater than $4,000\,\mu eq\,L^{-1}$ compared to maximum values of less than $200\,\mu eq\,L^{-1}$ at all other sites, and concentrations of SO_4^{2-} reached $7,000\,\mu eq\,L^{-1}$, compared to maximum concentrations below $120\,\mu eq\,L^{-1}$ at the other sites. Inverse geochemical modelling suggests that dissolution of pyrite, epidote, chlorite and minor calcite as well as the precipitation of silica and goethite best explain these elevated concentrations of solutes in the outflow of the rock glacier. Three component hydrograph separation using end–member mixing analysis shows that melted snow comprised an average of 30% of RG5 outflow, soil water 32%, and base flow 38%. Snow was the dominant source water in June, soil water was the dominant water source in July, and base flow was the dominant source in September. Enrichment of $\delta^{18}O$ from $-10‰$ in the outflow of the rock glacier compared to $-20‰$ in snow and enrichment of deuterium excess from $+17.5‰$ in rock glacier outflow compared to $+11‰$ in snow, suggests that melt of internal ice that had undergone multiple melt/freeze episodes was the dominant source of base flow. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS: rock glacier; chemistry; isotopes; deuterium excess; flowpaths

INTRODUCTION

Until recently, most of the research conducted on rock glaciers has primarily focused on their movement, origin, and climatic significance (Barsch, 1996). Only

a few studies have focused on their hydrology (e.g. White, 1971; Corte, 1976; Bajewsky and Gardner, 1989; Giardino *et al.*, 1992; Croce and Milana, 2002). These latter studies present mostly qualitative hydrological observations and so there is still little information about how melt water flows through active rock glaciers (Krainer and Mostler, 2002). Even less is known about the geochemical content of the water that drains rock glaciers. Giardino *et al.* (1992) noted that rock glaciers physically and chemically influence

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the water that passes through them and act as a concentrating rather than a filtering mechanism. The lack of information on the geochemistry of outflow from rock glaciers is partly because of the logistical constraints in collecting and analysing water samples for chemical content in rugged and isolated environments. Moreover, periglacial geomorphologists have been slow to focus attention on chemical weathering (Darmody *et al.*, 2000).

In contrast, there has been considerable progress in identifying flow sources and pathways in seasonally snow-covered catchments where the chemical and isotopic content of surface waters, soil water, and ground water have been used to provide quantitative, multi-component mass balance models of stream flow during snow melt (Maule and Stein, 1990; Wels *et al.*, 1990; Mast *et al.*, 1995; Sueker *et al.*, 2000; Laudon *et al.*, 2002). Variations in water quality have been used to parameterize simple, two-component mixing models for glacierized basins (e.g. Sharp, 1991; Tranter *et al.*, 1993; Sharp *et al.*, 1995). However, such models have not yet been applied to the outflow from rock glaciers.

Our first objective here is to characterize the geochemical and isotopic content in the outflow of the Green Lake 5 rock glacier (RG5), located in the Green Lakes Valley of the Colorado Front Range. We focus on the 2003 season from the initiation of snow melt to the start of the next snow accumulation season. We then use that information to identify flow sources and pathways using quantitative, multi-component mixing models. We build on a rich history of periglacial research in the Green Lakes Valley (e.g. White, 1971, 1976, 1981; Thorn, 1975; Caine, 1976, 1979; Janke, 2005). We support the results from 2003 with those from a longer time series (1998 to 2003). We evaluate whether the RG5 outflow has a unique geochemical signature or whether it is similar to other surface waters draining landscapes characteristic of alpine environments, including glaciers, blockslopes, late-lying snow patches, and alpine streams. We then use the solute chemistry and stable water isotopes in combination with end-member mixing analysis (EMMA) (Christophersen *et al.*, 1990; Hooper *et al.*, 1990) to determine source waters and flow paths that contribute to the outflow of the rock glacier. Last, we use this information to speculate on the internal structure of this rock glacier.

SITE

The upper Green Lakes Valley is an east-facing glacial valley, headed on the Continental Divide in the Colorado Front Range (40°03′N, 105°35′W). Named for a series of shallow paternoster lakes, the Green Lakes Valley is the headwaters of North Boulder Creek and lies within the City of Boulder Watershed. Green Lakes Valley is a Long-Term Ecological Research (LTER) network site. The upper valley is approximately 225 ha in area, and the elevation ranges from 4084 m at the Continental Divide to 3515 m at the outlet of Green Lakes 4 (GL4) (Figure 1). Most of the surficial deposits are of Holocene age, accumulated since deglaciation about 12,000 years ago (J. Harbor, unpublished masters thesis, University of Colorado, 1984).

The continental, high-mountain climate of Green Lakes Valley has been recorded continuously at the D-1 meteorological station on Niwot Ridge for over 40 years and for shorter periods on the valley floor (Greenland, 1989). Mean annual temperature at D-1 is −3.7°C (Williams *et al.*, 1996b). South-facing slopes of the Green Lakes Valley are warmer than north-facing slopes, which are underlain by discontinuous permafrost (Ives, 1973). Almost 80% of the approximately 1000 mm of recorded annual precipitation falls as snow (Caine, 1996). The bulk snow pack temperature remains below 0°C until late spring, introducing a lag in the hydrological cycle by concentrating the release of melt water in a short, intense period of runoff (Caine, 1996).

The 9-ha Arikaree glacier sits at the head of the valley and is the source of North Boulder Creek (Figure 1). The outflow of the Arikaree glacier drains into Green Lakes 5 (GL5). A blockfield on the east face of Niwot Ridge was sampled in the middle portion of the slope (M), and in the lower portion of the slope (L), the same locations as in Williams *et al.* (1997) and Liu *et al.* (2004) (called 'talus' for shorthand in both those papers). The 8-ha Martinelli catchment represents a snow-field dominated catchment and is located about 400 m from the Saddle site on Niwot Ridge; its outlet is at an elevation of 3,380 m (Figure 1). The Martinelli catchment has a poorly developed soil structure, little vegetation, and a deep winter snow cover (Caine, 1989).

Niwot Ridge, the northern boundary of the Green Lakes Valley, is the site of other experimental areas, including snow lysimeters, a subnivean laboratory and an aerometrics wet-chemistry precipitation collector at the Saddle site (Figure 1), as part of the National Atmospheric Deposition Program (NADP).

The floor of Green Lakes Valley has the stepped form of a glaciated mountain valley. The ridges defining upper Green Lakes Valley consist of bedrock or blockfield-covered, narrow ridges (arêtes) between glaciated cirques (White, 1976). Below these ridges,
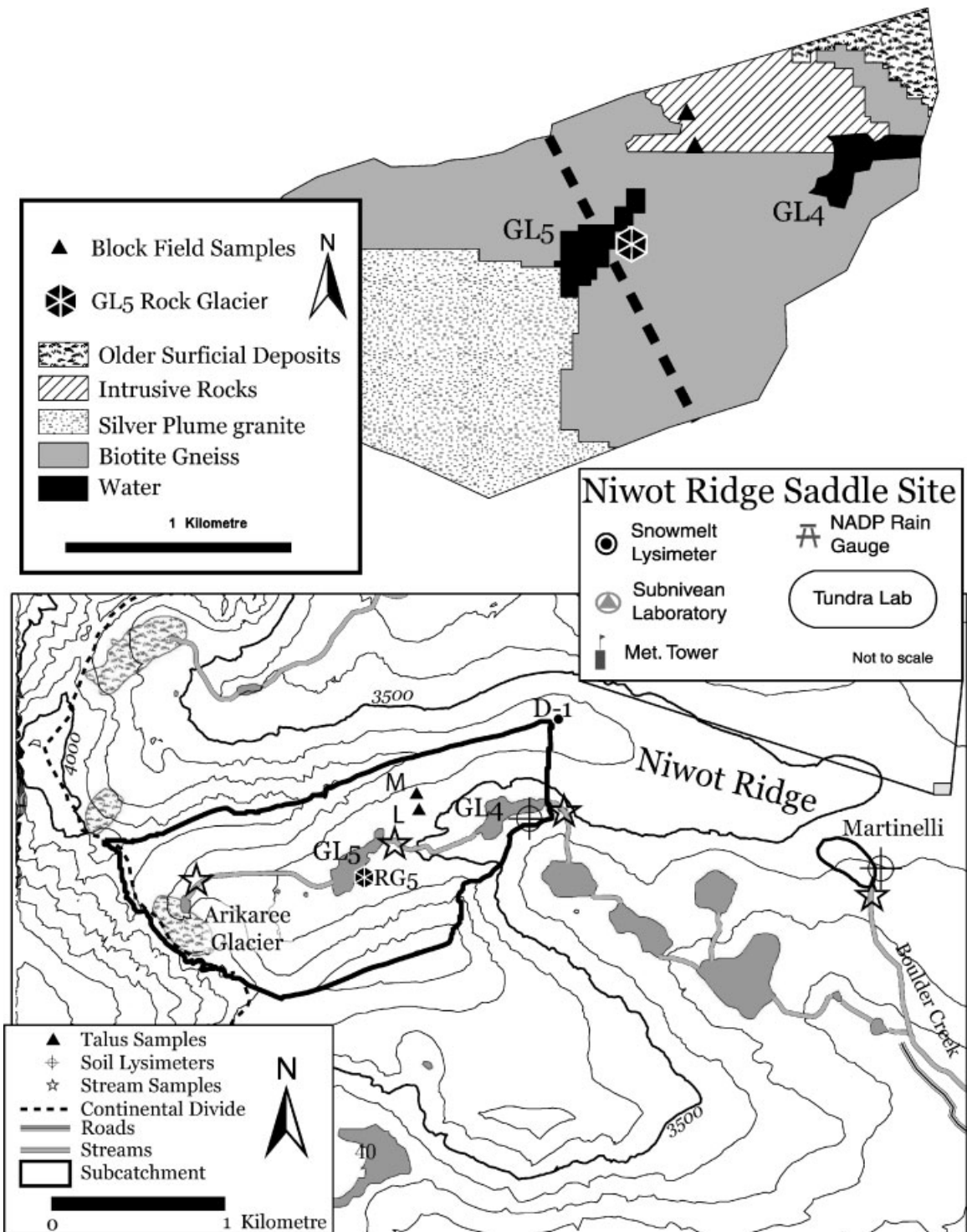
Figure 1   Location and geologic map of the Green Lakes Valley. Sampling sites are shown for snow, snow melt, glacial outflow, snow field discharge, blockslope flow, rock glacier outflow, and soil water.

