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Mechanisms for chemostatic behavior in catchments: Implications for CO_2 consumption by mineral weathering

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ABSTRACT

Concentrations of weathering products in streams often show relatively little variation compared to changes in discharge, both at event and annual scales. In this study, several hypothesized mechanisms for this "chemostatic behavior" were evaluated, and the potential for those mechanisms to influence relations between climate, weathering fluxes, and CO_2 consumption via mineral weathering was assessed. Data from Loch Vale, an alpine catchment in the Colorado Rocky Mountains, indicates that cation exchange and seasonal precipitation and dissolution of amorphous or poorly crystalline aluminosilicates are important processes that help regulate solute concentrations in the stream; however, those processes have no direct effect on CO_2 consumption in catchments. Hydrograph separation analyses indicate that old water stored in the subsurface over the winter accounts for about one-quarter of annual streamflow, and almost one-half of annual fluxes of Na and SiO_2 in the stream; thus, flushing of old water by new water (snowmelt) is an important component of chemostatic behavior. Hydrologic flushing of subsurface materials further induces chemostatic behavior by reducing mineral saturation indices and increasing reactive mineral surface area, which stimulate mineral weathering rates. CO_2 consumption by carbonic acid mediated mineral weathering was quantified using mass-balance calculations; results indicated that silicate mineral weathering was responsible for approximately two-thirds of annual CO_2 consumption, and carbonate weathering was responsible for the remaining one-third. CO_2 consumption was strongly dependent on annual precipitation and temperature; these relations were captured in a simple statistical model that accounted for 71% of the annual variation in CO_2 consumption via mineral weathering in Loch Vale.

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1. Introduction

Hydrolysis of silicate minerals by reaction with carbonic acid and water is an important mechanism for regulating CO_2 concentrations in the atmosphere (Berner, 1992; Berner et al., 1983; Urey, 1952; Walker et al., 1981). CO_2 is transferred from the atmosphere into soil by a combination of photosynthesis, root respiration, and microbial decomposition of organic matter. As a result, CO_2 concentrations often are 10 to 100 times higher in the soil than in the atmosphere (Drever, 1994). Some of the soil CO_2 dissolves in soil water forming carbonic acid, which promotes mineral weathering reactions that consume CO_2 and produce bicarbonate and other weathering products, as in the following reaction for albite feldspar:

$$\text{Albite} + 5.5H_2O + CO_2 = HCO_3^- + Na^+ + 2H_4SiO_4 + 0.5\text{Kaolinite} \quad (1)$$

Dissolved bicarbonate is transported by rivers to the ocean, where it may combine with Ca or Mg to form carbonate minerals that are subsequently buried in ocean sediments. CO_2 may be sequestered in this manner for millions of years until released by volcanism or metamorphism (Berner et al., 1983; Urey, 1952).

Carbon sequestration strategies have been proposed that take advantage of CO_2 consumption by silicate weathering via carbonic acid reactions (Oelkers et al., 2008). One of the main advantages of using carbonation reactions to sequester carbon is that the solid products (carbonate minerals) are environmentally safe and stable, and potential problems with leakage of CO_2 from underground storage sites are avoided. The primary disadvantage of silicate-carbonation reactions is that they are slow under earth surface conditions. Investigation of controls on silicate-carbonation reactions in natural settings may provide information that can be used for enhancing CO_2 sequestration via silicate weathering.

Estimates of current global consumption of CO_2 by mineral weathering range from 0.1 to 0.44 Gt C year^{-1} (Ammiotte-Suchet and Probst, 1995; Ammiotte-Suchet et al., 2003; Berner et al., 1983; Gaillardet et al., 1999; Holland, 1978). These estimates have significant uncertainty, however, largely because of the confounding effects of spatial variations in lithology, soil development, vegetation, precipitation, and temperature (Kump, 2000). In general, chemical weathering rates correlate well with lithology and runoff, but

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relations between weathering rates and soil development, vegetation, and temperature are equivocal (Ammiotte-Suchet et al., 2003; Gaillardet et al., 1999; Kump, 2000).

Problems with covariance among variables are inevitable when studying large river basins, as is common in global scale studies. White and Blum (1995) attempted to minimize the covariance problem by investigating relations between chemical weathering and climate in 68 small, mono-lithologic (granitic) basins distributed around the world. Fluxes of silica and sodium were positively correlated with precipitation, runoff, and temperature, suggesting that there may be a negative feedback between climate and chemical weathering that could help regulate atmospheric CO_2. There was, however, no correlation between fluxes of other weathering products and climate, which the authors attributed to only partial success in controlling for variations in lithology and other variables that may have obscured the climate signal (White and Blum, 1995).

It may be possible to obtain a more robust climate signal by using a temporal rather than a spatial approach when investigating relations between climate and weathering fluxes. Using data from a subset of sites where multiple years of data were available, White and Blum (1995) noted that inter-annual variations in weathering fluxes and runoff were more strongly correlated than spatial variations in weathering fluxes and runoff were among their 68 study sites. In another temporal analysis, a five-year field weathering experiment was conducted at a 39 m^2 alpine microcatchment in the Colorado Rocky Mountains (Clow and Drever, 1996). Water inputs were varied by supplementing precipitation with varying amounts of deionized water, and fluxes of weathering products were calculated based on outflow concentrations, discharge, and mineral surface area measurements (Clow and Drever, 1996). Concentrations of weathering products declined only modestly in response to increased water inputs, and as a result, weathering fluxes had a nearly 1:1 relation to discharge. Flushing of soil pore waters accounted for only a small part of the increased solute flux, indicating that concentrations of weathering products were regulated in some manner by reactions in the soil.

An investigation of concentration–discharge relations at 59 minimally-impacted, headwater catchments in the U.S. Geological Survey Hydrologic Benchmark Network (HBN) indicated that regulation of concentrations of weathering products is common (Godsey et al., 2009). When concentration–discharge relations are expressed as log concentration:log discharge, a ratio of −1 is consistent with simple mixing of dilute precipitation with concentrated groundwater, and a ratio of zero occurs when concentrations do not change in response to changes in discharge (Godsey et al., 2009). At most of the HBN sites, the log concentration:log discharge ratios were between −0.05 and −0.15, indicating that variations in solute concentrations typically were much smaller than variations in discharge; the authors referred to this phenomenon as "chemostatic" behavior (Godsey et al., 2009).

Chemostatic behavior in catchments has important implications for regulation of CO_2 in the atmosphere; if precipitation increases (or decreases) in response to climate change, consumption of CO_2 by chemical weathering may respond similarly, providing a negative feedback on atmospheric CO_2 concentrations. Recent observations and climate modeling indicate an intensification of the hydrologic cycle in response to global warming (Huntington, 2006), so quantifying the strength of the weathering feedback is important. Hypothesized mechanisms for chemostatic behavior include cation exchange, flushing of soil pore water and groundwater, seasonal dissolution/precipitation of amorphous aluminosilicates, changes in reactive mineral surface area, and decreased weathering rates through a chemical affinity effect (Burch et al., 1993; Clow and Drever, 1996; Drever and Clow, 1995; Drever et al., 1994; Swoboda-Colberg and Drever, 1993). Some of these mechanisms are recognized as important catchment processes (e.g., soil water flushing, cation exchange), but the importance of others in natural systems is uncertain (e.g., dissolution/precipitation of amorphous aluminosilicates, chemical affinity effects on weathering rates). Some of the hypothesized mechanisms consume CO_2 while others do not; this will have implications for the strength of the weathering feedback.

A critical evaluation of possible mechanisms for chemostatic behavior is needed in order to better understand feedbacks between climate and mineral weathering; these feedbacks are important parameters in global CO_2-weathering models such as GEM-CO_2 (Ammiotte-Suchet and Probst, 1995) and GEOCARB-III (Berner and Kothovala, 2001), which are used to understand past and predict future atmospheric CO_2 concentrations. Evaluation of chemostatic processes requires detailed physical and chemical information on the "critical zone", which is the outer layer of the Earth's surface where interactions between hydrosphere and lithosphere occur. These data are available for Loch Vale, which is a high-elevation catchment in the Colorado Rocky Mountains that has been extensively studied since the early 1980s, and is currently one of five study sites in the USGS Water, Energy, and Biogeochemical Budgets (WEBB) program (Baedecker and Friedman, 2000; Baron, 1992; Clow et al., 2000; Lins, 1994). The objective of this paper is to describe an investigation of hypothesized mechanisms for chemostatic behavior, and of relations between climate, weathering fluxes, and CO_2 consumption in Loch Vale. By focusing on a single, well-studied site, we were able to reduce uncertainty associated with confounding variables, such as lithology, soil type and amount, and vegetation.

