EXPRESSION OF GEOCHEMICAL CONTROLS ON
WATER QUALITY IN LOCH VALE, ROCKY
MOUNTAIN NATIONAL PARK

by
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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Hydrology).

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Department of Hydrologic Science and Engineering
ABSTRACT

Silicate mineral weathering over global scales provides negative feedback to increasing atmospheric CO$_2$ levels through geologic time. There is conclusive evidence of changes in hydrology due to changes in climate from increasing atmospheric CO$_2$; however, only a weak correlation between climate and chemical weathering has been identified in field observations, possibly due to non-linear behavior of geochemical processes or the complex interactions between geochemistry and hydrology in natural systems. For this study, we analyzed concentration-discharge (C-Q) relationships from an 18-year record in a snow-dominated high-alpine watershed to determine geochemical and hydrological processes that control solute concentrations seasonally. In winter months, when discharge from the watershed is low, the system is conceptualized as a batch reactor to estimate rates of chemical weathering from changes in solute concentrations in a stream. We evaluate temporal trends in these data to provide insight into changes in chemical weathering within a catchment over a decadal timescale during modern climate change. This study shows the importance of seasonality in a high alpine watershed, and looks for trends in weathering rates in a transport-limited system on a decadal timescale.
# TABLE OF CONTENTS

ABSTRACT ................................................................. iii
LIST OF FIGURES AND TABLES ........................................ vi
LIST OF SYMBOLS ......................................................... viii
ACKNOWLEDGMENTS ..................................................... ix

CHAPTER 1 INTRODUCTION ............................................. 1
  1.1 Purpose ............................................................... 2

CHAPTER 2 SITE DESCRIPTION ........................................ 4

CHAPTER 3 METHODS ................................................... 6
  3.1 Andrews Creek Data ............................................... 6
  3.2 Discharge, Concentration, and Mass Flux Data Analysis .......... 6
  3.3 Determining Solute Production Rates ............................. 7
  3.4 Calculating Weathering Rates ................................... 7

CHAPTER 4 RESULTS .................................................... 9
  4.1 Concentration, Discharge, and Mass Flux Relationships at Andrews Creek ... 9
  4.2 Solute Production Rates at Andrews Creek ..................... 11
  4.3 Oligoclase Weathering Rates at Andrews Creek ................ 12

CHAPTER 5 DISCUSSION ................................................ 16
  5.1 Concentration-Discharge Relationship, Mass Flux, and Seasonality .... 16
  5.2 Solute Production Rate’s Dependence on Hydrology ................ 17
  5.3 Using Batch Reactor Assumptions to Calculate Weathering Rates at Andrews Creek ... 18
LIST OF FIGURES AND TABLES

Figure 2.1 Map of Loch Vale Watershed, including Andrews Creek sub-catchment . . . . 5

Figure 4.1 Concentration of Si and total cation (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$), and average daily discharge plotted against time for the 2003 water year. The pattern seen here is similar for all years analyzed (1998-2015). The 2003 water year was displayed due to its large sample size. . . . . . . . . . . . . . . . . . . 10

Figure 4.2 Si and total cation (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$) concentrations plotted against average daily discharge for the 2003 water year. The pattern seen here is similar for all years analyzed (1998-2015). The 2003 water year was chosen due to its large sample size. . . . . . . . . . . . . . . . . . . 10

Figure 4.3 Log of Si and total cation (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$) concentrations plotted against log daily discharge data from 1992 to 2015. The horizontal line indicates chemostatic behavior, while the line with a slope of -1 indicates dilution. . . . . . . . . . . . . . . . . . . 11

Figure 4.4 Log of Si and total cation (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$) mass flux plotted against log daily discharge data from 1992 to 2015. The dashed line indicates an ideal case where concentration is constant over all discharge values. . . . . . . . . . . . . . . . . . . 12

Figure 4.5 Log of Oligoclase weathering rates calculated using a batch reactor assumption plotted against water year. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 13

Figure 4.6 Solute production rates of Si, total cations (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$), and Na plotted for each water year. Solute production rates corresponding to p-values greater than 0.1 were removed. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 14

Figure 4.7 Solute production rates of Si, total cations (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$), and Na and total volume of discharge for each water year plotted over time. Solute production rates corresponding to p-values greater than 0.1 were removed. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 15

Figure 5.1 Conceptual drawing of Andrews Creek as a batch reactor. Packets of water (blue squares) move through the subsurface via different flow paths (red arrows). The length of these paths results in different residence times for each packet of water. The residence time of each packet of water before it reaches Andrews Creek is equivalent to different sampling times in a batch reactor. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 20
Figure 5.2 Conceptual plots of weathering rate vs. fluid velocity, log mass flux vs. log discharge, and log concentration vs. log discharge showing the expected behavior of high alpine catchments at varying fluid velocities and discharge, and the expected relationship between mass flux and concentration, and weathering rates within a catchment. Dashed lines indicate interpretations.