Figure 2   Active front of the Green Lakes 5 rock glacier (RG5).

able to measure discharge, we did record flucuations in stage height.

LITHOLOGY

The bedrock of the upper Green Lakes Valley is primarily composed of Precambrian schists and gneisses, the Silver Plume quartz monzonite, and Audubon-Albion stock (R. G. Wallace, unpublished masters thesis, University of Colorado, 1967) (Figure 1). The Precambrian gneisses are quite variable in composition and include cordierite- and magnetite-bearing-sillaminite-biotite, biotite-quartz-plagioclase, and hornblende gneisses and migmatites. Exposed on the north slope of Kiowa Peak, above RG5, are cordierite- and magnetite-bearing-sillimanite-biotite gneisses. Above GL5 and extending to the Continental Divide, the Silver Plume quartz monzonite is a light to pinkish grey, coarse-grained, equigranular to porphyritic rock with distinctive white orthoclase phenocrysts up to several cm in length and etched into high relief on weathered surfaces (White, 1981). Silver Plume quartz monzonite is variable in composition but in general is comprised of microcline, quartz, and feldspar with lesser amounts of biotite and muscovite (Gable and Madole, 1976). The Audubon-Albion stock, exposed along the north side of GL5 and extending to the high point of Niwot Ridge, is monzonitic to quartz monzonitic in composition, dark grey in colour, with medium-grained texture consisting of plagioclase, hornblende, pyroxene, quartz, and minor biotite. A fault runs south from the Audubon-Albion stock on Niwot Ridge through GL5 and along the north slope of Kiowa Peak, through and above RG5.

The rocks exposed on the surface of RG5 are angular to subangular, variable in size from cobbles to boulders, and primarily gneissic with minor schistose layers. Gneisses exposed along the active front contain layers that have been propylitically altered and are primarily composed of epidote with minor chlorite, calcite, and pyrite. The origin of the hydrothermal fluids that caused this alteration is unclear, but the rock glacier is located at the edge of the Lake Albion mining district. Within a kilometre of RG5, the Snow Range vein produced lead, gold, and silver in the early 1900s. Alternatively, the fault that projects under the rock glacier may have been a channel for the hydrothermal fluids, or this mineral assemblage could be a result of low grade metamorphism caused by the intrusion of the Audubon-Albion stock. Further study is needed to better constrain the origin of the epidote, chlorite, and pyrite.

the alpine slopes of Green Lakes Valley fit the cliff-talus-sub-talus model that describes a rock-dominated system, the coarse debris system (Caine, 1974; Thorn and Loewenherz, 1987). The talus slopes of the valley above GL5 are predominately straight and steep, with angles in excess of 32° and a planar form (Rapp, 1960).

RG5 is a lobate rock glacier, approximately 8 ha in area, located in the talus foot zone on the north-facing side of Kiowa Peak at an elevation of 4,000 m (Figure 2), formed during the Holocene (White, 1981; Caine, 2001). It is a slow-moving rock glacier with a maximum surface velocity of about $2 \, cm \, yr^{-1}$, an order of magnitude less than flow rates of valley-floor rock glaciers in the Front Range (White, 1981; Benedict *et al.*, 1986). The top of RG5 supports patches of alpine tundra, similar to the talus and blockfields of the valley (Williams *et al.*, 1997). A deep and late-melting snow patch is located just above RG5 in a depression caused by movement of RG5 away from the cliff face. There is an outflow stream at the base of the most active area of the rock glacier. Measuring the discharge is very difficult because, like most rock glaciers, all or most of the flow is within boulder debris (Krainer and Mostler, 2002). We collected water samples for chemical and isotopic analyses in the outflow stream, and although we were not

METHODS

Sample Collection

Snow.

Physical and chemical properties of snow are routinely measured on a weekly basis at the Saddle site using sampling protocols presented in Williams *et al.* (1996a) and Williams *et al.* (1999). The same measurements were conducted on the snow field above RG5 approximately weekly starting on 19 June 2003 until melt out on 14 August. Snow pack melt water was collected at the Saddle site in 1-m^2 snow lysimeters before contact with the ground (Williams *et al.*, 1996a). Snow melt water flowed by gravity from the snow lysimeters about 5 m into a subnivean laboratory, where grab samples were collected approximately daily for solute chemistry and stable water isotope analysis. Annual snow surveys were conducted in the Green Lakes Valley at maximum accumulation from 1997 through 2003, following the protocol of Erickson *et al.* (2005). The number of snow depth measurements ranged from a low of 197 in 1997 to a high of 665 in 2000.

Surface Waters.

Surface waters were collected as grab samples during the 2003 season at the toe of RG5, Arikaree Glacier outflow, GL5 and Martinelli discharge, and blockfield flow (Figure 1). The same sites were sampled from 1998 to 2002 except for the blockfield discharge. Polyethylene bottles were soaked with deionized (DI) water overnight and then rinsed with DI water five times; bottles were further rinsed three times with sample water at the time of collection. Stream samples were collected about weekly starting with the initiation of snow melt runoff until freeze-up in the fall. All water samples were transported the same day as collection to our wet chemistry laboratory and treated the same as the snow samples.

Soils.

During 1996–99, surface temperatures of RG5 were logged (Ryan RL-100) at 5 h intervals from September to June each year. Since August 2002, this record has been extended through the year by Hobo H-8 (Onset Computer Corporation) loggers programmed with a log interval of 2 h (precision $\pm 0.1°C$). Instruments were placed at the centre of RG5 at a depth of about 20 mm and between boulders which shaded them from direct solar radiation. During June–August 1997, temperatures in the effluent stream from the rock glacier (at the point where water samples were collected) were logged (Ryan RL-100) on an hourly interval.

Zero-tension soil lysimeters, constructed of halved 400-mm long sections of PVC pipe 250 mm in diameter, capped on one end, and plumbed to drain into a 1-L storage bottle connected to the surface with tygon tubing, were installed in the mid-1980s (Litaor, 1993). At the GL4 catchment, four zero-tension soil lysimeters were installed along a hillslope catena with a northwestern aspect located with the bottom site just above lake level and about 20 m from the lake (Figure 1). Sample collection started when an area became snow free and continued at weekly to biweekly intervals. After the end of snow melt, the soil lysimeters rarely contained water except after rain events.

Laboratory Analyses

All water and snow samples were analyzed for pH, acid neutralizing capacity (ANC), conductance, major ions and reactive silicate (Si). Chemical analyses followed this protocol for all water samples including snow samples. Snow samples were stored frozen ($-20°C$) for 1 to 2 months until analysis. Blank samples of distilled DI water stored in sample bags for the same amount of time showed no significant contamination from the bags (Williams *et al.*, 1992). Snow samples were placed in covered polyethylene buckets and melted at room temperature. ANC and pH were measured immediately after melting for snow or after return to the laboratory for water samples using the Gran titration technique. Since waters in the Green Lakes Valley are primarily bicarbonate, ANC is considered to equal HCO_3^-, as suggested by Williams *et al.* (1993) for the alpine Emerald Lake basin in the Sierra Nevada. As Neal (2001) noted, the Gran titration may underestimate ANC, particularly at lower pHs (≤ 4.5). Since pH in our surface waters is usually around 6 or 7 (Caine and Thurman, 1990), it is believed that this underestimation should be insignificant.

Subsamples were immediately filtered through pre-rinsed (300 ml), 47-mm Gelman A/E glass fibre filters with ca. 1-μm pore size. Filtered samples were stored in the dark at 4°C for subsequent analyses within 1 to 4 weeks. Reactive silicate (Si) was measured by the silic-molybdate method (Strickland and Parsons, 1972). Anions were measured using ion chromatography (Dionex DX 500) employing chemical ion suppression and conductivity detection. Calcium (Ca^{2+}), magnesium(Mg^{2+}), sodium(Na^+), and potassium(K^+) were analysed with a Varian AA6 atomic absorption spectrophotometer using an air-acetylene flame. Lanthanum chloride was used to suppress chemical and ionization interferences during calcium and magnesium determinations. Duplicate

samples were separated by 10–15 samples in each run. Analytical precision for all solutes was less than 2% and detection limit less than $1\,\mu eq\,L^{-1}$ (Williams *et al.*, 2001).

Samples for stable water isotopes were collected in 2003 in 30-mL borosilicate vials with airtight caps. Analyses for $\delta^{18}O$ and δD were performed at the INSTAAR Stable Isotope Laboratory. The 1-σ precision was $\pm 0.05‰$ based on replicate samples. Isotopic compositions are expressed as a δ (per mil) ratio of the sample to the Vienna standard mean ocean water (VSMOW), where R is the ratio of $^{18}O/^{16}O$ or $^2H/^1H$

$$(\delta^{18}O, \delta D)_{sample} = \left[(R_{sample}/R_{VSMOW}) - 1\right] x 10^3 \tag{1}$$

Hydrograph Separation

Simple, two-component mixing models originally developed for fluvial systems (e.g. Sklash *et al.*, 1976; Hooper and Shoemaker, 1986) have been adapted for glacial systems

$$Q_b C_b = Q_q C_q + Q_d C_d \tag{2}$$

where Q is volume flow rate, C is concentration, and the subscripts describe the water source (b = bulk glacial outflow, q = quickflow, and d = delayed flow). Several conditions must be met for this two component model (Buttle, 1994), including: (1) tracer values of each component must be significantly different; (2) there are only two components contributing to stream flow; and (3) the tracer composition of each component is constant for the duration of the event, or the variation is known from measurements. The quick and delayed water components are considered end-members in this mixing model.

Unfortunately, subglacial hydrological interpretations based on such simple two-component mixing models are fraught with uncertainty, in part because the model assumes only two hydrological components (Brown, 2002). The same mass balance approach can be extended to three or more end-members using the following approach

$$f_i = x_i e_i^{-1} \tag{3}$$

where the subscript i denotes the ith stream sample, and f is the vector of runoff fractions for m components, which sum to 1. The term x is a $1x(p + 1)$ vector of stream chemistry where p orthogonal projections are used plus the last element of 1 that represents the constraint of total runoff fraction. The e term represents a $mx(p + 1)$ square matrix (Liu *et al.*,

2004). Note that this approach allows us to calculate the fraction contribution of each end-member to a stream sample even when we do not have discharge measurements.