1.1. Description of study site

Our approach was to evaluate possible mechanisms for chemostatic behavior in the Andrews Creek subcatchment, which is a small, steep, alpine basin in Loch Vale. The Andrews Creek subcatchment is 183 ha in size, has a median slope of 33°, and ranges in elevation from 3211 m at the stream gage to 4009 m on the Continental Divide, which forms the western boundary. The basin is underlain by granitic gneiss and Silver Plume granite, which have similar mineralogy and chemical composition (Mast, 1992). Mineral weathering reactions have been well defined for the Andrews Creek subcatchment by Mast (1992), who characterized bedrock and soil mineralogy using petrographic, chemical, and x-ray diffraction techniques. The dominant primary minerals include quartz (30–41%), oligoclase (26–28%), microcline (9–34%), and biotite (10–16%); trace amounts of accessory calcite are present in microcrystalline veins (Mast, 1992). Secondary minerals in the soil include smectite, kaolinite, and illite. Broad x-ray diffraction peaks indicate that much of the smectite is either poorly crystalline or was a mixed-layer smectite–illite (Mast, 1992). Amorphous clay minerals with a composition similar to kaolinite were identified by selective extraction on the <2 μm fraction (Mast, 1992). The Andrews Creek subcatchment is 75% unvegetated bedrock and talus, 23% tundra with low growing grasses and herbaceous plants, 1% wet meadow with sedges and grasses, and 1% spruce/fir forest (*Picea engelmanii* and *Abies lasiocarpa*) (Arthur, 1992) (Fig. 1). A 2 ha glacial tarn, which is the only standing water body in the subcatchment, exists at the base of an 8.3 ha glacier that occupies a headwall cirque. Estimated mean annual air temperatures range from 0.5 °C at the basin outlet to −5.0 °C on the Continental Divide (Clow et al., 2003). Mean annual precipitation during 1994–1999 was 101 cm, with 65% to 85% of it falling as snow that accumulates in seasonal snowpacks, which persist from November through June.

Discharge (streamflow) and climate are monitored continuously at three sites in Loch Vale, including one on Andrews Creek at the basin outlet. Stream chemistry is measured weekly during April through September, and monthly during the rest of the year. Soil moisture, temperature, and soil solution chemistry have been measured for varying lengths of time on talus slopes, in the meadow, and in the forest. Precipitation chemistry is measured on weekly composited samples as part of the National Atmospheric Deposition Program (NADP).

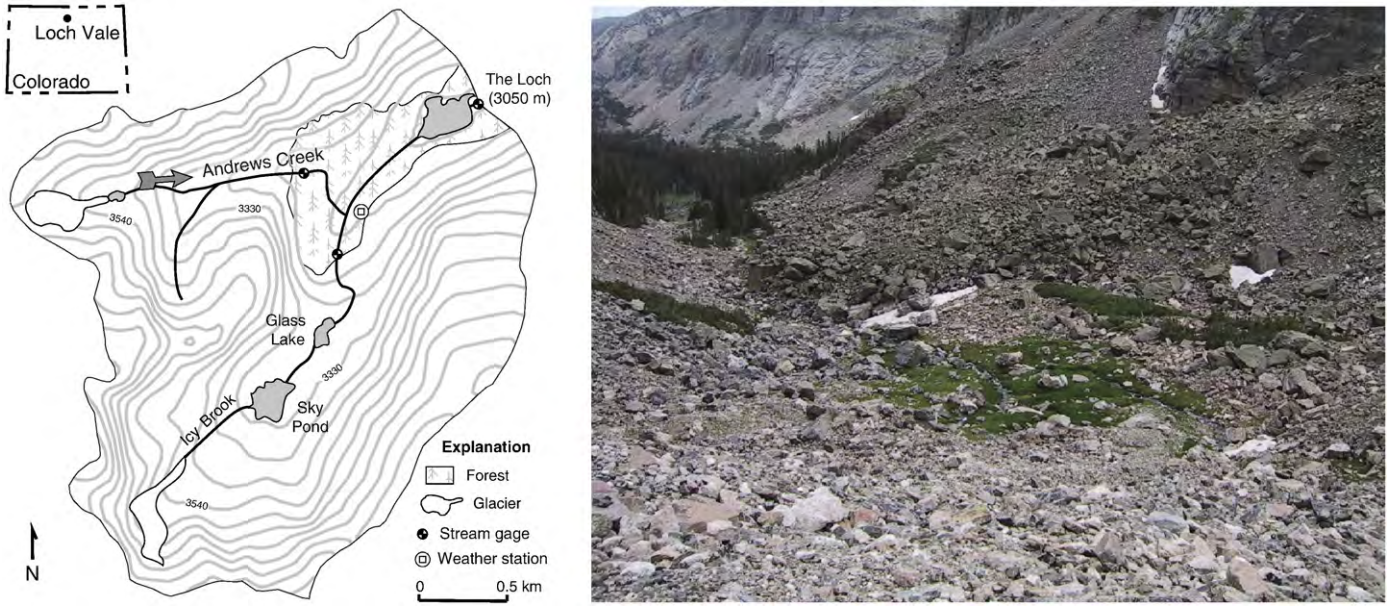

Fig. 1. Map of Loch Vale catchment and photograph of Andrews Creek subcatchment above stream gage, looking down valley. Arrow on map indicates location and direction of photo. Contour interval is 70 m.

2. Methods

2.1. Sample collection and analyses

Stream water samples were collected using standard USGS grab sampling methods along well-mixed reach of the stream (Wilde et al., 1998). Soil solutions were collected using suction lysimeters. Samples were kept cool and in the dark and were filtered within 24 h of collection through 0.45 μm polysulfone membrane filters. Samples were analyzed for bicarbonate alkalinity (HCO_3) by Gran titration, calcium (Ca), magnesium (Mg), silica (SiO_2), sodium (Na), potassium (K), and aluminum (Al) by inductively coupled plasma (ICP), chloride (Cl), sulfate (SO_4), and nitrate (NO_3) by ion chromatography, dissolved organic carbon (DOC) by ultra-violet promoted persulfate oxidation with infrared detection, and dissolved CO_2 using an infrared gas analyzer. pH was measured in the laboratory on air-equilibrated samples.

Quality assurance procedures included collection and analyses of field blanks and field splits, each of which comprised 5% of the total sample load. Solute concentrations in all of the field blanks were less than the detection limit for all constituents ($\leq$1 μmol L^{-1}). Median differences of field splits were $\leq$1 μmol L^{-1}, except for alkalinity and Ca, which had median differences $\leq$2 μmol L^{-1}.

2.2. Solute flux calculations

Stream solute fluxes are the product of discharge times concentration. Discharge was measured continuously, but because concentrations were measured at discrete intervals, it was necessary to estimate concentrations during the intervals between sampling events.

Solute concentrations were estimated using a regression modeling approach based on observed concentrations, discharge, and day of year, similar to the method described by Aulenbach and Hooper (2006). The method involves modeling concentration–discharge relations using a hyperbolic function (Johnson et al., 1969); the function is modified to account for seasonality effects using sine and cosine functions with periods of 1 year and 0.5 years, which captures asymmetrical annual cycles in concentrations (hysteresis) (Aulenbach and Hooper, 2006). Separate models, with a daily time step, were created for each solute. Estimated daily concentrations were multiplied by average daily discharge to obtain daily fluxes, which were summed to obtain annual fluxes for each water year (water years begin October 1 and end September 30).

2.3. Geochemical modeling

Geochemical modeling, including calculation of cation exchange equilibria, mineral saturation indices, and solute speciation, was performed using the PHREEQC (v2) software program; ion exchange selectivity coefficients, equilibrium constants, and rate constants were taken from the PHREEQC thermodynamic database (Parkhurst and Appelo, 1999). Multi-component cation exchange equilibria were calculated for 10 °C using the Gaines–Thomas equation (see Section 3.2), with exchangeable cation ratios taken from Baron et al. (1992). Saturation indices were calculated for Andrews Creek using measured water temperatures, pCO_2, and solute concentrations (see Section 3.4). The evolution of solute concentrations and saturation indices in deionized water–rock mixtures was simulated at 10 °C with pCO_2 fixed at 10^{-2} (see Section 3.5); these conditions are representative of summer soil conditions in Loch Vale.

2.4. Experimental methods

Laboratory experiments were used to test the importance of flow conditions on mineral dissolution rates; a detailed description of methods and results are provided in Clow (1992). Mineral soil collected from an alpine microcatchment in Loch Vale was sieved to obtain the 106–208 μm size fraction, which was cleaned by washing with deionized water. Mineral surface areas were quantified using BET nitrogen adsorption measurements (Brunauer et al., 1938; Clow and Drever, 1996). The soil material was split into two portions for use in mineral dissolution rate experiments. Mineral dissolution rates were measured using fluidized-bed reactors (Chou and Wollast, 1985) and saturated columns (White and Brantley, 2003); these two experimental systems provide fundamentally different hydrologic conditions. Fluidized-bed reactors keep mineral grains in suspension by injecting fluid from the bottom of the reaction vessel, and provide maximum contact between mineral grains and the fluid. In saturated columns, the mineral grains are at rest and fluid flows by gravity through the system; this provides hydrologic conditions that are more representative of nature than that of fluidized-bed reactors. Flexible

tubing connected to the bottom of the column was routed upward so that the outlet was slightly above the top of the sieved soil in the column; this maintained the soil material in a constantly saturated state.