Table 4.1 Solute Production Rates for Si, total cations (Mg, Ca, K, Na), and Na, and associated parameters.

Table 5.1 Oligoclase Weathering Rates
LIST OF SYMBOLS

Daily average discharge, for day $i$ $[m^3/sec]$ .............................................. $Q_i$

Number of days ............................................................................................. $t$

Cumulative sum of the volume of discharge .................................................. $q$

Volume of total annual discharge ................................................................. $V$

Mass flux, for solute $i$ ...................................................................................... $F_i$

Concentration, for solute $i$ .............................................................................. $C_i$

Average daily discharge .................................................................................. $Q$

Weathering rates ............................................................................................ $w$

Solute production rate, for solute $i$ ................................................................. $\frac{dC}{dt}_i$

Surface area .................................................................................................. $s$

Stoichiometric coefficient .............................................................................. $\beta$
ACKNOWLEDGMENTS

I would like to thank my advisor and committee for their support, and my friends and family for their encouragement.
CHAPTER 1
INTRODUCTION

Global weathering of silicate minerals plays a role in regulating atmospheric CO$_2$ levels through geologic time [1]. Geochemically, atmospheric PCO$_2$ equilibrates with surface waters forming carbonic acid, driving silicate mineral dissolution through hydrolysis reactions releasing Ca$^{2+}$ and Mg$^{2+}$ to solution that eventually precipitates as carbonate minerals in the ocean, sequestering carbon in mineral form. As atmospheric CO$_2$ concentrations rise, more carbonic acid forms and silicate mineral weathering rates increase providing a negative feedback on increasing atmospheric CO$_2$ concentrations [2][3][4]. Increased temperatures associated with increased atmospheric CO$_2$ concentrations lead to increased kinetic reaction rates and solubility of silicate minerals compounding the feedbacks between mineral weathering and CO$_2$ concentrations [5][6]. Observing and modeling the feedback between climate and weathering helps to unravel climate in geologic history and evaluate the future under rapidly increasing atmospheric CO$_2$ concentrations.

To date, only weak correlations between climate and chemical weathering have been observed [7] possibly because geochemical mechanisms, such as kinetic rate and solubility, are not always the controlling factor determining how fast minerals dissolve in natural systems. Weathering in many natural systems is transport-limited where weathering rates are tightly coupled to rates of fluid flow, and are thus governed by hydrology [8]. Weathering rate response to increases in temperature is weakened under transport-limited conditions [5]. Complex coupling of hydrology and geochemical reaction rates in heterogeneous systems is not fully understood and many non-linear relationships exist over spatial and temporal (annual and long-term) scales [9] making it difficult to parse hydrologic control from purely climatic controls on weathering. Thus, observing the response of silicate mineral dissolution to the current rapid rise in atmospheric CO$_2$ concentrations is complicated by a number of
factors, including the intricate relationships between hydrology and climate [10][11][12] and hydrology and weathering [5][6][13].

In order to identify relationships between climate and weathering, long-term geochemical data are needed in watersheds sensitive to climate change where the hydrology and geochemistry are at least partially decoupled during some portion of the year. Small, high alpine watersheds are sensitive to the effects of climate change [10][11][12], but changes in discharge driven by snowmelt-dominated hydrology might mask trends in solute production related directly to changes in geochemical processes, such as kinetic rates and solubility, driven by changes in climate. Concentration-discharge (C-Q) relationships allow for the analysis of coupling between geochemical processes that produce solutes (e.g. weathering) and hydrologic processes that change solute concentrations in surface water outflows. C-Q relationships have been used to identify times of the year when drivers on geochemical processes shift [14][15]. Here we use patterns in C-Q relationships in a high-alpine, snowmelt-dominated watershed in the Rocky Mountains, CO, USA to identify seasonal shifts in geochemical processes controlling solute production and transport over an 18-year record. Weathering rates are estimated using a batch reactor conceptual model during the winter when outflow within the high-alpine watershed was composed only of base-flow from the subsurface. We evaluate temporal trends in these data to provide insight into changes in chemical weathering within a catchment over a decadal timescale during modern climate change.