EMMA was used to determine the number and proportions of end-members contributing to RG5 outflow, following the procedures in Christophersen and Hooper (1992) and as demonstrated for the Green Lakes Valley by Liu *et al.* (2004). Stream flow samples and end-members were standardized for all conservative tracers using the mean and standard deviation of stream flow following the procedure of Hooper (2003) and Burns *et al.* (2001). Note that it is possible for some samples to lie outside the domain defined by the selected end-members. If this occurs, solutions would have negative fractions for some end-members, which are not realistic, and so these were forced to zero and the other fractions resolved geometrically, following Christophersen *et al.* (1990) and Hooper *et al.* (1990) and as applied by Liu *et al.* (2004) in the Green Lakes Valley.

RESULTS

Precipitation

The basin-averaged snow depth varied by more than a factor of two. Snow depth ranged from a high of 256 cm in 1997 to a low of 123 cm in 2002 (Figure 3). Mean snow depth in 2003 of 222 cm was similar to
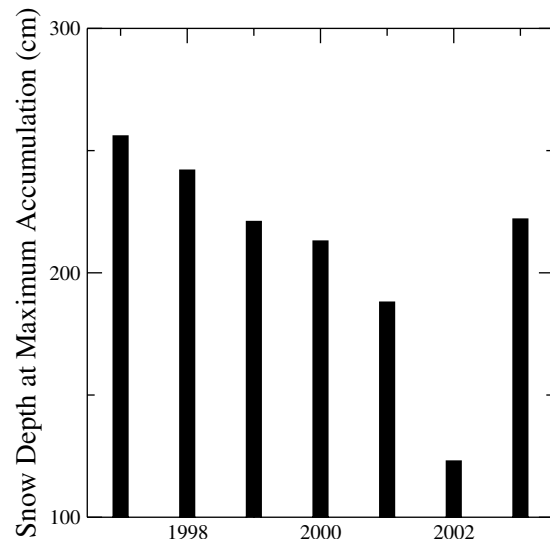
Figure 3   Annual mean snow depth measured at maximum snow accumulation from 1997 to 2003 for the 225-ha Green Lake 4 catchment. The number of snow depth measurements ranged from 197 in 1997 to 665 in 2000.

that of 1999. Annual precipitation in Colorado was below the long-term average for 1999 to 2003, with 2002 the driest year on record (National Oceanic and Atmospheric Administration (NOAA), 2002). These consecutive years of below-normal precipitation may have resulted in lower antecedent moisture than normal for all surface waters at the start of runoff in 2003.

Temperature

Surface temperatures at RG5 showed the predictable seasonal pattern, with daily mean temperatures near $15°C$ in summer and near $-20°C$ in winter (Figure 4). Sub-freezing temperatures were continuous from early-October to late-May, with mean temperatures for that period between $-7.2°C$ (2003–04) and $-8.2°C$ (1997–98). During winter, temperatures fluctuated on a daily (or shorter) frequency which suggests that the upper surface of the rock glacier does not carry a long-lasting snow cover. The lack of consistent snow cover during the winter on the upper surface of RG5 is consistent with occasional field observations.

During June–August 1997, temperatures logged on an hourly interval in the effluent stream from the rock glacier (at the point where water samples are collected) showed temperatures no higher than $1.0°C$, with a mean of $0.3°C$ (standard deviation of $\pm 0.4°C$). The consistent water temperatures near $0°C$ in RG5 outflow through the summer indicates that, within the rock glacier, liquid water is in contact with ice and frozen debris as suggested by Krainer and Mostler (2002).
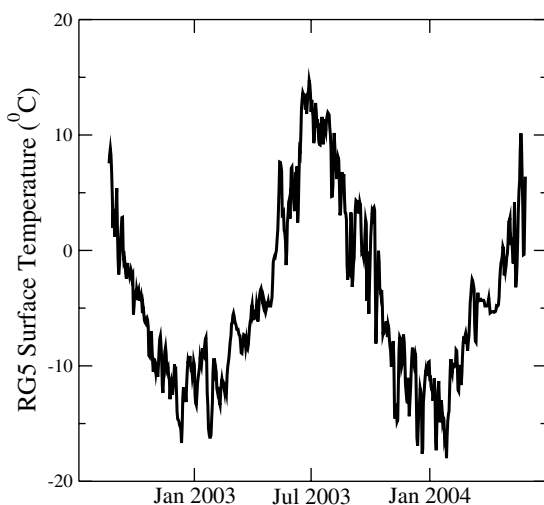

Figure 4   A time series of RG5 surface temperatures from 4 September 2002 to 14 June 2004.

Solute Content

We compare the solute content of outflow from RG5 with other surface flows in the Green Lakes Valley during 2003 (Figure 5). Concentrations of HCO_3^- in the outflow of RG5 were similar to other surface waters. Values in the outflow of the Arikaree Glacier were about $60 \mu eq \, L^{-1}$ at the initiation of snow melt, decreased to below $10 \mu eq \, L^{-1}$ during the summer, and then rose in the fall to near those at the initiation of snow melt. Bicarbonate concentrations at the other four sites were similar, ranging from about $50 \mu eq \, L^{-1}$ at the initiation of snow melt and then rising to about $80–100 \mu eq \, L^{-1}$ in the fall.

Reactive silicate in the outflow of RG5 was about $25 \mu moles \, L^{-1}$ at the initiation of snow melt and then gradually increased to about $100 \mu moles \, L^{-1}$ in the autumn. The concentrations of Si in the outflow of the Arikaree glacier and at GL5 were similar to those of RG5 at the initiation of snow melt and increased slightly with time. The concentrations of Si in blockfield waters and outflow from the Martinelli catchment were about twice that of RG5 at the initiation of snow melt and slightly lower than RG5 in the autumn.

Concentrations of Na^+ were generally less than $20 \mu eq \, L^{-1}$ at all sites through mid-July. However, starting in early August the concentrations of Na^+ in the outflow of RG5 rose steadily to about $80 \mu eq \, L^{-1}$. In contrast, concentrations of Na^+ in the other surface waters changed only slightly.

Concentrations of Mg^{2+} in the outflow of RG5 in the autumn were more than an order of magnitude greater than the other surface waters. Concentrations of Mg^{2+} in June and early July were less than $30 \mu eq \, L^{-1}$ at all sites. However, by late September concentrations of Mg^{2+} in the outflow of RG5 were more than $900 \mu eq \, L^{-1}$ compared to values of less than $40 \mu eq \, L^{-1}$ at all the other sites.

This large difference in solute concentrations between the outflow of RG5 and the other surface waters was even more striking for Ca^{2+} and SO_4^{2-}. As with Mg^{2+}, there was little difference between concentrations of these two solutes in the outflow of RG5 and the other surface waters into early July. However, in late September the outflow of RG5 had concentrations of Ca^{2+} greater than $4,000 \mu eq \, L^{-1}$ compared to maximum values of less than $200 \mu eq \, L^{-1}$ at all other sites. Concentrations of SO_4^{2-} in the outflow of RG reached $7,000 \mu eq \, L^{-1}$ in the autumn compared to maximum concentrations below $40 \mu eq \, L^{-1}$ at the other sites except for GL5 (into which the RG5 drains), where maximum concentrations of SO_4^{2-} reached $120 \mu eq \, L^{-1}$.
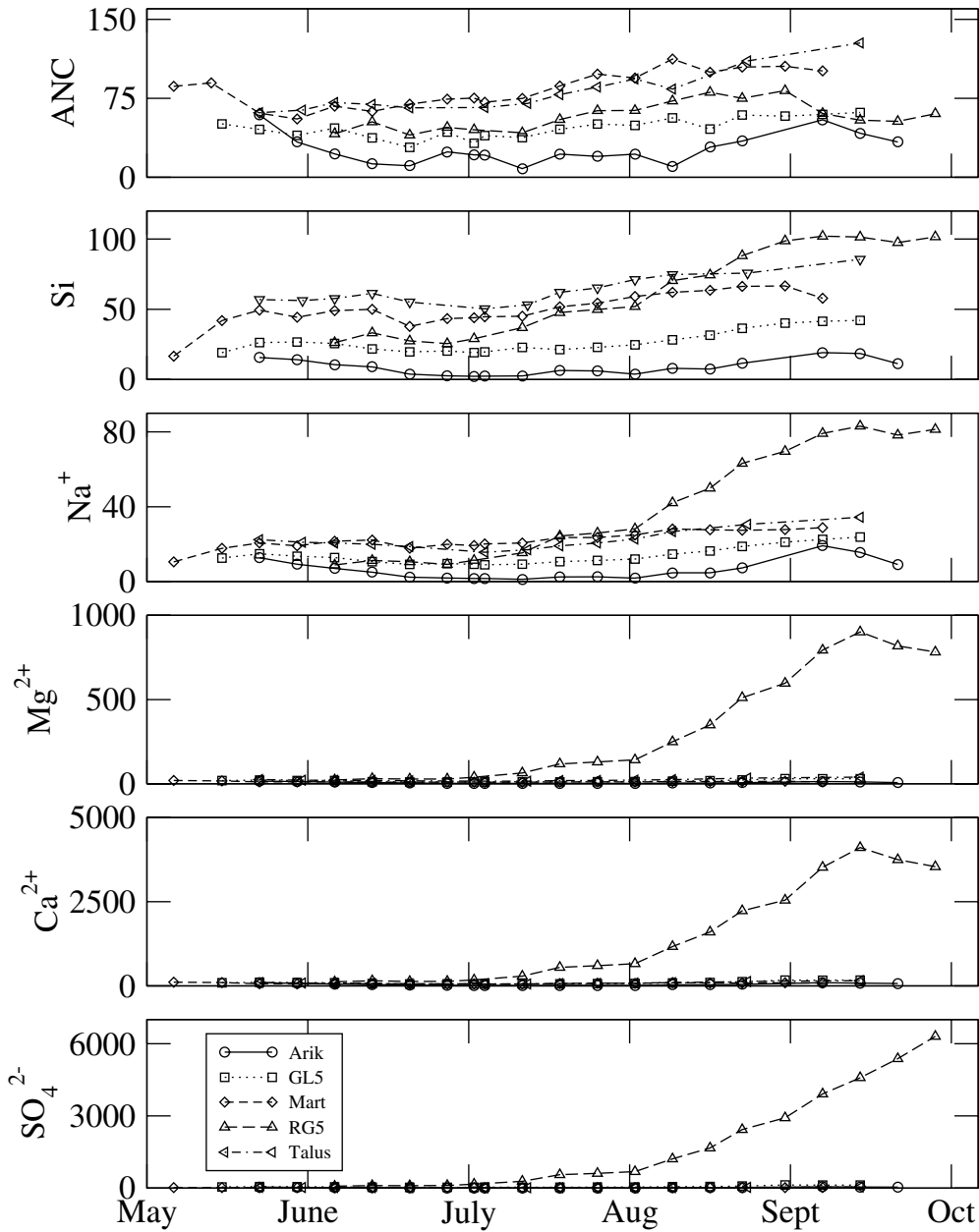
Figure 5   Time series of selected solute concentrations in surface waters of the Green Lakes Valley from 2003. All units are in μeq L^{-1} except for Si which is μmoles L^{-1}. Note that the scale for the y-axis varies by solute. Arik is Arikaree Glacier outflow; GL5 is the outlet of Green Lakes 5; Mart is the outlet of the Martinelli catchment; RG5 is the Green Lake 5 rock glacier outflow; Blockfield is the upper blockfield site.