The soil material was reacted with deionized water adjusted to pH 5.6 using 2 mM ammonium acetate. Temperatures were maintained at 19 ± 1.5 °C. Dissolution rates were calculated from solute release rates after the systems had reached steady state. The fluidized-bed reactors were operated for 960 h (40 days), and the saturated columns were operated for 2000 h (83 days). A metering pump was used to add and remove fluid from the fluidized-bed reactors at 6.2 ± 0.6 ml h^{-1}; the residence time in the fluidized-bed reactors was 3 h. The flow rate through the saturated columns was 5.3 ± 1.5 ml h^{-1}, and the residence time was 2 h.

After measuring pH, samples were acidified to pH 3 with high-purity nitric acid for preservation. Silica was measured using the silicomolybdate method; calcium, magnesium, sodium, and potassium were analyzed using flame AA on samples spiked with $SrCl_2$ to suppress interferences; aluminum was measured by graphite furnace atomic absorption spectrometry (Clesceri et al., 1999).

3. Results

3.1. Concentration–discharge relations and weathering fluxes

Concentrations of weathering products in Andrews Creek were inversely related to discharge, as has been documented for many other sites in previous studies (e.g., Godsey et al., 2009; Hall, 1970; Johnson et al., 1969). Interestingly, however, variations in concentration were much smaller than variations in discharge. Concentrations of silica, for example, varied by a factor of 3, from 20 to 63 μmol L^{-1} in Andrews Creek, while discharge varied over several orders of magnitude, from 0.001 to 0.4 $m^3 s^{-1}$ (Fig. 2a). The slope of the log Si:log discharge regression line was −0.12 (Fig. 2b), and log concentration:log discharge slopes for the other major weathering products (Ca, Mg, Na, K, alkalinity; not shown for clarity) ranged from −0.11 to −0.14. These results indicate that chemostatic behavior is important in the Andrews Creek subcatchment because the slopes were much closer to 0 than to −1; the slopes were slightly more negative than those documented for individual samples at most of the HBN watersheds (Godsey et al., 2009).

Chemostatic behavior also occurs at the annual time scale in Andrews Creek (Fig. 3a). Correlations between annual volume-weighted mean (AVWM) concentrations and annual runoff were relatively weak, as expected if solute concentrations are regulated by catchment processes; the squares of Pearson correlation coefficients (*r*-squares) for weathering products ranged from only 0.30 to 0.48, and *r*-squares for solutes derived primarily from atmospheric deposition (Cl, SO_4, and NO_3) were even weaker. Slopes of regressions of log annual volume-weighted mean (AVWM) concentrations of weathering products against log annual runoff ranged from −0.24 to −0.40 (Table 1), slightly more negative than the slopes were for individual samples (e.g., Fig. 2b). The AVWM slopes also were slightly more negative than those for most HBN sites (Godsey et al., 2009); however, this is not surprising given the relative scarcity of soil in the Andrews Creek subcatchment. The effect of processes that lead to chemostatic behavior should be proportional (although not necessarily linear) to the amount of soil in a given basin because the soil environment is where most geochemical reactions occur.

Annual fluxes of weathering products were strongly related to annual runoff, as expected given that AVWM concentrations were relatively invariant (Fig. 3b, Table 1). The *r*-squares for weathering products ranged from 0.47 to 0.90, and the slopes of the relations ranged from 0.63 to 0.79 (Table 1). Silica had the highest *r*-square and relative slope, suggesting that it may be more strongly influenced by chemostatic processes than other major weathering products. Dissolved organic carbon (DOC) also had a relatively high slope and

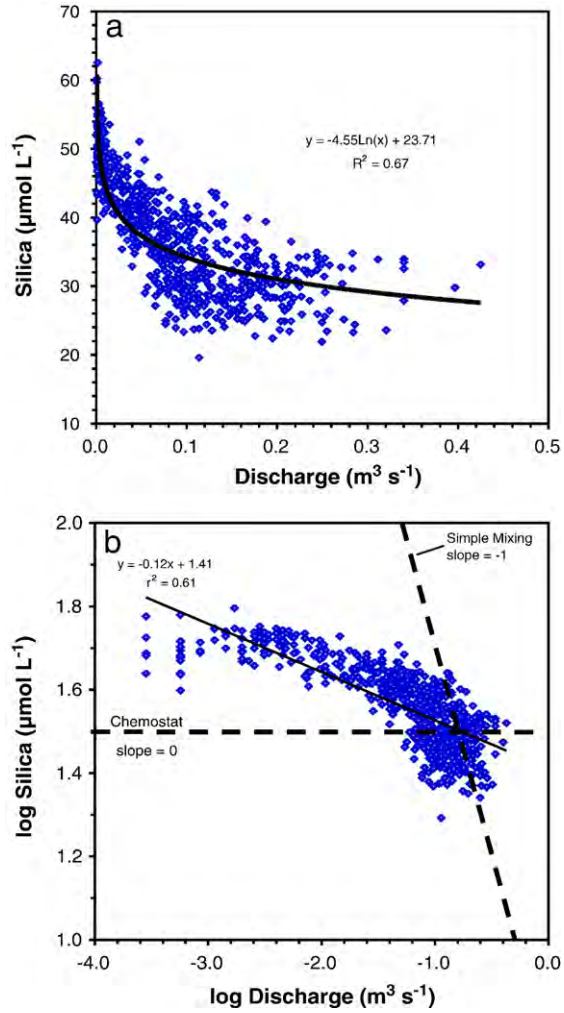

Fig. 2. Scatter plots showing (a) silica concentrations as a function of discharge, and (b) log silica concentrations as a function of log discharge in Andrews Creek, 1993–2007. Lines showing slopes of relations expected from simple mixing and chemostatic behavior are shown in (b) for reference.

r-square, indicating that production and/or flushing of decay products of organic matter are positively related to annual precipitation and runoff (Table 1).

3.2. Cation exchange

Cation exchange in Loch Vale soils is driven by seasonally varying inputs of carbonic, nitric, and sulfuric acids. Carbonic acid inputs to soils increase during spring as warming temperatures stimulate respiration and microbial decomposition of organic matter. When snowmelt begins, carbonic acid is supplemented by nitric and sulfuric acid released from the snowpack, and soils are flushed with dilute, slightly acidic melt water. Multi-component cation exchange equilibria indicate that the flushing should cause hydrogen in snowmelt to displace base cations (Ca, Mg, Na, K) from exchange surfaces and into soil solution. The hydrogen–base cation exchange reaction is reversed later in the year as hydrogen inputs from snowmelt decline, and new base cations are produced by mineral weathering.

To test for the importance of cation exchange in controlling stream water chemistry, seasonal patterns in Ca:Na, Mg:Na, DOC, and CO_2 concentrations in Andrews Creek were evaluated. Ca and Mg are by far the dominant base cations on cation exchange sites in Loch Vale alpine soils, accounting for 80% and 13% of base cations, respectively (Baron et al., 1992). Na is the least important exchangeable cation,

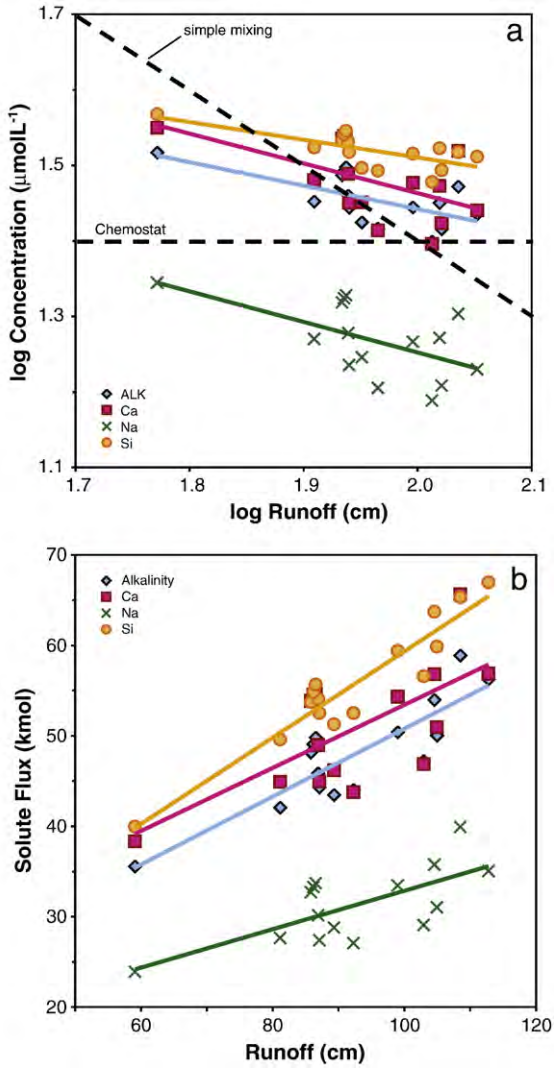

Fig. 3. Scatter plots for Andrews Creek (1993–2007) showing (a) log annual volume-weighted mean concentrations as a function of log annual runoff, and (b) solute fluxes as a function of annual runoff. Lines showing slopes of relations expected from simple mixing of dilute precipitation with relatively concentrated groundwater and from chemostatic behavior are shown in (a) for reference.

accounting for only 2 to 3% of base cations on the exchange pool. Even after taking differences in cation selectivity coefficients into account, the springtime pulse of acidity should release Ca and Mg from exchange sites in greater amounts than Na. If carbonic-acid-driven cation exchange is an important source of solutes to the stream, there should be springtime peaks in stream water Ca:Na and Mg:Na ratios as well as in products of organic matter decomposition, such as DOC and CO_2.

