The Pennsylvania State University

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WEATHERING DYNAMICS IN WATERSHEDS:

CONNECTING RIVER CHEMISTRY TO SUBSURFACE MINERAL DISTRIBUTIONS

A Dissertation in

Geosciences

by

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ABSTRACT

Mineral weathering significantly contributes to global biogeochemical cycles and is hypothesized to control Earth's long-term climate through release and removal of CO₂ to and from the atmosphere. Although it is known that underlying geology influences water quality and weathering, few studies consider the subsurface beneath a watershed with respect to weathering dynamics. This is because in most watersheds, subsurface mineral distributions remain largely uncharacterized. By exploring river chemistry in comparison to the subsurface architecture of a watershed, I sought insights into weathering mechanisms for different minerals. For a given mineral weathering reaction, it is often assumed that one step limits the rate, dictating the weathering regime in that watershed. Rate limiting steps such as water throughput (the regime of runoff limitation), delivery of weathering reagents other than H₂O (advective transport limitation), supply of fresh minerals (erosive transport limitation), and interfacial reaction kinetics (kinetic limitation) have been considered. But how the dominant weathering regimes change across spatial and temporal scales or for different compositional systems is generally unknown. In this dissertation I explore how weathering fluxes in rivers vary with discharge, watershed size, and climate to evaluate weathering regimes for a few compositional systems. I link this variability to subsurface mineral distributions through borehole observations, multivariate statistics, physically based models, and data driven techniques.

The first mineral whose weathering I assess is pyrite – a ubiquitous iron sulfide mineral that releases much of the sulfate in rivers that flows to the ocean. When pyrite oxidizes, it releases sulfuric acid, dissolving minerals in proximity and often releasing CO_2 . Additionally, some of the oxidant (O_2) can be incorporated into the sulfate byproduct from pyrite oxidation. Oxygen isotopes in sulfate deposits could, therefore, help to reconstruct Earth's atmospheric oxygen history; however, we need a better understanding of modern pyrite oxidation mechanisms to

accurately interpret historic or long-term geologic oxidation dynamics. In my first study I developed a machine learning-based mixing model to discern the signal of pyrite oxidation from other sources of sulfate in rivers. This model leverages the fact that different minerals dissolve along deep and shallow flowpaths, leading to unique chemical signatures that can be detected in streams. I apply this model to three extensively studied watersheds to investigate modern and long-term weathering-CO₂ dynamics. I found that watersheds intermittently switch between acting as CO₂ sources and CO₂ sinks depending on whether the dominant flowpath sampled by the stream is deep or shallow, respectively. Comparing soil chemistry to river chemistry, I found that long-term CO₂ dynamics (recorded in soils) are roughly consistent with short-term CO₂ dynamics (recorded in soils) are roughly consistent with short-term CO₂ dynamics (recorded in soils) are roughly consistent with construction and agent and has reduced the short-term capacity of the watersheds to sequester CO₂. Only recently have the watersheds begun recovering from the impacts of acid rain.

From my first study, I observed that pyrite-derived sulfate concentrations changed with time, and that concentrations were highest in the dry season and lowest in the wet season. To explore these temporal dynamics, I coupled the machine learning-based mixing model to a physically based-oxidation model that describes how pyrite-derived sulfate concentrations vary with discharge. Utilizing concentration and discharge data from 15 watersheds in the northeastern United States and ~300 watersheds in the western United States, I fit the oxidation model using a non-linear least squares regression. From these modeling results, I found that, in the northeastern United States, concentrations vary little with discharge when coal mining is absent within the drainage area, and that concentrations decrease with discharge when coal is mined in the basin. I interpreted this trend as a shift in the rate limiting step of oxidation from advection of dissolved oxygen to interfacial reaction kinetics as a result of mining-related exhumation of pyrite. Coal mining and spatial scale co-vary in the Susquehanna River Basin of the northeastern United

States (i.e., only small watersheds contain no coal); therefore, it is difficult to disentangle their effects on concentration-discharge (C-q) dynamics. In the western United States, I was able to deconvolve some of these relationships by focusing on watersheds without agriculture and with low inputs of acid rain. I found that C-q behaviors are consistent with the pyrite reaction front becoming shallower as drainage areas of watersheds increase. This could indicate that pyrite-derived sulfate fluxes in small watersheds tend to be limited by transport of reagent (short timescales) or supply of fresh mineral (long timescales).

In the first two studies, I focused on pyrite weathering, which shows relatively fast reaction kinetics. As a comparison, I sought to explore the other end of the weathering spectrum, namely slow-dissolving silicate minerals. For my third study, I aggregated data for water quality, discharge, climate, and catchment characteristics for 148 shale-underlain watersheds across the United States to explore the rate limiting step of silicate weathering. Shales cover a significant proportion of global land area, but most weathering studies focus on granitic and basaltic systems. I found that when potential evapotranspiration (PET) is much larger than mean annual precipitation (MAP), weathering is limited by the throughput of water in the system (i.e., runoff). For humid watersheds, I found that weathering rates show a dependence on erosion rate, temperature, and precipitation rate, which is consistent with a mixture of weathering regimes and rate limiting steps. When watersheds are small and characterized by steep slopes on average, the silicate weathering rate is only dependent on temperature and precipitation. When watersheds are large and are characterized on average by gentle slopes, the weathering rate is predominantly dependent upon the erosion rate. I quantify the weathering dependencies for different groups of watersheds via regression analysis. For US shale-underlain watersheds, 48%, 37%, and 7% of their land area is limited by runoff, erosion, and reaction kinetics, respectively. The remaining 9% represent a mixed weathering regime. Weighting these land fractions by the average fluxes

observed for each weathering regime, I found that 17%, 56%, 11%, and 16% of silicate weathering fluxes from shale watersheds in the US are limited by runoff, erosion, reaction kinetics, or a mixture, respectively.