1.1 Purpose

The purpose of this study is to identify a relationship between climate and geochemical processes, and the effect climate change may have on weathering rates using field data. Our study was motivated by the following questions:

1. Can C-Q relationships be used to capture geochemical processes affecting solute transport?

2. If so, can we capture changes in climate signal on a decadal timescale?
The following study attempts to answer these questions using long-term water quality and discharge data from a snow-melt dominated high alpine watershed. Using C-Q relationships, mass flux, and solute production rates we evaluate temporal trends in these data to provide insight into changes in chemical weathering within a catchment over a decadal timescale.
CHAPTER 2
SITE DESCRIPTION

C-Q relationships are examined from long-term water quality and discharge records from Andrews Creek located within the Loch Vale watershed in Rocky Mountain National Park, Colorado (Figure 2.1). The Andrews Creek catchment is composed of approximately 75% exposed bedrock (granitic gneiss and Silver Plume granite) and bedrock derived talus, 23% tundra with low growing grasses and herbaceous plants, 1% wet meadow, and 1% spruce/fir forest [16][17], and includes an approximately 7.5 ha drift glacier that feeds Andrews Creek [18][19]. Primary mineralogy of the bedrock includes quartz, oligoclase, microcline, and biotite with trace amounts of calcite [17]. Secondary minerals found in the soil include smectite, kaolinite, and illite [17]. Estimated mean annual temperature of the catchment is 0.5°C [20], with mean annual precipitation 101 cm, the majority (65% -85%) falling as snow from 1994 to 1999 [12]. Andrews Creek flows continuously throughout the year with discharge varying from 0.0001 m$^3$/s during the winter to 0.65 m$^3$/s during snowmelt in the spring. Peak discharge occurs in late spring, typically April or May.
Figure 2.1: Map of Loch Vale Watershed, including Andrews Creek sub-catchment [12].
CHAPTER 3
METHODS

3.1 Andrews Creek Data

All data analyzed in this study came from the USGS Andrews Creek stream gage in Loch Vale, CO from 1992 to 2015 [21]. The data analyzed included daily discharge and water quality data, including the concentrations of calcium (Ca), magnesium (Mg), silica (SiO$_2$), sodium (Na), potassium (K), and chloride (Cl). All days where the daily discharge was recorded as 0 m$^3$/s were removed for a total of 11 days removed from the long-term record of 8769 days. For the water quality data, all field blanks were removed, and duplicates were averaged. Due to lack of concentration data, all annual analyses that involved concentration data used observations from 1998 to 2013.

Water quality sampling occurred approximately once per week from May to October (summer), and once per month for the remaining months (winter). Winter sampling did not begin until 1998. For the purposes of our study, only water years where sampling occurred during the winter and summer (1998 to 2015) were analyzed for annual trends. All temporal analyses were based on the water year running from October 1$^{st}$ to September 31$^{st}$, not the calendar year from January 1$^{st}$ to December 31$^{st}$.

3.2 Discharge, Concentration, and Mass Flux Data Analysis

Daily discharge at Andrews Creek varied seasonally. The total annual volume of discharge was used for some analyses by summing average daily discharge values. Dry and wet years were identified by comparing total annual discharge to the median for all years analyzed (1992-2015), where a dry year has less and a wet year more than the median, respectively.

Concentration and mass flux data were analyzed based on whether they were measured before or after peak discharge. The date of peak discharge was defined as the date when 50% of the volume of total annual discharge passed through the system using
\[ q(t) = \sum_{i=1}^{t} Q_i \times 86400, \]
\[ q(t) < V/2, t : \text{Before Peak Discharge} \]
\[ q(t) > V/2, t : \text{After Peak Discharge} \]

where, \( Q_i \) is the daily average discharge for day \( i \) in units of \( \text{m}^3/\text{s} \), \( t \) is the number of days since the start of the water year, 86400 is the number of seconds within a day, \( q \) is the cumulative sum of the volume of discharge up to day \( t \), and \( V \) is the volume of total annual discharge. Daily mass flux was calculated using

\[ F_i = C_i \times Q_i \]

where \( F_i \) is the daily mass flux for a given solute \( i \), \( C_i \) is the concentration of a solute, and \( Q_i \) is the average daily discharge for the date that solute was sampled.