Modeled Ca:Na, DOC (calculated as described in Section 2.2), and smoothed discharge are shown in Fig. 4a; seasonal patterns in Mg:Na and CO_2 concentrations are omitted for clarity but were very similar to Ca:Na and DOC, respectively. Seasonal variations in Ca:Na and Mg:Na occurred as hypothesized, with highest ratios during the rising limb of the snowmelt hydrograph and lowest ratios during low flow conditions in late summer and winter (Fig. 4a). Interestingly, a second peak in Ca:Na and Mg:Na occurred during fall, probably in response to rain storms, which may have flushed dissolved organic acids through the soil. Seasonal patterns in DOC and CO_2 were similar to Ca:Na and Mg:Na, although the DOC and CO_2 concentration peaks were slightly shifted towards earlier in the year (Fig. 4a). This suggests that carbonic acid inputs may slightly precede nitric and sulfuric acid inputs to soils.

If we make a simplifying assumption that cation exchange is the dominant process affecting seasonal variations in stream water Ca:Na, we may estimate the relative importance of cation exchange in controlling stream water Ca fluxes. The AVWM Ca:Na in Andrews Creek during 1993–2007 was 3.25 ± 0.03 (average $\pm$ 1 standard deviation). Differences in Ca:Na from the 1993–2007 AVWM Ca:Na (ΔCa:Na) were calculated at a daily time step (ΔCa:Na = AVWM Ca:Na − modeled daily stream water Ca:Na). ΔCa:Na values were positive during snowmelt and negative during the remainder of the year. Daily fluxes to and from the exchange pool were calculated

Table 1
Statistical relations between log annual volume-weighted mean (AVWM) concentrations (μeq L^{-1}) and log annual runoff (m), and between solute fluxes (kmol) and runoff (m) at Andrews Creek, 1993–2007.

Solute	Log AVWM concentration: log discharge		Flux:runoff	
	Slope	*r*-square	Slope	*r*-square
ALK	−0.39	0.40	0.72	0.75
Ca	−0.39	0.30	0.63	0.47
Mg	−0.40	0.30	0.64	0.48
Na	−0.36	0.32	0.63	0.49
K	−0.24	0.30	0.67	0.55
Si	−0.24	0.48	0.79	0.90
Cl	−0.50	0.30	0.77	0.79
SO_4	−0.48	0.10	0.55	0.38
NO_3	−0.08	0.24	0.55	0.25
DOC	–	0.05	0.88	0.82

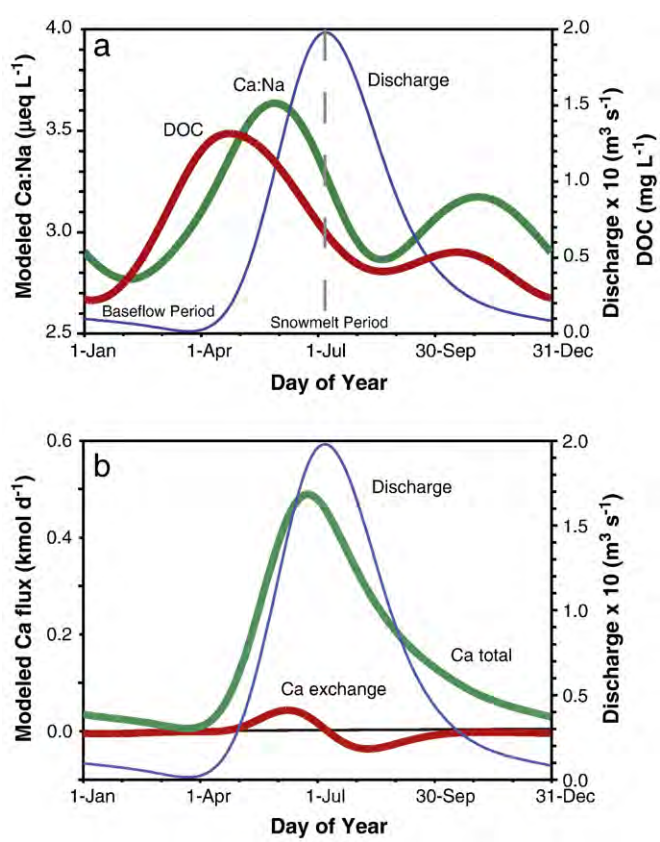

Fig. 4. Seasonal patterns in (a) Ca:Na concentrations, dissolved organic carbon (DOC) concentrations, and discharge, and (b) fluxes of calcium (Ca) in Andrews Creek. Concentrations were modeled based on discharge and day of the year using data from 1993–2007.

based on ΔCa:Na and daily discharge (Fig. 4b). Results indicate that on a seasonal basis, cation exchange increased stream water Ca fluxes by up to 11% during snowmelt, decreased stream water Ca fluxes by up to 13% during late summer, and had a minimal affect at other times of the year (Fig. 4b). It is worth noting that although cation exchange affects stream water chemistry and seasonal patterns in solute fluxes, it should not result in any net consumption of CO_2 on an annual basis unless there are long-term trends in atmospheric deposition or climate that alter soil acidity. Furthermore, it should not affect net annual cation fluxes in areas unaffected by acidic deposition.

3.3. Flushing of subsurface waters

Flushing of water from the subsurface by snowmelt and rain is a well-documented phenomenon that contributes weathering products to streams (e.g., Christophersen and Hooper, 1992; Hall, 1970; Hooper et al., 1990). Log concentration:log discharge ratios for Andrews Creek and the HBN catchments are close to zero (−0.11 to −0.14), however, indicating that flushing alone cannot explain observed concentration–discharge relations (Fig. 2; Godsey et al., 2009). The relative contribution of subsurface water flushing can be evaluated by performing hydrograph separation analyses using conservative tracers, such as the $\delta^{18}O$ of water (Mast et al., 1995; Maule and Stein, 1990; Moore, 1989). This method relies on differences in the isotopic or chemical signature of "new" water, such as precipitation, and "old" water that is flushed from the subsurface (Genereux and Hooper, 1998; Rodhe, 1998). The fraction of old water in the stream (X) may be calculated as:

$$X = (C_s - C_n) / (C_o - C_n) \quad (2)$$

where C_s, C_n, and C_o are tracer concentrations in the stream, precipitation, and subsurface water, respectively (Mast et al., 1995; Rodhe, 1998).

Mast et al. (1995) used $\delta^{18}O$ in a hydrograph separation analysis to quantify new and old water in Loch Vale for the 1994 snowmelt period. Results indicated that snowmelt was the dominant contributor to streamflow, and old water was rapidly flushed from the subsurface (Mast et al., 1995). Using the methods described in Mast et al. (1995), we extended their analysis to include six full years of data (1994–1999). The purpose was to characterize variability in the fraction and volume of old water contributions to the stream during snowmelt. In this context, we define old water as water that resided in the subsurface during winter and was flushed into the stream by infiltrating snowmelt.

An example of the new hydrograph separation results is provided in Fig. 5. Old water accounted for 100% of streamflow during late winter and during the first part of the snowmelt period. The relative contribution of old water to the stream began to decline shortly after snowmelt began, and the absolute amount (flux) of old water generally peaked about mid-way through the rising limb of the snowmelt period (Fig. 5). Thereafter, relative and absolute amounts of old water contributions gradually declined until snowmelt began the following year.

The amount of old water flushed from the subsurface during each annual snowmelt cycle was calculated as the sum of the daily old water fluxes from April 1 to March 31 of the following year. During the six annual snowmelt cycles investigated, old water accounted for 26 ± 6 cm of runoff or 26 ± 6% of total annual streamflow. This is approximately 33% of total storage capacity of subsurface materials in Loch Vale, which have been estimated to be equivalent to 78 ± 12 cm (Clow et al., 2003). Assuming all of the old water had the composition of stream water measured during winter (baseflow), old water accounted for 47 ± 12% and 45 ± 11% of annual fluxes of Na and SiO_2 in the stream. This indicates that even in the Andrews Creek subcatchment, which has relatively little well-developed soil, subsurface storage contributes a substantial fraction of the annual solute load to the stream.