Measurements of solute concentrations in the out-flow of RG5 during snow-free seasons from 1998 to 2002 show a similar pattern of elevated concentrations of Ca^{2+} and SO_4^{2-} as in 2003 (Figure 6). However, there are interesting year-to-year variations. Concen-trations of Ca^{2+} and SO_4^{2-} during the first week of September (which is common to all years) of about 1600 μeq L^{-1} during the drought years from 2000–03 were four times the mean value of about 400 μeq L^{-1} for each solute in the pre-drought years of 1998 and
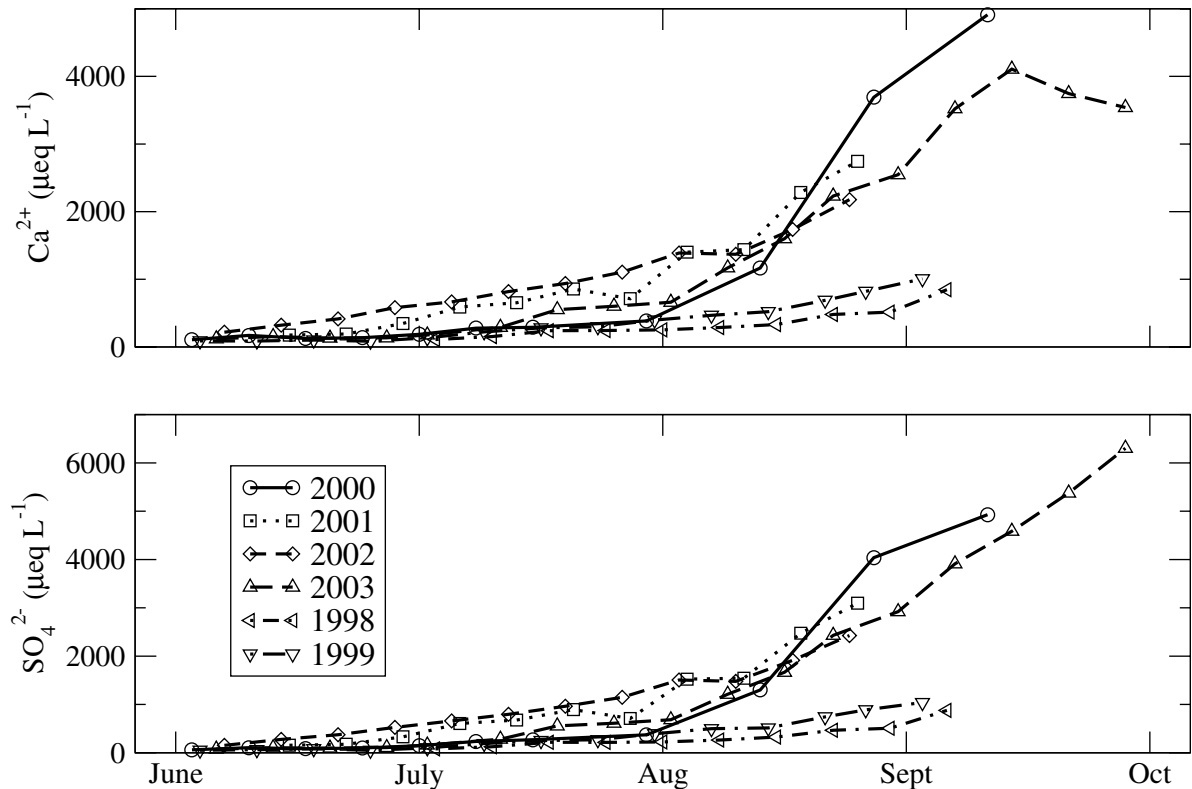
Figure 6   Time series of Ca^{2+} and SO_4^{2-} concentrations in the outflow of RG5 during the snow-free season from 1998 to 2003.

1999. Concentrations of Ca^{2+} and SO_4^{2-} were also elevated in June and July during the two driest years of 2001 and 2002 relative to the other four years. Concentrations of Ca^{2+} and SO_4^{2-} in the outflow of RG5 appear to be highest at the end of the season during low snowfall years.

Boxplots showing the median and quartiles of selected solutes and isotopes are presented in Figure 7 for potential end-members in the hydrographic mixing models. Potential end-members include snow, snow melt, soil water, RG5 outflow, Arikaree Glacier outflow, GL5 stream, Martinelli stream, and the two blockfield sites. Solute concentrations in snow and snow melt were generally lower than other types of water. The median value of most solute concentrations in the soil solution was similar to that of RG5, though the range in values was greater for RG5 than for soil water.

Water Isotopes

The $\delta^{18}O$ from the outflow of RG5 was similar to that of the other water bodies at the initiation of snow melt

but at the end of summer was enriched compared to the same water bodies (Figure 8). The $\delta^{18}O$ of snow was around $-20‰$ at the initiation of snow melt in mid-May. Snow then became more enriched with time to near $-15‰$. The $\delta^{18}O$ from the outflow of the Arikaree Glacier was near $-20‰$ at the start of snow melt and then became gradually enriched to near $-16‰$, similar to snow pack values. The $\delta^{18}O$ outflow of GL5 and the blockfield site showed a similar enrichment pattern with time to that of the Arikaree Glacier but with slightly enriched values, near $-18‰$ at the start of snow melt and about $-14‰$ at the end of the summer. The $\delta^{18}O$ of $-17.5‰$ in outflow from RG5 was similar to that of GL5 and the blockfield at the start of snow melt. However, the $\delta^{18}O$ of the RG5 outflow became substantially more enriched with time starting in early July, before levelling off at about $-13‰$ in early August(Figure 8). In mid-August there was an inflection point where the $\delta^{18}O$ values of the RG5 outflow rapidly become more enriched. In September the $\delta^{18}O$ values of RG5 were near $-10‰$, almost $5‰$ more enriched than any of the other water sources. The $\delta^{18}O$ values from the outflow of RG5 are
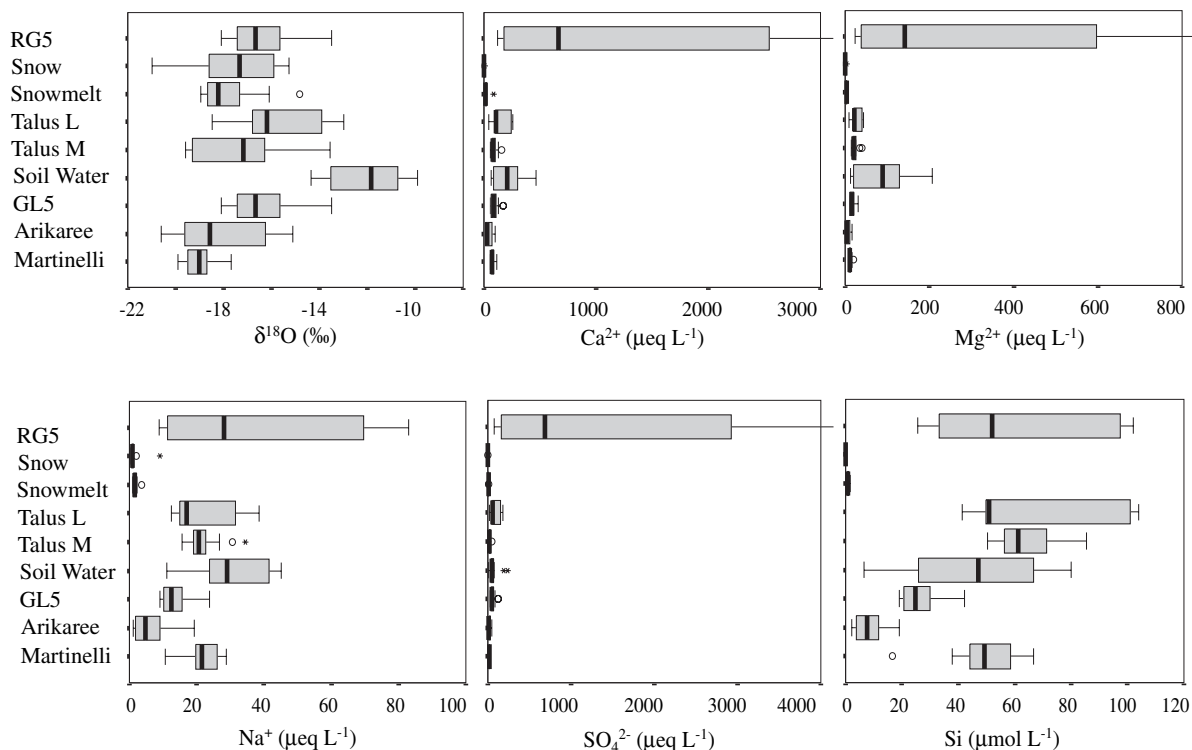
Figure 7 Boxplots from 2003 showing median and quartiles (box for 25% and 75% and whisker for 5% and 95%) for Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, Si, and $\delta^{18}O$ values in snow, snow melt, stream waters, glacial and rock glacier outflow, blockfield waters, and zero-tension soil lysimeters. Asterisks indicate outliers within the sample population for a given sample type/location. Median values are emphasized because EMMA uses median values to parameterize end-members in the PCA.

consistent with a snow melt source in June but have a unique value in September with respect to other water bodies.