### 3.3 Determining Solute Production Rates

Data was filtered to find the period of time each year when the system could be conceptualized as a batch reactor. These conditions allowed us to estimate weathering rates. Simple linear regressions were fit annually to the sum of cation (\( \text{Mg}^{2+} + \text{K}^+ + \text{Ca}^{2+} + \text{Na}^+ \)), Si, and Na concentrations during periods of time when their temporal patterns appeared to fit the batch reactor assumptions from 1998 to 2013. This time period typically lasted from late October to April within the water year. The slopes of the annual simple linear regressions represent the solute production rate \( \left( \frac{dC_i}{dt} \right) \), for solute \( i \) with units of concentration per time. The significance of regression was determined using p-values. A p-value at a significance level of 10% was deemed significant. Any years that resulted in a p-value higher than 10% were removed for analysis.

### 3.4 Calculating Weathering Rates

Weathering rates \( w \) were calculated from the solute production rates using a batch reactor assumption [22] and the equation

\[ w = \frac{dC_i}{dt} \times \frac{1}{(\beta \times s)} \]
where $\frac{dC}{dt}$ is the change in concentration over time of solute $i$, also known as the solute production rate, $s$ is the surface area of rock 1 L of water is exposed to in the system, and $\beta$ is the stoichiometric coefficient [22]. A BET measured surface area of 0.15 m$^2$ g$^{-1}$ for weathered Silver Plume granite from Loch Vale was used [23]. The surface area exposed to 1 L of water was calculated from porosity, which was assumed to be 20% [19], and the average density of granite 2.7 g/cm$^3$ [24]. The surface area per 1 L of water was calculated to be 1620 m$^2$ using

$$\frac{4 \text{L of rock}}{1 \text{L of water}} \times \frac{1000 \text{cm}^3}{1 \text{L}} \times \frac{2.7 \text{g}}{\text{cm}^3} \times \frac{0.15 \text{m}^2}{\text{g}} = 1620 \frac{\text{m}^2}{1 \text{L of rock}} \tag{3.4}$$

To calculate the weathering rate for oligoclase the solute production rate for Na ($\frac{dC}{dt} \text{Na}$) was used, since feldspar is the only possible source of Na within the catchment. A $\beta$ of 0.73 was used based on the following chemical reaction for the oligoclase present in Loch Vale [17].

$$\text{Oligoclase} + 1.27 \text{CO}_2 + 4.82 \text{H}_2\text{O} \rightarrow 0.64 \text{Kaolinite} + 0.27 \text{Ca}^{2+} + 0.73 \text{Na}^+ + 1.46 \text{H}_4\text{SiO}_4 + 1.27 \text{HCO}_3^- \tag{3.5}$$

Since the solute production rates used where calculated during the winter, when the assumptions for a batch reactor are met, the weathering rates calculated will reflect the winter weathering rates of the system.
4.1 Concentration, Discharge, and Mass Flux Relationships at Andrews Creek

In all years of analyzed data (1998-2015), the concentration of solutes are higher during winter months, when discharge is low, compared to the spring and summer months when discharge is high (Figure 4.1). Maximum solute concentrations occur before snowmelt in May, due to increasing discharge. A notable spike in cation concentrations around this time may be attributed to release of organic acids from the snow pack releasing Ca from the mineral exchange pool (Figure 4.1) [12]. Solute concentrations increase gradually through the winter to this maximum concentration. Minimum concentrations typically occur in August to September on the falling limb of the hydrograph, after which concentrations begin to increase again through the fall and winter months (Figure 4.1). A pattern of hysteresis is apparent in annual C-Q plots for all solutes over the period of analyzed data (1998-2015), with higher concentrations occurring prior to peak discharge (Figure 4.2).

Utilizing all available solute concentration data (1992-2015), the C-Q relationship changes based on magnitude of discharge (Figure 4.3). For daily discharge, less than 0.03 m$^3$/s, the slope of the log C-Q relationship is approximately zero, indicating chemostatic behavior (Figure 4.3) [12][25]. For discharge greater than 0.03 m$^3$/s, the C-Q plot shows a negative slope of approximately one indicating dilution (Figure 4.3) [25]. All observations after peak discharge follow this dilution trend (Figure 4.3).