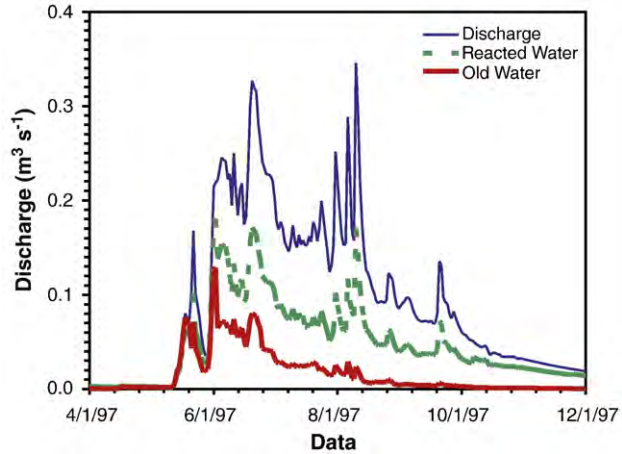

Fig. 5. Discharge and calculated amounts of "old" water and "reacted" water in Andrews Creek during May–July 1997. Old water refers to isotopically heavy water stored in the subsurface during winter and flushed into the stream during snowmelt. Reacted water refers to any water that flowed through the subsurface and acquired silica during transport (Mast et al., 1995).

3.4. Seasonal precipitation/dissolution of amorphous aluminosilicates

In contrast with hydrograph separations using $\delta^{18}O$, which quantify new and old water, hydrograph separations using weathering products, such as SiO_2, provide an indication as to the importance of water routed through the subsurface (Mast et al., 1995). The subsurface water component consists of old water, which contains weathering products produced during the winter, and new snowmelt water that moves through the subsurface and acquires SiO_2 during transport. We refer to any water that has moved through the subsurface and acquired SiO_2 as "reacted water", which may be quantified by substituting SiO_2 for $\delta^{18}O$ in Eq. (2) (Mast et al., 1995).

As shown in Fig. 5, the amount of reacted water far exceeds the amount of old water in the stream during most of the year. The difference in amounts of old and reacted water is indicative of the importance of reactions in the soil that release SiO_2 to solution relatively rapidly. Weathering of primary silicate minerals in the bedrock probably cannot account for the regulation of SiO_2 at seasonal and sub-seasonal time scales because rates of silicate mineral dissolution are too slow. Hydrologically driven seasonal cycles of precipitation and dissolution of amorphous or poorly crystalline secondary minerals is a more likely explanation. To investigate this possibility, mineral saturation indices (Ωs) were calculated for plausible secondary minerals based on Andrews Creek chemistry during 2001. Saturation indices are a measure of disequilibrium or degree of oversaturation or undersaturation with respect to specific minerals, and may be calculated as:

$$\Omega = \log(IAP / K_{eq}) \quad (3)$$

where IAP is the ion activity product and K_{eq} is the equilibrium constant for the reaction (Drever, 1997).

Saturation indices varied seasonally for important mineral phases, including plagioclase (albite), kaolinite, quartz, amorphous silica, smectite (Na-beidellite), and amorphous aluminosilicate (Fig. 6). Saturation indices for quartz and smectite (Na-beidellite) were negative during snowmelt (April through July), indicating undersaturation, and were positive during winter, indicating oversaturation (Fig. 6). In theory, smectite and quartz could help regulate cation and silica concentrations through seasonally cycles of precipitation and dissolution; the minerals would tend to dissolve during snowmelt when soils are flushed with dilute melt water, and precipitate during

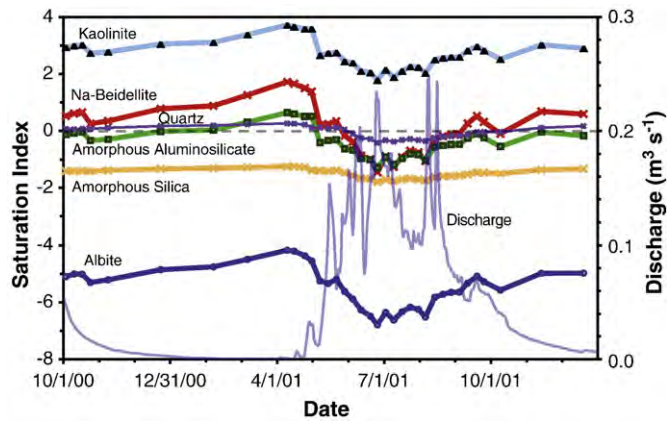

Fig. 6. Discharge and saturation indices for kaolinite, amorphous kaolinite, and albite in Andrews Creek during October 2000–December 2001.

winter when solute concentrations in the soil increase due to increased water residence times. Seasonal variations in temperature compound the effect; cold temperatures during winter make Ωs more positive, and warmer temperatures during summer make Ωs more negative.

Regulation of cation and silica concentrations by poorly crystalline smectite is plausible; it is kinetically labile and has been identified in Loch Vale soils. However, the kinetics of quartz dissolution and precipitation are too slow for it to exert substantial control on stream water silica concentrations. An amorphous silica phase would react more quickly than quartz, but amorphous silica was undersaturated in the stream throughout the year, and thus is unlikely to regulate stream water silica concentrations (Fig. 6). An amorphous aluminosilicate with a composition similar to kaolinite has been identified in Loch Vale soils, and may be a more likely candidate for controlling stream water silica concentrations (Mast, 1992). Calculating a saturation index for this phase is problematic, however, because equilibrium constants for amorphous aluminosilicates are not available. In order for it to regulate silica concentrations in Andrews Creek, it would need to have a K_{eq} of approximately 10^{13}. Obviously, this K_{eq} value has high uncertainty and is not necessarily transferable to other locations. This raises the issue of uncertainty in thermodynamic data in general; mineral solubility constants can vary substantially among databases, particularly for poorly crystalline phases (Yang and Steefel, 2008). In addition, equilibrium constants are not available for some common minerals, such as oligoclase and smectite, because they form part of a solid-solution series; thus, approximations are required, such as substitution of albite for oligoclase and Na-beidellite for smectite, as was done in this study when calculating saturation indices. Despite these uncertainties, the interpretation that seasonal variations in mineral saturation indices occur in nature and may lead to cyclical precipitation and dissolution of amorphous mineral phases is robust.

These results are consistent with observations by Garrels (1967) and Garrels and Mackenzie (1967) that the composition of water from igneous rock terrains often appears to be controlled by equilibrium with kaolinite and smectite. Garrels and Mackenzie (1967) also noted that the controlling solids were not necessarily crystalline. Poorly crystalline secondary minerals, such as amorphous silica, amorphous aluminosilicates, or poorly crystalline smectite, may be precursors to crystalline minerals or intermediate phases during transitions between two crystalline minerals (Mast, 1992). We suggest that lack of crystallinity may be a prerequisite for chemostatic behavior at seasonal and sub-seasonal time scales. Amorphous phases tend to precipitate and dissolve relatively rapidly (Drever, 1997), whereas the kinetics of precipitation/dissolution of highly crystalline secondary minerals probably are too slow to explain chemostatic behavior.

3.5. Chemical affinity

Flow through soils exhibits substantial spatial and temporal variability, which may affect dissolution rates of primary minerals, and thus, CO_2 consumption by mineral weathering. Heterogeneous flow through soils leads to spatial variability in water residence times, concentrations of weathering products, and saturation states. Solutions in regions of low flow rates (micropores and microcracks) tend to have long residence times, high concentrations of weathering products, and are closer to saturation with respect to primary minerals than solutions in macropores.

Early, simple linear models of weathering rates suggested that soil solutions typically were too far from equilibrium with respect to most primary minerals to be affected by saturation indices. According to transition state theory, dissolution rates are a function of distance from equilibrium (Aagard and Helgeson, 1982; Drever, 1997). For a simple linear reaction:

$$Rate = k[1-\exp(\Delta Gr / RT)] \quad (4)$$

where k is the forward rate constant, R is the gas constant, and T is absolute temperature. ΔGr is the chemical affinity of the reaction and is related to Ω:

$$\Delta Gr = RT\,2.303\Omega. \quad (5)$$

After rearranging, we obtain the dissolution rate as a function of saturation index:

$$Rate = k[1-\exp(2.303\Omega)]. \quad (6)$$

Recent experiments, however, suggest that for some minerals, including feldspars, the relation between dissolution rate and Ω is not well explained by this simple linear model (Burch et al., 1993; Hellmann and Tisserand, 2006; Taylor et al., 2000). Parallel reactions occur, leading to a sigmoidally-shaped relation between dissolution rate and Ω (Fig. 7) (Hellmann and Tisserand, 2006). Albite dissolution rates reach their maximum at Ωs far from equilibrium (<-8), but are strongly dependent on Ω between -8 and -2 (Hellmann and Tisserand, 2006). At $\Omega > -2$, dissolution rates decrease slowly until they reach zero at $\Omega = 0$.