The possible importance of evaporation in concentrating geochemical weathering products in the outflow of RG5 was evaluated by investigating the $\delta D - \delta^{18}O$ relationship in snow and surface waters. Empirical results have shown that δD and $\delta^{18}O$ values in precipitation co-vary and are generally described by the relationship (Craig, 1961):

$$\delta D = 8\delta^{18}O + 10‰ \qquad (4)$$

which is defined as the Global Meteoric Water Line (GMWL). Deuterium values in the snow pack were highly correlated with $\delta^{18}O$ ($R^2 = 0.99$; $n = 11$) (Figure 9). Our local meteoric water line (LMWL) has a similar slope but a different y-intercept:

$$\delta D = 7.7\delta^{18}O + 5.1‰ \qquad (5)$$

The similar values in slope between our LMWL (7.7) and the GMWL (8.0) suggests an absence of complex kinetic fractionation processes affecting the

$\delta D - \delta^{18}O$ relationship of snow fall or storage in the snow pack.

In contrast, the $D - \delta^{18}O$ relationship for the outflow of RG5 was:

$$\delta D = 8.5\delta^{18}O + 19.1‰ \qquad (6)$$

These results suggest that source waters for the outflow of RG5 are subjected to little if any evaporation. The slope of 8.5 for the $\delta D - \delta^{18}O$ relationship in the outflow of RG5 is slightly higher than the LMWL and GMWL. Evaporation would cause enrichment of $\delta^{18}O$ in source waters and a decrease in the slope of the $\delta D - \delta^{18}O$ relationship. The lack of a decrease in slope of the $\delta D - \delta^{18}O$ relationship in the outflow of RG5 indicates little if any evaporation is occurring in this system, consistent with a coarse debris system and limited vegetation characterized by high infiltration rates.

Steig *et al.* (1998) have shown that elevated deuterium excess (d_{excess}) values provide insight into the importance of melt-freeze cycles within a rock glacier. Deuterium excess was calculated for
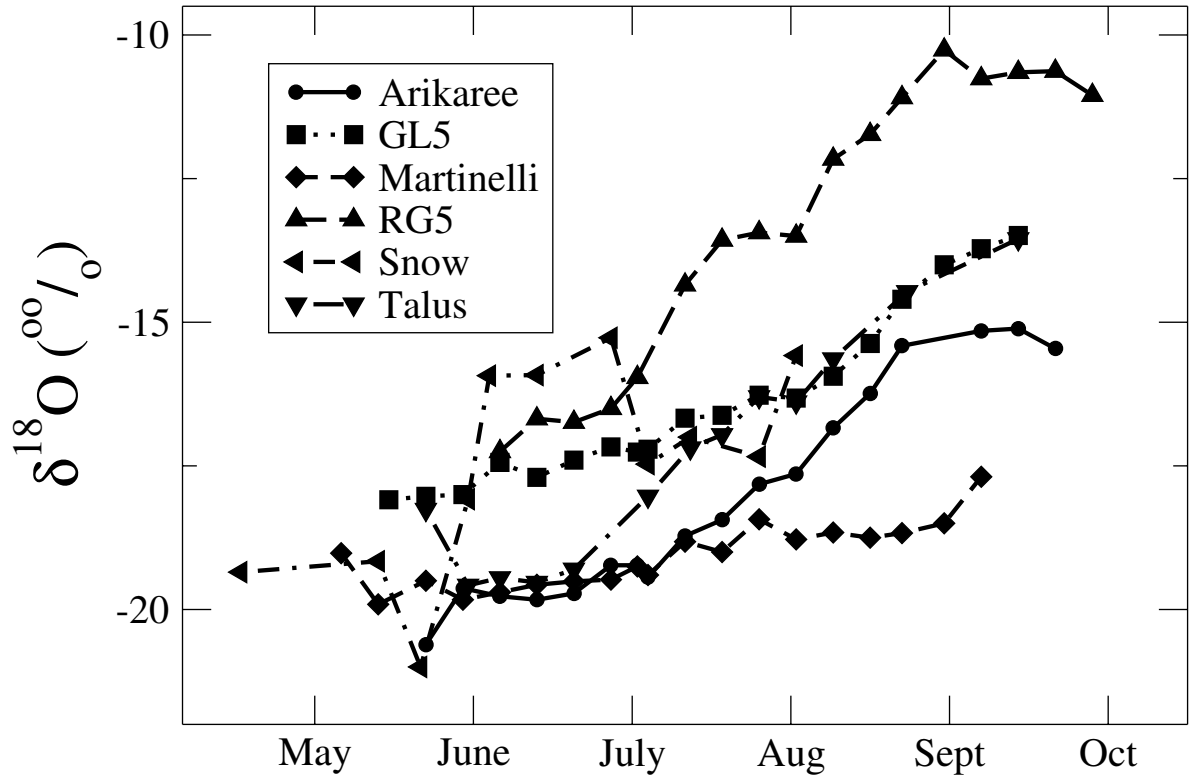
Figure 8   A time series of δ^{18}O values from snow and from the outflow of the Arikaree Glacier, Martinelli snowpatch, Green Lake 5, blockfield sites L and M, and the GL5 rock glacier, 2003.
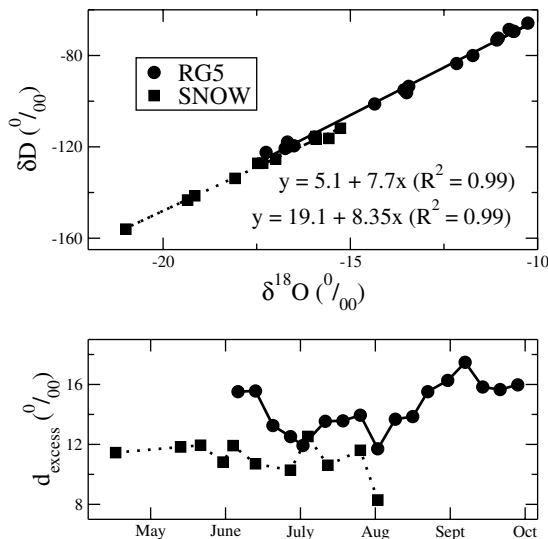

Figure 9   Upper panel: Global meteoric water line (GMWL) and the local meteoric water line (LMWL) from snow samples collected prior to the initiation of snow melt on 14 May 2003 to melt out on 14 August 2003. Lower panel: A time series of the d_{excess} values for the snow pack and for the RG5 outflow.

individual samples following the protocol developed by Johnsen and White (1989) based on the equation for the GMWL (Craig, 1961):

$$d_{\mathrm{excess}} = \delta D - 8\delta^{18}O \qquad (7)$$

The d_{excess} values for the RG5 outflow ranged from $+11.7‰$ early in the melt season to $+17.5‰$ in the autumn, with a mean of $+14.5‰$ (Figure 9). In contrast, the d_{excess} values for the snow pack of around $+11$ to $+12‰$ were generally similar to that of RG5 outflow early in the snow melt but about 5‰ lower than RG5 outflow in the autumn. There appears to be some process that causes an increase of d_{excess} in the outflow of RG5 in September and October.

Mixing Model: Flowpaths

EMMA was used to determine possible sources of water in the RG5 outflow. Conservative tracers were evaluated using mixing diagrams following the protocols of Christophersen *et al*. (1990) and Hooper *et al*. (1990). Tracer compositions of streamflow samples were plotted along with median and quartiles of

potential end-members. Potential end-members considered are the ones presented in Figure 7. Base flow was assumed to be defined by the last sample collected in 2003 from the outflow of RG5, following the protocol of Liu *et al.* (2004) to use EMMA to identify end-members for the Martinelli and GL4 catchments of the Green Lakes Valley. Tracers were considered acceptable if streamflow samples were bounded by potential end-members, as demonstrated in Figure 10. Note that for these two examples the mixing model suggests that base flow, snow, and soil water might be appropriate end-members. A total of 55 mixing diagrams were evaluated, including all potential combinations of paired tracers for Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, ANC, Si, $\delta^{18}O$, and conductance. Six tracers were found acceptable at RG5, including Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, Si, and $\delta^{18}O$.

A Principle Component Analysis (PCA) was performed to obtain eigenvalues and eigenvectors for the six solutes selected. The first two PCA components explain 99% of the total variance of the streamflow data. Based on Christophersen and Hooper (1992) and Liu *et al.* (2004), three end-members appear to be

Figure 11 Orthogonal projections of end-members into U space defined by RG5 outflow chemistry. End-members are shown by their medians along with their 25% and 75% quartiles. The six tracers used were Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, Si and $\delta^{18}O$.

sufficient to explain the total variance of solute and isotopic content of the outflow from RG5 (end-members equal PCA components plus one). The stream data were standardized and projected onto U space defined by the first two eigenvectors, along with all end-members (Figure 11). Source waters were determined using the first two U-space projections.

The same three end-members used in the mixing diagrams above appear to be geometrically correct in binding the RG5 outflow. Snow comprised an average of 30% of RG5 outflow, soil water 32%, and base flow 38%. However, it was the changes in the time of year for which each of the components influenced the water chemistry of RG5 that was most interesting (Figure 12). From the initiation of sampling on 19 June to 15 July 2003, snow was the dominant source water in RG5 outflow. During the middle part of the
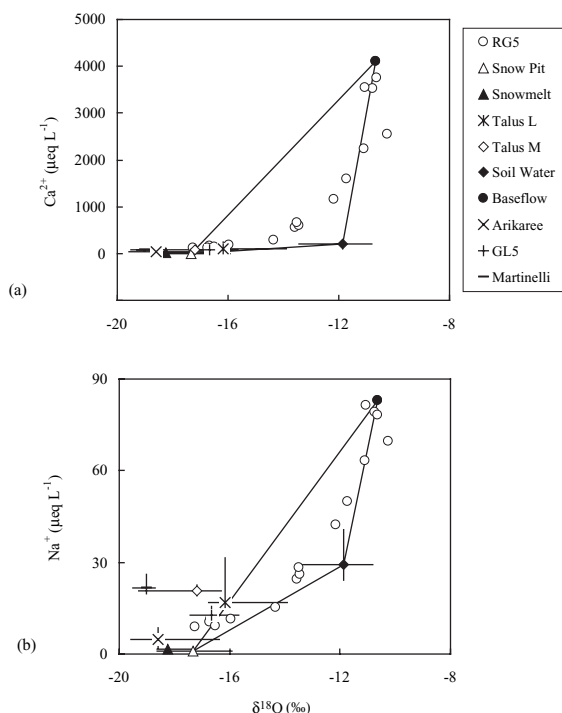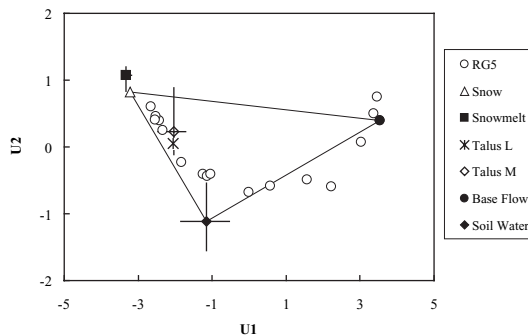