Mass flux values, calculated by multiplying concentration by discharge, did not show a change in trend based on magnitude of discharge (Figure 4.4). Using all available mass flux values, a log plot of mass flux versus discharge shows a positive linear trend with a slope of approximately one (Figure 4.4). For mass flux observations that occurred after peak discharge, a positive linear trend is still present; however, the line appears to be shifted down
Figure 4.1: Concentration of Si and total cation (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$), and average daily discharge plotted against time for the 2003 water year. The pattern seen here is similar for all years analyzed (1998-2015). The 2003 water year was displayed due to its large sample size.

Figure 4.2: Si and total cation (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$) concentrations plotted against average daily discharge for the 2003 water year. The pattern seen here is similar for all years analyzed (1998-2015). The 2003 water year was chosen due to its large sample size.
indicating a decrease in solute mass for a given discharge within Andrews Creek, which may be due to dilution from overland flow.

![Graph](image)

Figure 4.3: Log of Si and total cation (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$) concentrations plotted against log daily discharge data from 1992 to 2015. The horizontal line indicates chemostatic behavior, while the line with a slope of -1 indicates dilution.

### 4.2 Solute Production Rates at Andrews Creek

Solute production rates for total cations (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$) ($\frac{dC}{dt}$), SiO$_2$ ($\frac{dC}{dt}$ Si), and Na$^+$, ($\frac{dC}{dt}$ Na) show no discernable linear trend over time or with discharge using a simple linear regression (Figure 4.6) (Table 4.1). Based on visual inspection, the solute production rates for total cations and Na$^+$ appears to follow a similar trend as discharge, with a possible lag between discharge and solute production rate (Figure 4.7). Within the standard error of each solute production rate there is no significant trend, however (Figure 4.6). Solute production rates were calculated for total cations (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$), Si, or Na in years where a linear increase in these solute concentrations was identified over the winter months (p-value < 0.1). In years with p-values >0.1, either the sample size was too small (e.g. 2006 and 2012), samples were collected at irregular intervals, or the geochemical reactions producing the solutes changed over the winter months. In particular, only 8 of the
Figure 4.4: Log of Si and total cation (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$) mass flux plotted against log daily discharge data from 1992 to 2015. The dashed line indicates an ideal case where concentration is constant over all discharge values.

17 years had linear increases in SiO$_2$ concentrations over the winter months. In years where a linear trend was not observed the SiO$_2$ concentration increased initially but transitioned to approximately constant values, possibly indicating control of the SiO$_2$ concentrations by geochemical reactions at equilibrium in the subsurface.

### 4.3 Oligoclase Weathering Rates at Andrews Creek

Using the batch reactor assumption, weathering rates of oligoclase were calculated from the solute production rate of Na ($\frac{dC}{dt}$$_{Na}$) using equation 1 (Figure 4.5). The average calculated weathering rate for oligoclase is 4.0x10$^{-16}$ mol m$^{-2}$ s$^{-1}$. The calculated weathering rates show a similar trend to the solute production rates of Na ($\frac{dC}{dt}$$_{Na}$) (Figure 4.6 and Figure 4.5). This is expected, since the weathering rates are simply the solute production rates of Na scaled by surface area and a stoichiometric coefficient, which we assumed to remain constant over time.
Figure 4.5: Log of Oligoclase weathering rates calculated using a batch reactor assumption plotted against water year.

Table 4.1: Solute Production Rates for Si, total cations (Mg, Ca, K, Na), and Na, and associated parameters.