Some minerals are more likely to be affected by chemical affinity than others. Saturation indices for K-feldspar and albite in Loch Vale

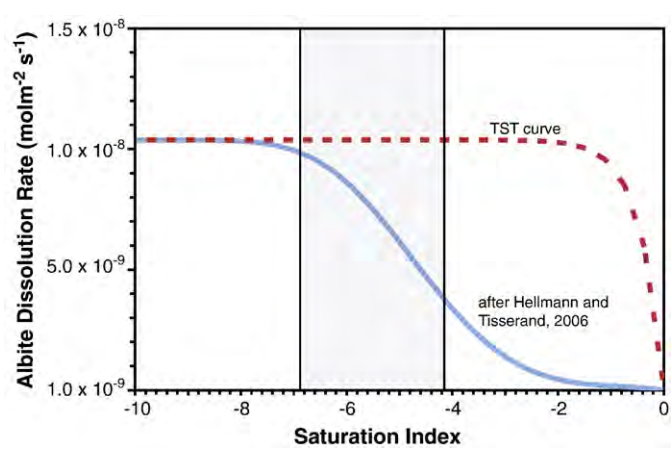

Fig. 7. Theoretical dissolution rates for albite at 10 °C based on transition state theory (TST; dashed red curve; Aagard and Helgeson, 1982) and on experimental data presented in Hellmann and Tisserand (2006; solid blue curve). Shaded area shows range of saturation indices for albite at Andrews Creek during October 2000–December 2001.

soil solutions typically range from 10^{-3} to 10^{-4} and 10^{-4} to 10^{-7}, respectively. These Ωs are well within the range where a strong dependence of weathering rates on Ω is expected (Hellmann and Tisserand, 2006).

Recent field studies have confirmed the importance of chemical affinity effects in natural weathering situations (Maher et al., 2009), indicating that chemical affinity may help explain the dependence of weathering fluxes on hydrologic conditions. In solutions far from equilibrium ($\Omega < -8$), dissolution rate is independent of solute concentration and thus will not be influenced by flow rate (Fig. 7). In solutions closer to equilibrium ($\Omega = -8$ to -2), increased flow will lead to greater flushing, lower solute concentrations, and faster dissolution rates (Hellmann and Tisserand, 2006; White and Brantley, 2003). Saturation indices for feldspars in Loch Vale soil solutions fall within this range. Thus, feldspar weathering rates may change dramatically in response to variations in precipitation and flushing of soils. This has important implications for rates of CO_2 consumption by mineral weathering; increased precipitation would cause greater flushing, lower Ωs, faster weathering rates, and greater CO_2 consumption. Decreased precipitation would have the opposite effect.

Saturation indices in soils are not spatially uniform due to heterogeneous flow paths, residence times, and solute concentrations (Steefel, 2008). Water in micropores, microcracks in mineral surfaces, and small, poorly connected channels has relatively long residence times, allowing solute concentrations to build up over time. Water in macropores tends to have relatively short residence times and thus lower solute concentrations than water in micropores and other slow-flow zones.

It is useful to consider how long it takes for solute concentrations to build up enough to approach saturation with respect to primary minerals under various flow conditions. This question was investigated by simulating the evolution of solute concentrations when reacting 1 g of granite with varying amounts of distilled water (1, 10, and 100 ml) over a period of 50 days using the computer program PHREEQC (Parkhurst and Appelo, 1999). These water:mineral ratios were intended to simulate reactions in saturated soil with heterogeneous flow paths, with the highest ratios corresponding to reactions within macropores, and the lowest ratios corresponding reactions in the soil matrix. In each simulation, Ωs for quartz and kaolinite increased with time and solutions quickly reached saturation (Fig. 8). In contrast, Ωs for calcite were very strongly affected by water: mineral ratios. In the 1:1 solution, calcite reached saturation after 10 days ($\Omega = 0$), but in the 100:1 solution, calcite was still substantially undersaturated after 50 days ($\Omega = 10^{-2.9}$; Fig. 8). Saturation indices for K-feldspar and albite also were affected by water:mineral ratios, although to a lesser extent than calcite (Fig. 8). After 50 days in the 1:1 solution, Ωs for K-feldspar reached $10^{-1.8}$, and Ωs for albite reached $10^{-4.5}$, again within the range where weathering rates show a strong dependence on Ω. It should be noted that these water: mineral ratios are relatively high; water:mineral ratios in the vadose zone often will be much less than 1:1, so soil solutions will be closer to equilibrium, resulting in slower weathering rates. The results from these simulations are consistent with pore network modeling performed by Li et al. (2007), which predicted that mineral weathering rates should be strongly dependent on hydrodynamic conditions.

3.6. Variations in reactive mineral surface area

Mineral weathering rates are directly dependent on reactive mineral surface area (Lasaga, 1995). In catchments, reactive mineral surface areas vary temporally in response to changing hydrologic conditions. During dry periods, soil moisture in the unsaturated zone may decline to the point that a large fraction of the total mineral surface area becomes essentially unreactive. This can occur if mineral surfaces dry out or if evapotranspiration concentrates soil solutions enough that they approach saturation with respect to primary minerals. At Andrews Creek, soil moisture generally is moderate during winter, increases sharply during snowmelt, and gradually declines to annual minima during late summer (Fig. 9). Summer rain causes short-term increases in soil moisture that may flush some solutes from the soil, temporarily lowering concentrations in bulk soil solutions and increasing the reactive soil mineral surface area. Fall rains provide a more sustained increase in soil moisture that persists through winter due to relatively low evapotranspiration rates.

Flushing by rain or snowmelt also may affect reactive surface area in the saturated zone. Micropores, microcracks, and small channels can make up a large fraction of total soil water volume; Hornberger et al. (1990) performed bromide tracer experiments in 10 m^2 plots in forest soils in Maine, and determined that the ratio of mixing volume to total soil water volume ranged from 0.25 to 0.39. They inferred that most of the total soil water volume is relatively immobile. Subsequent work has shown that macropore flow is particularly important during storm events and snowmelt periods (Gwo et al., 1995, 1996; Jaynes et al., 1995; Lange et al., 1996; Ray et al., 1997). Zones of mobile/immobile water can be important within aquifer material as well; tracer tests indicate that the mobile water fraction often is only 2 to 10% of total aquifer porosity (Payne et al., 2008). Mineral surfaces in zones of immobile water may be considered essentially unreactive because weathering rates are limited by transport of weathering products away from mineral surfaces (Drever and Clow, 1995). Flushing by snowmelt or rain can cause a transient increase in reactive surface area by increasing advection of solutes from zones of slow flow, allowing them to contribute to the overall soil solute flux.

Changes in the water table also will strongly affect the reactive surface area. During snowmelt and rain events, the water table rises and the saturated zone expands vertically and horizontally up the hillslope, which can dramatically increase the reactive surface area.

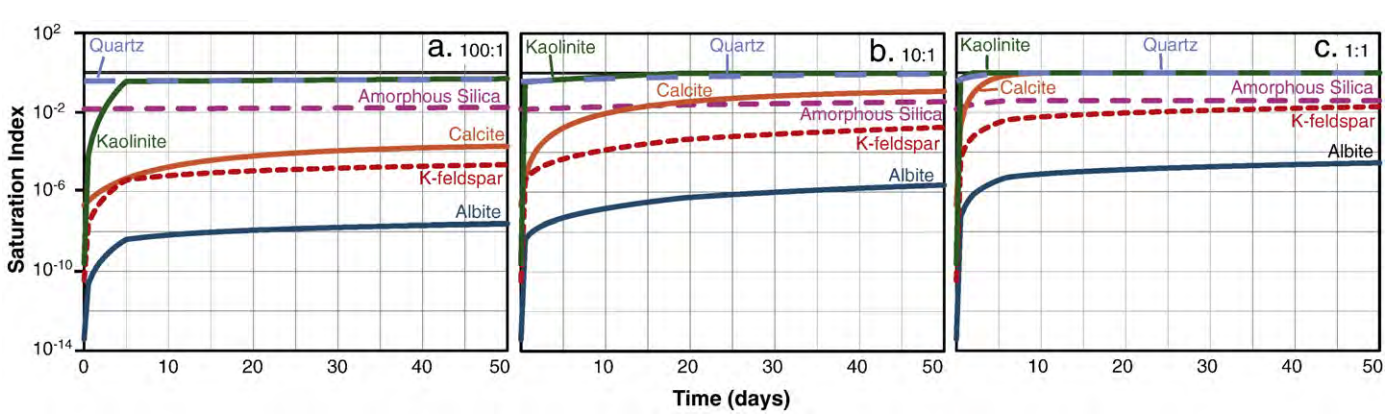

Fig. 8. Modeled evolution of saturation indices over time for 1 g of granite reacting at 25 °C with (a) 100 ml distilled water, (b) 10 ml distilled water, and (c) 1 ml distilled water.