Figure 10 Conservative tracers were evaluated by plotting medians and quartiles of potential end-members along with the values in RG5 outflow. A total of 55 mixing diagrams were evaluated. Here we show the results using (a) $\delta^{18}O$ and Ca^{2+} and (b) $\delta^{18}O$ and Na^+.
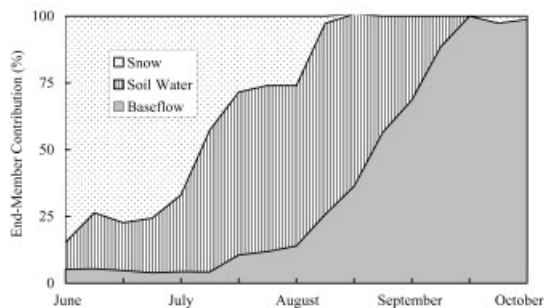

Figure 12 Time series of the percentage contribution of each of the three end-members to the solute chemistry of the RG5 outflow, 2003. Snow was the dominant source of RG5 outflow in June through mid-July. Soil was the dominant source from mid-July to early September. Base flow was the dominant source to the RG5 outflow in the autumn months.
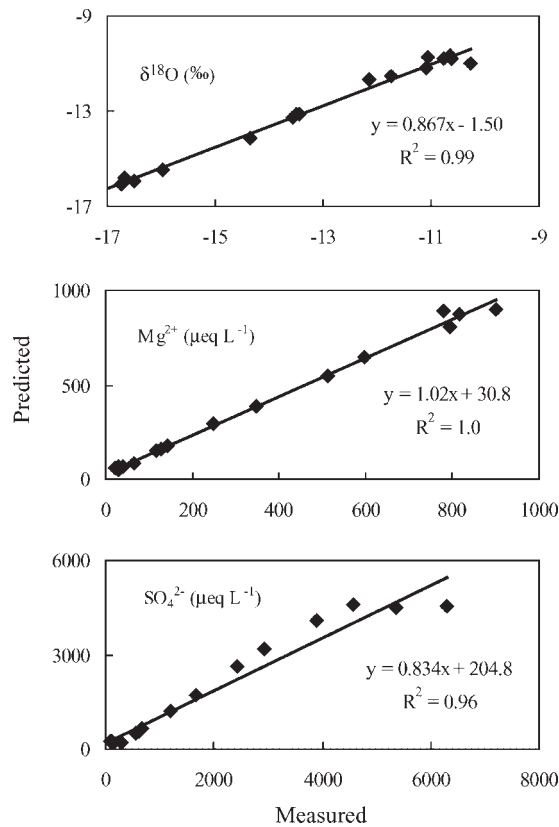
Figure 13   The mixing model results were evaluated by plotting observed versus predicted concentrations. For the three examples, the R^2 values were greater than 0.95 and slopes were near 1, indicating that the model performance was adequate.

summer, from 24 July to 28 August, soil water was the dominant water source. Finally, from 28 August to the end of the season on 10 October, base flow was the major component of RG5 outflow. Furthermore, from

17 September on, base flow comprised about 90% of RG5 outflow.

The EMMA solutions were evaluated by reproducing concentrations of all conservative tracers from the EMMA model and comparing them to the measured values. In general, EMMA reproduced the measured concentrations well. For example, the R^2 values for $\delta^{18}O$, Mg^{2+}, and SO_4^{2-} were all greater than 0.95 with slopes near one (Figure 13). The Pearson correlation coefficient was greater than 0.95 for all six conservative tracers (Table 1). The difference of the means was less than 15% for all conservative tracers.

DISCUSSION

Geochemistry

The elevated concentrations of cations and anions in the outflow of RG5 are consistent with the results of Giardino *et al.* (1992), who noted that water exiting rock glaciers in the San Juan Mountains of Colorado acquired a significant dissolved load during movement through the rock glaciers. Weathering in cold regions has long been believed to be dominated by mechanical processes (Hutton, 1795). The predominant mechanical process is generally considered to be freeze-thaw or frost-shattering (Hall *et al.*, 2002). Moreover, chemical weathering has intuitively been considered minimal in periglacial environments because low temperatures inhibit chemical reactions. However, Thorn (1992) clearly pointed out that these are only assumptions that lack substantive corroboration, let alone unequivocal 'proof' (Hall *et al.*, 2002). A number of investigators have shown that chemical weathering can be important in periglacial environments (Reynolds and Johnson, 1972; Thorn, 1975; Caine, 1976; Caine and Thurman, 1990; Dixon *et al.*,

Table 1   Results of the EMMA model for conservative tracers in the outflow of GL5 RG. Units are $\mu eq\,L^{-1}$ or $\mu moles\,L^{-1}$ (Si) or ‰ ($\delta^{18}O$). Difference (%) between observed and predicted means is normalized by dividing the sum of observed and predicted means.

	Observed means	Predicted means	Per cent difference	Slope	y-intercept	Pearson correlation coefficient
Ca^{2+}	1487	1604	7.8	1.05	43.7	0.99
Mg^{2+}	329	366	11.1	1.02	30.8	0.99
Na^+	40	40	0.4	0.97	1.2	0.99
SO_4^{2-}	1829	1730	5.4	0.83	204.8	0.95
Si	62	53	14.5	1.11	−16.1	0.98
$\delta^{18}O$	−13	−13.1	1.9	0.87	−1.5	0.99

1995; Anderson *et al.*, 1997). The enhanced geochemical content of RG5 outflow supports the contention of these investigators that a renewed interest in chemical weathering processes in periglacial environments may be warranted.

During June and July the geochemical content of the outflow of RG5 does not appear to differ substantially from that of other types of surface waters in the Green Lakes Valley. Thus, for this alpine ecosystem at this time of year there does not appear to be large differences in water quality among rock glacier outflow, glacier and blockslope discharge, and discharge from small alpine catchments. However, water quality in the outflow of RG5 showed strong seasonal differences that the other surface waters did not, with elevated concentrations of Mg^{2+}, Ca^{2+}, and SO_4^{2-} from early August into October. Longer-term measurements from 1998 to 2002 show the same pattern of elevated concentrations of these solutes in the autumn, suggesting that the 2003 results were not specific to that year. The mineral weathering that contributed to the elevated concentrations of Mg^{2+}, Ca^{2+}, and SO_4^{2-} in the outflow of RG5 relative to the other surface waters in the Green Lakes Valley during autumn merits further analysis.
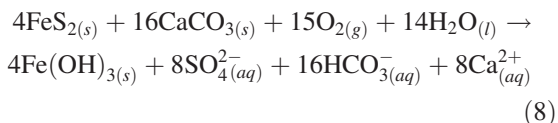
Glacial melt waters generally demonstrate significant chemical enrichment over relatively short distances (e.g. a few km), between their origin as dilute snow and ice-melt (ionic strength of about $10 \, \mu eq \, L^{-1}$) and their emergence at the glacial portal, where ionic strengths may exceed $1000 \, \mu eq \, L^{-1}$ (Tranter *et al.*, 1993; Brown, 2002). The contrast between dilute snow (about $10 \, \mu eq \, L^{-1}$) and the late-season base flow leaving the rock glacier (where the ionic strength exceeds $10,000 \, \mu eq \, L^{-1}$) is greater by an order of magnitude than that characteristic of typical subglacial hydrological systems. Furthermore, if the seasonal snow patch located directly above RG5 were the main source of water into the rock glacier, the observed enrichment of three orders of magnitude occurred over the short distance of several hundred metres.

Evaporative concentration is one potential mechanism that may explain the very high concentrations of solutes in the late-season outflow of RG5. Summer time evaporation/sublimation of water/ice has been suggested to explain unexpectedly lower ground temperatures in blockfields in the Alps (Harris and Pedersen, 1998). If evaporation is an important process at RG5, the slope of the $\delta D - \delta^{18}O$ relationship in the RG5 outflow should be significantly lower than the local meteoric water line. Furthermore, you would need to have about 99% evaporative concentration.

The isotopic results suggest that evaporation was not an explanatory factor for the large increase in solute concentration.

Moreover, the geochemical composition of the outflow of RG5 appears to differ widely from the expected solute products produced from mineral dissolution of crystalline bedrock. Depending on the specific mineralogy, chemical weathering of crystalline bedrock generally produces Si and HCO_3^- in about equal proportions to the sum of base cations (Williams *et al.*, 1993). This ratio does appear to hold true for surface waters in June and July at RG5 outflow, glacier outflow, blockslope flow, and discharge from GL5 and Martinelli catchments. However, in September and October the concentrations of Mg^{2+} and Ca^{2+} at RG5 were an order of magnitude greater than for Si or HCO_3^-. Mast *et al.* (1990) present evidence that preferential weathering of calcite within crystalline bedrock is the major source of Ca^{2+} and HCO_3^- for high-elevation catchments of the Colorado Front Range. However, HCO_3^- concentrations in the outflow of RG5 were not sufficient to support preferential weathering of calcite. Moreover, the elevated concentrations of SO_4^{2-} and Mg^{2+} need to be accounted for.

Pyrite oxidation coupled to carbonate dissolution is another potential weathering mechanism (Sharp, 1991; Tranter *et al.*, 1993):

$$4FeS_{2(s)} + 16CaCO_{3(s)} + 15O_{2(g)} + 14H_2O_{(l)} \rightarrow$$
$$4Fe(OH)_{3(s)} + 8SO_{4(aq)}^{2-} + 16HCO_{3(aq)}^- + 8Ca_{(aq)}^{2+}$$
$$(8)$$

The stoichiometry of this reaction produces equal-parts Ca^{2+} and SO_4^{2-}, similar to the outflow of RG5.