<table>
<thead>
<tr>
<th>Year</th>
<th>Total Cations</th>
<th>Si</th>
<th>Na</th>
<th>Number of Observations</th>
<th>Total Cations</th>
<th>Si</th>
<th>Na</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
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<td>5 6 5</td>
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<td>1.79E-03</td>
<td>1.06E-02</td>
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<tr>
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<td>0.051</td>
<td>4 5 5</td>
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<td>2.72E-02</td>
<td>2.96E-03</td>
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<td>2000</td>
<td>0.223</td>
<td>0.071</td>
<td>0.036</td>
<td>12 10 12</td>
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<td>1.15E-06</td>
<td>1.66E-04</td>
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<tr>
<td>2001</td>
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<td>0.025</td>
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<td>2003</td>
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<td>8 11 8</td>
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<tr>
<td>2004</td>
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<td>0.075</td>
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<tr>
<td>2006</td>
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<td>3.04E-03</td>
<td>1.97E-03</td>
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</table>
Figure 4.6: Solute production rates of Si, total cations (Mg$^{2+}$ + K$^+$ + Ca$^{2+}$ + Na$^+$), and Na plotted for each water year. Solute production rates corresponding to p-values greater than 0.1 were removed.
Figure 4.7: Solute production rates of Si, total cations ($\text{Mg}^{2+} + \text{K}^+ + \text{Ca}^{2+} + \text{Na}^+$), and Na and total volume of discharge for each water year plotted over time. Solute production rates corresponding to p-values greater than 0.1 were removed.
CHAPTER 5
DISCUSSION

To test geochemical responses to changes in climate within our system, we analyzed concentration-discharge relationship, mass flux, and field calculated weathering rates within the Andrews Creek sub-catchment.

5.1 Concentration-Discharge Relationship, Mass Flux, and Seasonality

The concentration-discharge relationship in Andrews Creek shows chemostatic behavior, defined as slope of zero on a plot of concentration as a function of discharge (Figure 4.3), during low flow. This indicates possible decoupling of concentration and discharge where buildup and storage of solutes within a system effectively buffers the solute concentrations against changes in discharge or episodic inputs [26][27][25][28][29]. During high flow, a pattern of dilution is evident defined as a negative slope in a C-Q relationship (Figure 4.3) [30][31]. For Andrews Creek, C-Q relationships dependence on magnitude of flow indicates the importance of seasonality on solute production within the system. During the winter, when flow is low, solutes appear to build up within the subsurface, while in the spring and summer, when flow is high due to snow melt, dilution is evident and most likely due to overland flow. Previous studies have shown that seasonality is one of the strongest predictors of C-Q behavior for less-reactive elements, such as Cl, Mg, and Ca, which is the case at Andrews Creek as well [14].

The impact of seasonality on concentration within Andrews Creek is further evident in the pattern of hysteresis present on an annual scale between concentration and discharge (Figure 4.2). For all analyzed solutes (Ca, Na, Mg, K, Si), the concentration of solutes before peak discharge are greater than concentrations after peak discharge at similar values of discharge (Figure 4.2). This pattern has been attributed to the flushing out of solutes due to spring snow melt in Andrews Creek [32]. Overall, the dependence of concentration
on seasonality complicates the analysis of long-term trends, and thus the effect of changes in climate on solute production in the Andrews Creek watershed. To remove the effects of seasonality due to discharge, mass flux was examined.

For all available data, mass flux plotted against discharge follows a constant linear trend (Figure 4.4). Mass flux data also shows the importance of dilution and seasonality. After peak discharge, the mass flux data appears to have the same slope as the rest of the mass flux data; however, the linear trend is shifted down (Figure 4.4). This shift indicates a decrease in solute production at similar values of discharge, and may be due to dilution from overland flow or the flushing out of solutes.

### 5.2 Solute Production Rate’s Dependence on Hydrology

We were not able to identify any statistically significant trends in solute production rates over time or with discharge (Figure 4.6 and Figure 4.7). However, time series trends in solute production rate appear to mirror discharge, with the exception of Si (Figure 4.7). This relationship suggests there may be another parameter linked to discharge, such as residence time, that is more closely coupled to reaction rates within the system and would better capture the variation in solute production rate. Si production rates may not follow the same pattern due to biological processes, such as the uptake of SiO$_2$ by phytoplankton [32]. It is also possible that a temporal lag between solute production rate and discharge exists in the dataset, especially given the definition of a water year from October 1$^{st}$ to September 31$^{st}$ as precipitation from the previous year contributes to subsurface flow for the next year. A temporal lag would make the correlation analysis between solute production rates and discharge more complex, the analysis of which lies outside the scope of this study.