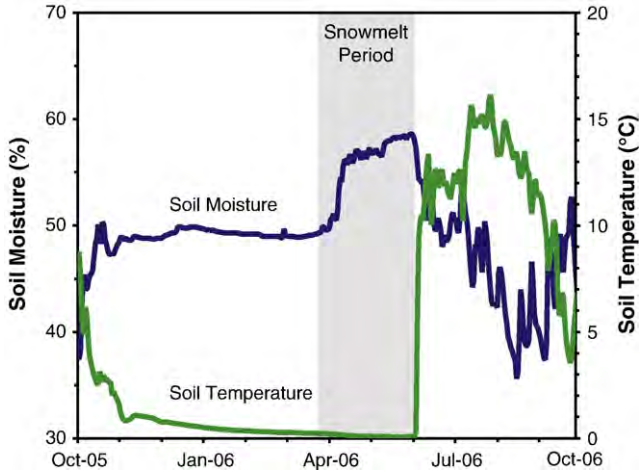

Fig. 9. Typical annual cycle of soil moisture and temperature conditions in seasonally wetted alpine meadow in Andrews Creek catchment. Shaded area indicates timing of snowmelt.

Thus, variations in precipitation amount and frequency could have an important influence on weathering fluxes.

3.7. Laboratory experiments

Laboratory experiments provide additional evidence for hydrologic control on mineral weathering rates, with relatively few potentially confounding variables. Mineral dissolution rates were measured on the 106–208 μm size fraction of soil collected from an alpine microcatchment in Loch Vale (see Section 2.4 for a description of the experiments). Dissolution rates were measured using fluidized-bed reactors, which maintain maximum contact between mineral grains and fluid by keeping the grains in suspension, and saturated columns, which provide hydrologic conditions more representative of nature because the grains are at rest within the columns. The effects of cation exchange, flushing of subsurface water, and seasonally-alternating precipitation/dissolution of amorphous mineral phases probably were minimal in the laboratory experiments because of the experimental design (see Section 2.4 for a description of the experiments). Evaluation of any differences in dissolution rates, therefore, may be constrained to effects of chemical affinity and variations in reactive mineral surface area.

After accounting for differences in temperature, oligoclase dissolution rates in the saturated columns were similar to those measured in the field (Fig. 10) (Clow and Drever, 1996). Oligoclase dissolution rates in fluidized-bed reactors, however, were 8 times higher than in saturated soil columns. The differences in mineral dissolution rates

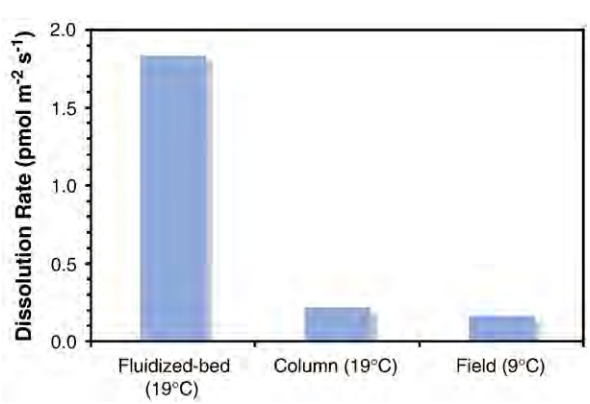

Fig. 10. Oligoclase dissolution rates from laboratory and field experiments. Adjustment of laboratory experiment results to 9 °C would lower the dissolution rates by approximately 20 to 60%, depending on activation energy.

probably were not due to the chemical affinity effect because column outflow solutions were far from equilibrium with respect to oligoclase; Ωs of outflow solutions were $<10^{-8}$.

Fluidized-bed reactors provide a fundamentally different flow regime than soil columns by keeping mineral grains in suspension. As a result, more of the total surface area is in contact with quickly moving water. In columns, flow rates are slower and more variable, analogous to the situation in natural soil systems with heterogeneous porosity. The mechanism(s) responsible for the slower dissolution rates in saturated columns compared to fluidized beds may be linked to the reactive surface area concept. The most likely explanation for slower dissolution rates in the columns is that zones of immobile water existed in the soil matrix that reduced the reactive mineral surface area.

4. Discussion

4.1. Implications for consumption of CO_2 by chemical weathering

The influence of the chemostatic processes examined in this study on regulation of CO_2 in the atmosphere is diverse. Some of the mechanisms responsible for chemostatic behavior consume CO_2, while others do not. Seasonal dissolution/precipitation of amorphous aluminosilicates, for example, are important chemostatic processes but they have no direct effect on carbon cycling. Carbonic acid mediated cation exchange consumes CO_2 on a seasonal basis, but these reactions are reversible, and on a long-term basis the cations are resupplied by mineral weathering, otherwise, soil acidification would occur. It is the chemostatic mechanisms associated with mineral weathering that are most important with respect to regulation of atmospheric CO_2.

To calculate the amount of CO_2 consumed by mineral weathering in a catchment, one must characterize the mineral weathering reactions occurring in the study area; different types of weathering reactions result in different rates of CO_2 consumption. Carbonic acid weathering of silicate minerals, such as albite for example, consumes one mole of CO_2 for each mole of bicarbonate produced:

$$\text{Albite} + 5.5H_2O + CO_2 = HCO_3^- + Na^+ + 2H_4SiO_4 + 0.5\text{Kaolinite} \quad (7)$$

Carbonic acid weathering of carbonate minerals consumes only half as much CO_2 per mole of bicarbonate produced:

$$\text{Calcite} + H_2O + CO_2 = 2HCO_3^- + Ca^{2+} \quad (8)$$

Strong acid mediated weathering does not consume any atmospheric CO_2. If the mineral weathering reactions are known, one can use the mass-balance approach to back-calculate the moles of CO_2 consumed via weathering (Drever, 1997; Garrels and Mackenzie, 1967; Mast, 1992). The method involves solving a set of linear equations that account for solute inputs from atmospheric deposition and production of bicarbonate, base cations, silica, and aluminum by each of the major weathering reaction. CO_2 consumption is calculated based on reaction stoichiometry and the amount of bicarbonate produced via each weathering reaction.

In the Andrews Creek subcatchment, long-term changes in storage of cations in biota and the cation exchange pool were assumed negligible due to the paucity of vegetation and soil in the basin. Results of mass-balance calculations for Andrews Creek included moles of minerals dissolved and CO_2 consumed via weathering on an annual basis (Table 2). Weathering of silicate minerals, primarily plagioclase and biotite/chlorite, accounted for approximately two-thirds of the CO_2 consumption via mineral weathering; calcite weathering accounted for the other third (Table 2).

The availability of long-term records of climate, runoff, and stream water chemistry at Andrews Creek provides an opportunity to investigate relations between climate and CO_2 consumption via

Table 2
Annual runoff, precipitation (precip.), mean air temperature (AirT), and amount of CO_2 consumed by mineral weathering in the Andrews Creek subcatchment.

				kg CO_2 consumed km^{-2}		
Year	Runoff (m)	Precip. (m)	AirT (°C)	By silicates	By calcite	Total
1993	0.92	1.14	0.2	1522	714	2236
1994	0.87	1.18	1.9	1308	797	2106
1995	1.03	1.42	1.0	1680	792	2473
1996	1.05	1.25	1.2	1702	841	2543
1997	1.13	1.48	1.0	2058	967	3025
1998	1.05	1.00	0.8	2116	918	3035
1999	0.89	1.09	1.4	1622	671	2293
2000	0.86	0.88	2.4	1948	839	2788
2001	0.87	0.97	2.2	1801	771	2573
2002	0.59	0.61	1.6	1355	478	1833
2003	1.08	0.84	2.0	2374	918	3292
2004	0.81	1.02	1.2	1657	720	2377
2005	0.99	1.01	1.9	2017	895	2912
2006	0.86	0.77	1.6	1890	584	2474
2007	0.87	0.87	2.2	2008	858	2866

CO_2 consumption was calculated based on solute fluxes and mineral mass-balance calculations as described in Mast (1992).

mineral weathering at single, well-studied catchment. Statistical comparison of climate and CO_2 consumption data for Andrews Creek indicate that CO_2 consumption is positively related to runoff, precipitation, and temperature (Fig. 11; Table 2).

In several previous studies (Brady and Carroll, 1994; White and Blum, 1995), solute fluxes have been modeled as a function of precipitation and temperature using an equation of the form:

$$Q = (aP)\exp[(-E_a/R)((1/T)-(1/T_0))] \quad (9)$$

where Q is solute flux (mol ha^{-1} $year^{-1}$), a is a constant that describes the linear relation between solute flux and precipitation (P, in mm), E_a is a constant for the solute of interest that is analogous to an activation energy for a single chemical reaction (kJ mol^{-1}) (Drever and Clow, 1995), R is the gas constant (kJ mol^{-1} °K^{-1}), T is temperature (°K), and T_0 is a reference temperature (273.4° K, which was the minimum annual average temperature during the study period). Runoff is sometimes substituted for precipitation because the two variables usually are highly correlated, and runoff data generally are more widely available and reliable.