Brown *et al.* (1996) evaluated changes in the relative contribution of various weathering reactions in glacial meltwaters using the C-ratio $[HCO_3^- / (HCO_3^- + SO_4^{2-})]$. A ratio of 1 signifies weathering by carbonation reactions whereas a ratio of 0.5 signifies coupled sulphide oxidation and carbonate dissolution reactions (equation 8 above). Tranter *et al.* (1997) adopted a variation of this procedure called the S-ratio $[SO_4^{2-}/(HCO_3^- + SO_4^{2-})]$, which gives a ratio of 0.5 for coupled sulphide/carbonate dissolution and zero for carbonation. For the RG5 outflow, the C-ratio is at 0.35 during snow melt and then gradually decreases to near zero in the autumn (Figure 14). These results suggest that neither carbonation reactions nor coupled sulphide/carbonate dissolution were important processes. The S-ratio provides similar information, with a value of 0.65 during snow melt that increases to almost 1.0 in the autumn.
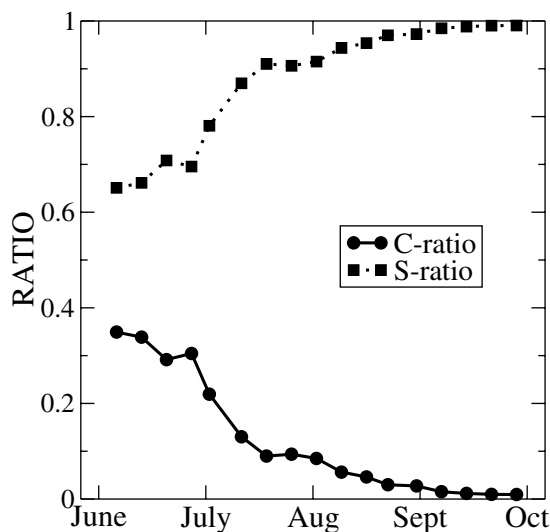
Figure 14 The C-ratio $[HCO_3^-/(HCO_3^- + SO_4^{2-})]$ and S-ratio $[SO_4^{2-}/(HCO_3^- + SO_4^{2-})]$ for the RG5 outflow, 2003. A C-ratio of 1 signifies weathering by carbonation reactions whereas a ratio of 0.5 signifies coupled sulphide oxidation and carbonate dissolution reactions. The S-ratio is 0.5 for coupled sulphide/carbonate dissolution and zero for carbonation.

Dissolution of gypsum could result in elevated levels of Ca^{2+} and SO_4^{2-} without producing Si or HCO_3^-:

$$CaSO_4 \cdot 2H_2O_{(s)} \leftrightarrow Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} + 2H_2O_{(aq)}$$

$$(9)$$
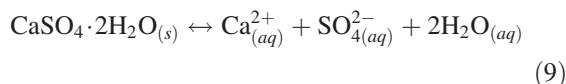
Darmody *et al.* (2000) have shown that pyrite oxidation coupled with gypsum dissolution/precipitation is a significant source of both Ca^{2+} and SO_4^{2-} in the alpine Kärkevagge catchment of northern Sweden. A linear regression does show a significant relationship between the solutes, with $SO_4^{2-} = 1.35Ca^{2+} - 175 (R^2 = 0.93, p \leq 0.001, n = 17)$. However, the presence of gypsum or anhydrate would be unusual in this crystalline metamorphic rock. Moreover, a simple linear regression between Ca^{2+} and Mg^{2+} is also significant, with $Mg^{2+} = 0.22Ca^{2+} - 1.9 (R^2 = 0.99, p \leq 0.001, n = 17)$. Mineral weathering of gypsum will not produce Mg^{2+}.

We conducted a mineral investigation on the active face of RG5 and found extensive amounts of freshly exposed mineral faces. Although we did not find any presence of gypsum, pyrite is present. Additionally, iron-staining was common, which is consistent with pyrite oxidation and precipitation of ferric hydroxide at the 6–7 pH range of RG5 outflow. Somewhat

surprisingly, epidote was found in abundance. Epidote is a calcium-silicate mineral with lesser amounts of Mg^{2+}. The production of sulphuric acid from pyrite oxidation followed by preferential weathering of epidote is consistent with the elevated SO_4^{2-}, Ca^{2+}, and Mg^{2+} concentrations in the autumn months for RG5 outflow. Reactive siliate becomes increasing insoluble with decreasing water temperatures. Thus, much of the Si produced from the weathering of epidote would be precipitated as amorphous silicate forms such as imogolite (Williams *et al.*, 1993).

Glacierized catchments experience high rates of mechanical erosion which can exceed rates of chemical weathering (Sharp *et al.*, 1995). The high rates of mechanical weathering may lead to enhanced chemical weathering, because the freshly ground material may remove organic and inorganic weathering rinds on grains that decrease the rate of chemical weathering (Drever and Zobrist, 1992). A possible contributing process to the elevated concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} is preferential weathering of reactive minerals such as pyrite and epidote in combination with the production of new reactive faces of these minerals caused by mechanical weathering processes in the active rock glacier (Hoch *et al.*, 1999). Hall *et al.* (2002) have suggested that weathering in cold regions is not temperature-limited but rather is limited by moisture availability. Within the rock glacier, moisture may always be available to both enhance chemical weathering and transport weathering products because of a combination of infiltrating snow melt and rain water along with internal ice melt.

To further constrain the weathering reactions that control the enrichment of Ca^{2+}, Mg^{2+}, and SO_4^{2-} during the late summer months, inverse geochemical models based on measured water chemistry and mineralogical data were constructed using NETPATH (Plummer *et al.*, 1994). Since trace metal data were not collected during this study, we chose to focus on the major solute constituents. We chose to model mineral reactions responsible for chemical changes from snow (using the mean value of each solute from our snow pits), to the 25 September 2003 water sample collected from the rock glacier outflow. This sample was collected late in the season and had a low charge imbalance. Two models were found that satisfy chemical and mineralogical data. Model one calls for the dissolution of pyrite, epidote, chlorite, and minor calcite and the precipitation of silica and goethite, and model two called for the dissolution of gypsum, pyrite, chlorite, and calcite and the precipitation of silica and goethite. To date no gypsum has been observed in the vicinity, so the first model appears to be more reasonable.

Source Waters and Flowpaths

Our multi-component mixing model suggests three source waters for the outflow of RG5: new water from snow melt and soils and old water from base flow. These results appear to be robust. Liu *et al.* (2004) conducted EMMA on discharge from the GL4 and Martinelli catchments in the Green Lakes Valley and reported Pearson correlations as low as 0.8. Our Pearson correlations were all greater than 0.95. Similarly, xy scatterplots of modelled versus measured concentrations all had R^2 greater than 0.95 and slopes near 1. Thus, the three source waters identified by the mixing model appear to explain the majority of the variance in the concentrations of the conservative tracers. However, because our mixing model is based on weekly measurements of water quality, this model represents average flow conditions and does not account for short-term events that last less than a week in duration.

Based on measurements of discharge and electrical conductivity from rock glaciers in Austria, Krainer and Mostler (2002) suggested that the hydrographs of active rock glaciers are characterized by two components: quickflow and base flow. They show that water released as quickflow occurred primarily in the spring and summer, was mainly derived from snow melt and rainfall, and was only subordinately derived from melting of ice. Results from our mixing model show qualitative agreement with this study. Outflow from RG5 from June into August was predominantly new water from melted surface snow and soils.

Cecil *et al.* (1998) estimated the source waters and age of melt water draining the Galena rock glacier in Wyoming using a combination of isotopic tracers, including $\delta^{18}O$, ^3H, and ^{35}S. They report that the melt water from the Galena rock glacier is composed primarily of melted surface snow and rain water rather than melted glacier ice. The $\delta^{18}O$ values in the RG5 outflow from June into August are consistent with the values that Cecil *et al.* (1998) report for the Galena rock glacier.

Somewhat surprisingly, our mixing model indicates that outflow from RG5 in July was dominated by water characterized by our zero-tension soil lysimeters placed in well-developed alpine soils. Previous research in the Green Lakes Valley has shown that fine-grain substrates on talus and blockfields behave similarly to well-developed alpine soils with respect to water and nutrient processes (Williams *et al.*, 1997; Bieber *et al.*, 1998; Ley *et al.*, 2004). Cannone and Gerdol (2003) have shown that vascular plants are common on fine-grain substrates on the surface of rock glaciers even with surface movement rates as

high as $35\,cm\,yr^{-1}$. Brown (2002) emphasizes that inputs and outputs from the soil exchange pool may potentially influence dissolved solute concentrations and hence chemical denudation rates in glacierized systems. Here it appears that fine-grained substrates on and near the surface of RG5 modify the chemical content of subsurface water in similar fashion to that of well-developed soils.

Base flow was the dominant water source from RG5 in September and October and is characterized by concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} near $1,000\,\mu eq\,L^{-1}$. An outstanding question is what is base flow? Krainer and Mostler (2002) suggest that base flow in their rock glacier system is largely derived from groundwater. Base flow is the dominant water source for the Green Lakes Valley in September and October (Liu *et al.*, 2004). Assuming that base flow at GL5 is predominantly groundwater, the $\delta^{18}O$ value of about $-14‰$ for GL5 is $4‰$ more depleted than the $-10‰$ in outflow from RG5. Similarly, the concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} in outflow from RG5 during base flow are almost a magnitude greater than in the outflow of GL5 (Figure 5). Thus, the groundwater of the Green Lakes Valley does not appear to be a major contributor to the base flow component of RG5 outflow.