The calculation of solute production rates are sensitive to sample size, and the cutoff for determining this sample size. For our study, the cutoff was based on the time of year (October to April) and discharge ($<0.03$ m$^3$/s), which resulted in sample sizes that ranged from 3 to 12 observations (Table 4.1). Smaller sample sizes made it harder to determine if the trend in concentration was linear, and thus whether the system was far from equilibrium. More
research is required to determine the accuracy of these rates. A sampling regime designed with these limitations in mind could be used to produce more reliable results.

5.3 Using Batch Reactor Assumptions to Calculate Weathering Rates at Andrews Creek

To calculate weathering rates from the observed concentration and discharge data at Andrews Creek, the sub-catchment could be modeled as a batch reactor during the winter, and a flow-through reactor during the summer. During the spring and summer, overland flow will complicate these calculations, and dilution would need to be accounted for. For this reason, our study focuses on calculating weathering rates using a simple batch reactor assumption using winter concentration data when overland flow, and thus dilution, is not present.

Based on the linear trends in concentration over time during the winter, the sub-catchment can be conceptualized as batch reactor (Figure 4.1). For our conceptual batch reactor model, Andrews Creek will behave as the outlet, and different flow paths lengths leading to the stream will be equivalent to different sampling times (Figure 5.1). For example, a packet of water that takes 10 days to travel through the catchment to Andrews Creek is assumed to be the same as sampling a batch reactor after 10 days. This conceptual model requires the following assumptions: there are no fluid inputs to the system, the fluid within the watershed is well mixed, the volume of water entering Andrews Creek is small compared to the total volume of water available in the Andrews Creek sub-catchment, and the system is far from equilibrium. The Loch Vale watershed is essentially a closed system with the only input being precipitation [19]. During the winter, the ground is frozen and precipitation falls as snow. Thus, there are minimal additional inputs to Andrews Creek from precipitation, and the base flow in Andrews Creek is due to subsurface flow [12]. The watershed’s mineralogy is homogenous with the two major types of bedrock, Biotite Gneiss (80%) and silver plume granite (20%), being chemically similar [17]. Having a homogenous system satisfies the well-mixed assumptions. This assumption is over simplified, and does not include possible alternation
zones or an analysis of fracture flow, however, the results are instructive to examine trends over time comparing relative values, but the calculated rates not necessarily representative of absolute rates. Based on an assumed porosity of 20% and an approximate regolith depth of 1 m [19] the total volume of water flowing through Andrews Creek, during the winter, is 17% of the estimated total holding capacity of the Andrews Creek sub-catchment, or 17% of the initial water within the batch reactor was removed.

To calculate a weathering rate based on the batch reactor assumptions, the solute production rates are divided by the surface area of rock 1 L of water will be in contact with based on Equation 3. As long as we can assume porosity or surface area does not change over time, the water to rock ratio will remain constant and the trends observed in solute production rate will reflect trends in weathering rates. This may not be the case, for example, if porosity decreases with depth and the water table fluctuates over time causing the average porosity to decrease. However, the natural variation in porosity and granite density is so small, varying within an order of magnitude, they have very little control over the weathering rate. At no point in the calculations does discharge come into play (besides the inherent relationship between concentration and volume of water), thus the observed coupling between the solute production rates and discharge is due to hydrology’s impact on the geochemical processes.

5.4 Comparison of Oligoclase Weathering Rates

The average calculated oligoclase weathering rate using the batch reactor assumption was $4 \times 10^{-16}$ mol m$^{-2}$ s$^{-1}$. This rate is 2 orders of magnitude lower than any rates previously calculated at Loch Vale; however, it is within the range of previously calculated oligoclase weathering rates (Table 5.1). This difference may be due to our incorporation of seasonality into our calculation of rates. Weathering rates are typically calculated annually. Our method calculated weathering rates during the winter, when flow is low and residence time is high. These rates are expected to be slower than in the spring or summer due to the buildup of solutes, and long residence times (Figure 5.2). Using the batch reactor assumption, reaction time may be a lot longer than can be accounted for from the nanocatchment experiment or
weathering rates calculated using a mass-balance approach due to the differences in length of reaction time [33]. Experiment and field rates calculated at Loch Vale most likely represent summer rates or the annual average of rates, while the rates calculated in this study represent winter rates.