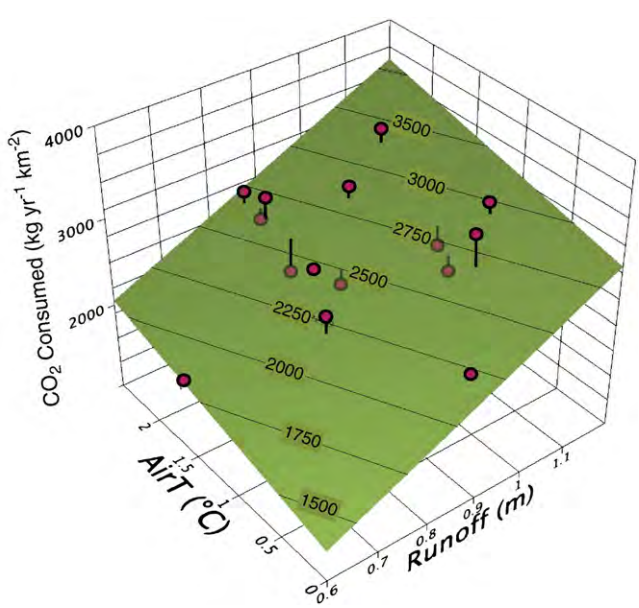

Fig. 11. CO_2 consumption by mineral weathering as a function of air temperature (AirT) and runoff in the Andrews Creek catchment during 1993–2007. The surface is the optimized fit through the data based on Eq. (9) (after White and Blum, 1995).

Using the annual Andrews Creek flux and climate data, Eq. (9) was solved numerically for a and E_a. Separate values of a and E_a were calculated for CO_2 consumption, and Na, SiO_2, and HCO_3 production. Values for a ranged from 0.16 for Na to 0.53 for CO_2 (Table 3), indicating that CO_2 consumption is strongly dependent on precipitation and runoff. Values for E_a ranged from 27.2 for SiO_2 to 83.4 for CO_2 (Table 3), indicating that CO_2 consumption also is quite sensitive to variations in temperature. The model explained 71% of the variance in CO_2 consumption calculated using the mass-balance method (Table 2; Fig. 12). Runoff was the most important explanatory variable, accounting for 53% of the variance in CO_2 consumption, while mean annual temperature accounted for an additional 18% of the variance.

The observed positive relation between CO_2 consumption and runoff in Loch Vale is consistent with results from White and Blum (1995) and other studies that used a spatial approach to investigate controls on solute fluxes and CO_2 consumption by mineral weathering (e.g., Ammiotte-Suchet et al., 2003; Gaillardet et al., 1999). The positive relation between air temperature and CO_2 consumption in Loch Vale is as expected given dependence of weathering reactions on temperature indicated by the Arrhenius equation (White, 2008). Few multi-catchment studies found strong relations between temperature and CO_2 consumption, probably because of confounding variables, such as variations in lithology, elevation, soil, and vegetation (White, 2008). The relations between CO_2 consumption and climatic variables are perhaps more clear in the present study because the effects of confounding variables were minimized by using a temporal approach at a single catchment.

Results from this study have important implications in light of observed warming and intensification of the hydrologic cycle (Christensen et al., 2007; Diaz and Eischeid, 2007; Huntington, 2006). Predictions for increases in global average air temperatures range from 1.7 to 4.4 °C by 2100 under the A1B emissions scenario of the IPCC (IPCC, 2007), but warming is expected to be greatest at high latitudes and high elevations (Christensen et al., 2007). In Loch Vale, average annual air temperatures rose by 3.1 °C during 1983–2007, and similar increases have been observed at other high-elevation sites in Colorado. Predictions for long-term changes in precipitation are less certain, but an intensification of the hydrologic cycle has already been observed (Huntington, 2006), and additional intensification seems likely based on energy balance considerations related to warming ocean temperatures.

The positive correlations observed in this study between CO_2 consumption, runoff, precipitation, and temperature indicate that chemostatic processes related to mineral weathering exert a negative feedback on CO_2. This is consistent with the well-established role of mineral weathering in regulating atmospheric CO_2 concentrations over geologic time scales (Berner and Kothovala, 2001; Walker et al., 1981). Mineral weathering helps regulate atmospheric CO_2 concentrations and global air temperatures at short time scales as well, and carbon sequestration strategies are being explored that exploit the mineral weathering process. Results from this study suggest that increasing hydrologic flushing rates could enhance CO_2 consumption via mineral weathering.

Table 3
Parameter estimates for equations relating runoff and temperature to CO_2 and solute fluxes.

Parameter	a	E_a	r-square
Na	0.16	74.3	0.64
SiO_2	0.31	27.2	0.90
HCO_3	0.26	46.1	0.81
CO_2	0.53	83.4	0.72

a is related to the dependence of fluxes on runoff, and E_a is related to the dependence of fluxes on temperature.

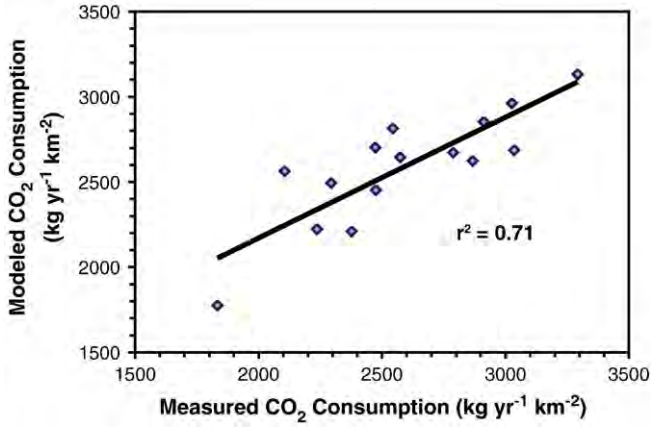

Fig. 12. Regression of measured against predicted mass of CO_2 consumed by mineral weathering in the Andrews Creek subcatchment during 1993–2007. Measured CO_2 consumption was calculated based on measured solute fluxes in Andrews Creek using the mineral mass-balance method described in Mast (1992). Modeled CO_2 consumption was calculated using Eq. (9).

The strength of the mineral weathering feedback is an important component of carbon cycling models used to predict future atmospheric CO_2 concentrations, but is still highly uncertain at the global scale. While this study quantified the weathering feedback in Loch Vale, the strength of the feedback is likely to vary spatially. Additional site-specific studies are needed to help quantify the importance of climate in controlling CO_2 regulation via mineral weathering.

5. Summary and conclusions

This paper documents the evaluation of several hypothesized mechanisms for chemostatic behavior and of how those processes may influence relations between climate, weathering fluxes, and CO_2 consumption via mineral weathering. The investigation used detailed physical and chemical information collected over a 15-year period (1993–2007) in Loch Vale, an alpine catchment in the Colorado Rocky Mountains. Cation exchange and seasonal precipitation and dissolution of poorly crystalline aluminosilicates appear to be important processes that help regulate solute concentrations in the stream; however, those processes have no direct effect on CO_2 consumption in catchments.

Hydrograph separation analyses using $\delta^{18}O$ indicated that old water (water stored in the subsurface over the winter) could account for $26 \pm 6\%$ of annual streamflow. Old water makes a surprisingly large contribution to annual fluxes of weathering products, accounting for $47 \pm 12\%$ and $45 \pm 11\%$ of annual fluxes of Na and SiO_2 in the stream. These results indicate that flushing of old water by snowmelt contributes substantially to chemostatic behavior in the Andrews Creek subcatchment.

Temporal variations in hydrologic flushing of subsurface materials, driven by snowmelt at the seasonal scale and by annual precipitation variability at the annual scale, contribute to chemostatic behavior by changing the chemistry of subsurface water and by changing reactive mineral surface area. The variations in hydrologic flushing cause changes in saturation indices for primary minerals in soil solutions that appear sufficient to substantially affect mineral weathering rates. Variations in snowmelt and annual precipitation also may affect weathering rates by changing reactive mineral surface area through vertical and lateral expansion/contraction of the groundwater reservoir, and by altering advection of solutes from micropores and other areas of slowly moving water.

Annual variations in runoff and air temperature were strongly and positively correlated with CO_2 consumption by mineral weathering in the Andrews Creek subcatchment. A statistical model that used runoff and temperature as explanatory variables accounted for 71% of annual CO_2 consumption. The positive correlations between CO_2 consumption and runoff and temperature indicate that they provide a negative feedback on atmospheric CO_2 concentrations. Quantifying the strength of the feedback in a range of catchments is needed to help improve model projections of future atmospheric CO_2.

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