Post-depositional alteration of the original isotopic values of the internal ice of RG5 may explain the large deviations in the $\delta^{18}O$ and d_{excess} values for RG5 outflow in September and October compared to other surface waters in the Green Lakes Valley. Recent findings have shown a systematic enrichment in the isotopic composition of snow melt caused by fractionation of the melt water as it percolates through the snow pack (Taylor *et al.*, 2001; Unnikrishna *et al.*, 2002). The temporal enrichment of the $\delta^{18}O$ values in snow melt is a result of depletion of $\delta^{18}O$ in the liquid water due to isotopic fractionation between the liquid phase and solid phase (Maule and Stein, 1990; Taylor *et al.*, 2001). Thus, more depleted isotopes are preferentially removed in melt water, leaving the remaining snow enriched in $\delta^{18}O$, with subsequent melt water becoming progressively enriched with time. Taylor *et al.* (2002) show that the temporal variation of $\delta^{18}O$ in annual snow melt is on the order of $+4‰$ for a variety of catchments in maritime and continental climates, including Green Lakes Valley. Liu *et al.* (2004) has shown that in the Green Lakes Valley the enrichment of $\delta^{18}O$ in melt water increases as the amount of snow melt increases. Steig *et al.* (1998) report that post-depositional processes occurring during firnification of the Galena rock glacier caused similar enrichment in the $\delta^{18}O$ values of the ice core. They report that multiple melt/freeze episodes over
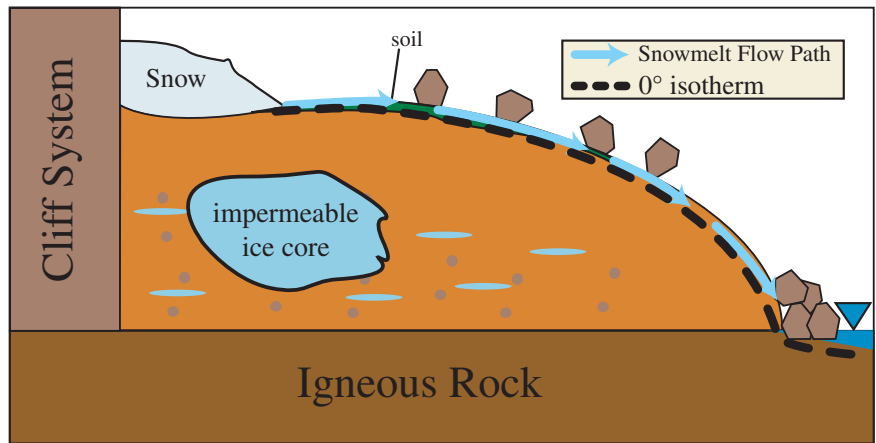
Early-Summer (Snowmelt)
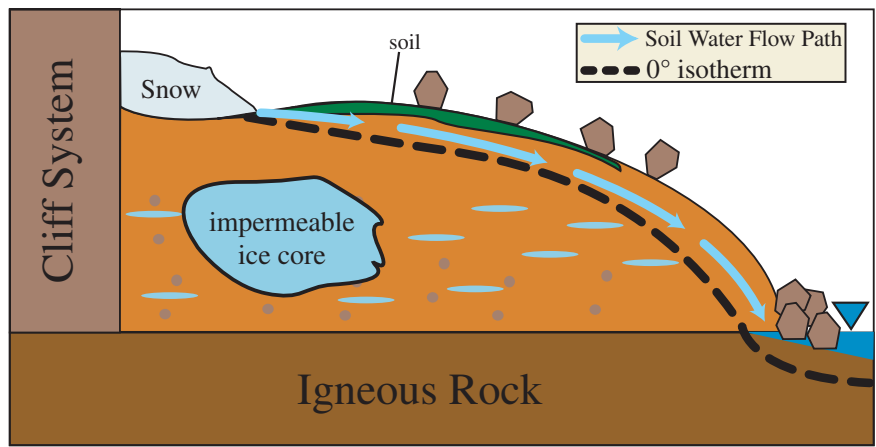
Mid-summer (soil water)
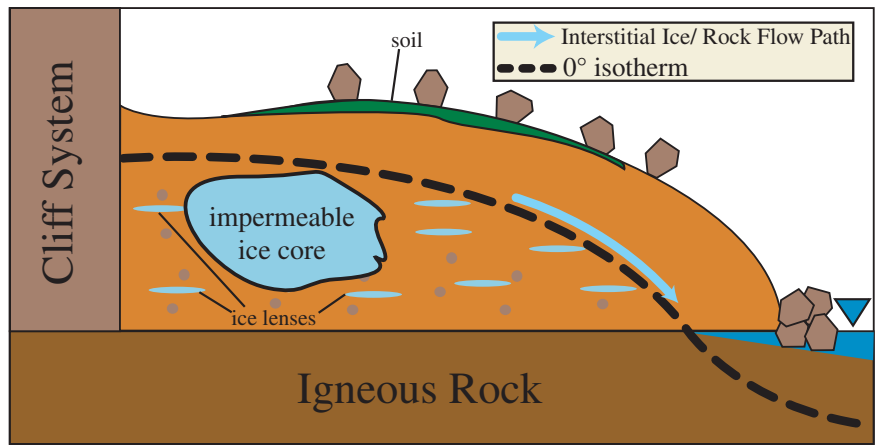
Late-summer (Base flow)

Plate 1   Schematic of hypothesized internal structure of the rock glacier, along with source waters and flowpaths as a function of time.

the course of the summer caused an enrichment of about 4‰ in the upper ice core of the Galena rock glacier.

The enrichment of $\delta^{18}O$ in the outflow of RG5 may be consistent with ice in the interior of the rock glacier that has undergone extensive melt/freeze episodes. Isotopic fractionation between infiltrating liquid water and ice will preferentially remove the lighter isotopes, leaving the heavier isotopes behind. Thus, the ice in contact with infiltrating waters would be progressively enriched in $\delta^{18}O$. If and when this ice melts and contributes to RG5 outflow, the $\delta^{18}O$ values will be enriched. Thus, the increase of $\delta^{18}O$ in the outflow of RG5 during the autumn months to -10‰, an enrichment of 4–6‰ relative to the other surface waters, is consistent with the source of the water being interior ice, originally from snow with an $\delta^{18}O$ near -20‰ that has been eluted numerous times by infiltrating liquid water.

Alternatively, some combination of isotopically-enriched rain water and ice melt could potentially provide the same isotopic values in the outflow of RG5 during September and October. The $\delta^{18}O$ of rain in the Green Lakes Valley is enriched relative to snow, with the most enriched values close to 0‰ (Liu *et al.*, 2004). However, because rainfall contributes only about 15% of annual precipitation to the Green Lakes Valley (Caine, 1986), the contribution of rain to the enriched isotopic value in the outflow of RG may be minimal. Moreover, such a rain signal is not seen in the isotopic values of other surface waters in the Green Lakes Valley.

The enrichment of d_{excess} from the outflow of RG5 during the autumn months may also be consistent with ice that has undergone multiple melt-freeze cycles. Hermann *et al.* (1981) found experimentally that the runoff of melt water from a snow pack causes enrichment of d_{excess} in the melt water. Steig *et al.* (1998) report that multiple melt-freeze cycles increased the d_{excess} in an ice core collected from the Galena rock glacier from the base value of $+11$‰ to enrichment near $+18$‰. The d_{excess} for snow at our site had a mean value of about $+11$‰, similar to the base value for the ice core from the Galena rock glacier (Steig *et al.*, 1998). The d_{excess} in RG5 outflow of near $+17.5$‰ in the autumn months was an enrichment of about $+6$‰ compared to snow. Both the d_{excess} value for RG5 outflow of $+17.5$‰ and the enrichment of $+6$‰ compared to snow are similar to the values for sections of the ice core from the Galena rock glacier that had undergone multiple melt-freeze cycles. Thus, multiple melt-freezes episodes in the interior ice of RG5 is consistent with the enriched values of $\delta^{18}O$ and d_{excess} in its outflow.

We use this information to speculate on the internal structure of this rock glacier (Plate 1). There remains much research to be done on the role of ice in rock glaciers, particularly as to whether there is a central ice core, dispersed ice throughout the rock glacier, or some combination of these scenarios (Barsch, 1996). We hypothesize that the rock glacier has an internal ice core surrounded by interstitial ice intermixed with coarse debris. The $0°C$ isotherm within the rock glacier was near the surface at the initiation of snow melt. As the surface temperature increased during the summer months (Figure 4), the $0°C$ isotherm extended lower in the rock glacier (Plate 1). In September and October of 2003, the $0°C$ isotherm extended into the interstitial ice, and some of the interstitial ice melted, contributing to base flow.

While this conceptual model of the internal rock glacier is speculative, it is consistent with source waters and flowpaths. Snow melt runoff was the dominant water source during early summer (Figure 11). Krainer and Mostler (2002) note that their dye tracer tests indicate that melt water flow through their rock glaciers in Austria most likely occurs in channelized flow along a network of conduits. At RG5, early in the melt season there most likely is substantial seasonal frost in the near-surface environment in areas with fine clasts and/or soil-like properties (Figure 4). Water at this time may percolate through the rock glacier in the void spaces created by the larger clast material where there is little seasonal frost, similar to the network of conduits suggested by Krainer and Mostler (2002). That infiltrating meltwater most likely flows near and around the permanently frozen interior of the rock glacier. The contribution of soil water increases with time as the fine-grained soils begin to melt (Plate 1).

During mid-summer, snow melt decreases in importance as the large snow field directly above RG5 melts out. Soils have gradually warmed above freezing and store some of the infiltrating melt water, chemically changing the water quality. Water above field capacity in the soil-like near surface substrate percolates through the rock glacier, providing an increasing fraction of RG5 outflow (Plate 1).

By late August, the snow field has melted and soils were below field capacity, removing those sources of water. There are no external inputs of water into the rock glacier. In 2003 the $0°C$ isotherm drops below the interstitial ice (Plate 1). The internal ice is in contact with liquid water and undergoes isotopic fractionation. Melt/freeze episodes are likely as well, causing further isotopic enrichment. It is possible that the liquid water moves along ice/rock interfaces, since the relatively high thermal conductivity of the rocks

will cause ice melt at their edges. This ice melt is in direct contact with the newly eroded rock faces, enhancing mineral weathering and transport of geochemical weathering products. Base flow thus consists predominantly of internal ice melt with enriched isotopic and geochemical values.

There may be a climate interaction with these proposed scenarios. In high snow years it is likely there is little if any ice melt from the interior of the rock glacier, consistent with the much lower concentrations of geochemical weathering products during September and October in 1998 and 1999 (Figure 6). Conversely, the highest concentrations of geochemical weathering products and the earliest occurrence of elevated geochemical weathering products in the outflow of RG5 occurred during the two most extreme drought years of 2001 and 2002. In 2001 and 2002 there may have been more interior ice melt than in 2003 because of the drought conditions during those two years. These speculations suggest that the mass balance of rock glaciers in the Colorado Front Range may be very sensitive to small changes in climate.

CONCLUSIONS

We present the first comprehensive measurements of the major solute chemistry and isotopic content of the outflow from a rock glacier. Concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} in September and October were an order of magnitude greater than in waters from glacier and blockslope discharge, and discharge from small alpine catchments. We also use the measurements of solute chemistry and isotopic content to provide the first application of hydrograph separation models to outflow from rock glaciers. Three component hydrograph separation using EMMA shows that melted snow comprised an average of 30% of RG5 outflow, soil water 32%, and base flow 38%.

Our conceptual model on the interior of the rock glacier suggests future research directions. An outstanding question is the location of the $0°C$ isotherm and how the position of the isotherm changes intra- and inter-annually. The possibility of channelized flowpaths within the rock glacier is intriguing. If they do exist, do the channels last longer than a season? Another question is whether sections of the rock glacier remain above freezing year-round, potentially keeping flowpath channels open?

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