5.5 Implications

Based on the linear relationship between mass flux and discharge, we expect the reaction rates within our system to change seasonally, with winter rates being lower than summer rates due to the change in fluid flow within the subsurface (Figure 5.2). This relationship also indicates that rates within this sub-catchment always depend on fluid velocity, or are transport-limited. Transport-limited systems are more dependent on changes in hydrology than other consequences of climate change, such as changes in temperature or PCO$_2$ [5][15]. The lack of a linear trend in our calculated weathering rates supports this finding that reaction rates in transport-limited systems are closely coupled to hydrology. Also, it is
Table 5.1: Oligoclase Weathering Rates

<table>
<thead>
<tr>
<th>Rate (mol m$^{-2}$ s$^{-1}$)</th>
<th>Location</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.63 x 10^{-12}</td>
<td>Plastic Lake, Ontario, Canada</td>
<td>Field: Soil mass balance [34]</td>
</tr>
<tr>
<td>9 x10^{-13} - 4.0 x10^{-12}</td>
<td>Loch Vale, CO</td>
<td>Field: Nanocatchment Soils [35]</td>
</tr>
<tr>
<td>7.7x10^{-13}</td>
<td>Loch Vale, CO</td>
<td>Experiment: Flow-through Reactor [35]</td>
</tr>
<tr>
<td>9.5x10^{-14}</td>
<td>Loch Vale, CO</td>
<td>Experiment: Long-term flow through column [23]</td>
</tr>
<tr>
<td>9x10^{-14}</td>
<td>Loch Vale, CO</td>
<td>Experiment: Saturated Column [35]</td>
</tr>
<tr>
<td>4x10^{-16}</td>
<td>Loch Vale, CO</td>
<td>Field: Winter stream concentrations (This Study)</td>
</tr>
<tr>
<td>1.26x10^{-16}</td>
<td>Merced River, CA</td>
<td>Field: Soil Chronosequences [36]</td>
</tr>
</tbody>
</table>

important to note that even though our sub-catchment is small, with high relief, and fast fluid flow through the system, the system never becomes kinetically-limited (Figure 5.2).

With climate change causing snow melt to occur earlier in the season the period of low flow in Andrews Creek, and similar alpine systems will be shortened [37]. With shorter periods of low flow, it is expected that the average weathering rate will increase. This increase in average silicate weathering rate may help to provide negative feedback on increasing atmospheric CO$_2$ concentrations, as expected by Berner & Caldeira [1], and others. Overall, looking at weathering rates on a decadal time scale did not produce a statistically significant trend that could be linked directly to a change in climate due to changes in kinetic rates and solubility. Instead, hydrology appears to play a bigger role in geochemical processes complicating long-term trends within field data.
Figure 5.2: Conceptual plots of weathering rate vs. fluid velocity, log mass flux vs. log discharge, and log concentration vs. log discharge showing the expected behavior of high alpine catchments at varying fluid velocities and discharge, and the expected relationship between mass flux and concentration, and weathering rates within a catchment. Dashed lines indicate interpretations.
CHAPTER 6
CONCLUSIONS

Understanding how geochemical processes are affected by climate change will determine how efficiently CO$_2$ is regulated by silicate weathering. Through the analysis of field data in a snow-melt dominated watershed the following points can be concluded:

- The analysis of the Andrews Creek sub-catchment water quality data shows the important role seasons play in controlling the mass output in a snow-melt dominated system. During the winter, when flow through the system is slow and residence times are low, concentrations build up in the subsurface. In the spring/summer, snowmelt flushes out the subsurface, decreasing concentrations. In future analysis, it may be helpful to examine data by season instead of annually, especially if sampling frequency changes between winter, when concentrations are high, and spring/summer, when concentrations are lower.

- There are no significant trends on the decadal scale in the solute production rates or weathering rates calculated based on winter concentrations in Andrews Creek.

- In this system, hydrology has a stronger effect on geochemical processes then climate directly. Based on the mass flux analysis, the system remains transport-limited throughout the spring-summer. Weathering rates in transport-limited systems are not as susceptible to changes in atmospheric CO$_2$ and climate, as kinetically limited systems [15]. However, geochemical processes in transport-limited systems are more susceptible to changes in hydrology [6], indicating any direct affect climate is having on the system will be masked by changes in hydrology.

With hydrology complicating the effects of climate change on geochemical processes, looking at the predicted behavior of hydrology due to climate change may help predict the...
trends in weathering rates. In addition, since mass production varies seasonally due to hydrology the changes in weathering rate may be due to changes in duration of seasons.
REFERENCES CITED