Overall, the results presented in this dissertation shed new light on the impact of subsurface mineral distributions on weathering dynamics in watersheds. I present a new interpretive framework for evaluating the CO₂ sequestration efficiency of weathering using both stream and soil chemistry. This has implications for evaluating CO₂-weathering dynamics over geologically relevant timescales. I also present a new method for evaluating C-q relationships with respect to depths of groundwater flowpaths and reactive minerals. This has implications for predicting legacy contamination and the transport of redox-sensitive species. Lastly, I evaluate and quantify the silicate weathering dependencies in shale watersheds. I classify weathering regimes in these watersheds based on climatic and geomorphologic characteristics of a watershed. Results in this dissertation can improve future hydrologic and geochemical models through integrating subsurface mineral distributions across scales.

TABLE OF CONTENTS

LIST OF TABLES	XV
ACKNOWLEDGEMENTS	XV
Chapter 1 Motivation and Outline	1
1.1 Motivation	1
1.1.1 Introduction	1
1.1.2. Modalities of Weathering	2
1.1.3. Modalities of Concentration-Discharge Relationships	6
1.1.4. Weathering Across Space and Time	
1.1.5. Connecting Mineral Distributions to Weathering Dynamics	
1.2Chapter Summaries	
1.2.1 Summary of Chapter 2	
1.2.2 Summary of Chapter 3	
1.2.3 Summary of Chapter 4	
1.3Tables	
1 4 Figures	23
1 5 References	26
Chapter 2 Machine Learning Deciphers CO ₂ Sequestration and Subsurface F	lowpaths
Chapter 2 Machine Learning Deciphers CO ₂ Sequestration and Subsurface F from Stream Chemistry	lowpaths 32
Chapter 2 Machine Learning Deciphers CO ₂ Sequestration and Subsurface F from Stream Chemistry	lowpaths 32
Chapter 2 Machine Learning Deciphers CO ₂ Sequestration and Subsurface F from Stream Chemistry	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Surplustic Detector 	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 2.3 Results and Discussion 	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 2.3 Results and Discussion 2.3.1 Synthetic Data Model 	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 2.3 Results and Discussion 2.3.1 Synthetic Data Model 2.3.2 Application to Shale Hills 	lowpaths 32 33 37 37 37 38 38 40 41 41 41
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 2.3 Results and Discussion 2.3.1 Synthetic Data Model 2.3.2 Application to Shale Hills 2.3.3 Rates of Weathering and CO₂ Sequestration at Shale Hills 	lowpaths 32 33 33 37 37 38 38 40 41 41 41 41
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 2.3 Results and Discussion 2.3.1 Synthetic Data Model 2.3.2 Application to Shale Hills 2.3.3 Rates of Weathering and CO₂ Sequestration at Shale Hills 2.3.4 East River 	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 2.3 Results and Discussion 2.3.1 Synthetic Data Model 2.3.2 Application to Shale Hills 2.3.3 Rates of Weathering and CO₂ Sequestration at Shale Hills 2.3.4 East River 2.3.5 Hubbard Brook 	lowpaths 32 33 33 37 37 38 38 40 41 41 41 41 41 41 41 41 41 41 41 41 41
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 2.3 Results and Discussion 2.3.1 Synthetic Data Model 2.3.2 Application to Shale Hills 2.3.3 Rates of Weathering and CO₂ Sequestration at Shale Hills 2.3.4 East River 2.3.6 Predicting CO₂ release or drawdown from rock chemistry 	lowpaths 32 33 37 37 37 38 38 38 40 41 41 41 41 41 41 41 41 41 41 41 41 41
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry. Abstract 2.1 Introduction 2.2 Methods 2.2.1 Study Sites 2.2.2 Data Acquisition 2.2.3 Machine Learning Model 2.2.4 Synthetic Dataset 2.3 Results and Discussion 2.3.1 Synthetic Data Model 2.3.2 Application to Shale Hills 2.3.3 Rates of Weathering and CO₂ Sequestration at Shale Hills 2.3.4 East River 2.3.5 Hubbard Brook 2.3.6 Predicting CO₂ release or drawdown from rock chemistry 	lowpaths 32 33 37 37 37 38 38 40 41 41 41 41 41 41 41 41 41 41 41 41 41
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry	lowpaths
 Chapter 2 Machine Learning Deciphers CO₂ Sequestration and Subsurface F from Stream Chemistry	lowpaths 32 33 33 37 37 38 38 40 41 41 41 41 41 41 41 41 41 41 41 41 41

Abstract	63
3.1 Introduction	64
3.2 Methods	66
3.2.1 Data Acquisition	66
3.2.2 Water Sampling and Analysis	67
3.2.3. Rock Sampling and Analysis	69
3.2.4 Machine Learning Model	69
3.2.5 Data Analysis	71
3.3 Results	71
3.3.1 Sources of Sulfate	71
3.3.2 Dissolved Oxygen Dynamics	73
3.3.3 Streambed Pyrite in Shaver's Creek	73
3.3.4 Concentrations Across Watershed Scale	74
3.4 Discussion	74
3.4.1 Oxidation Model	74
3.4.2 Oxidation Model for Shale Hills	78
3.4.3 C-q Analysis	80
3.4.4 Explanations for Observed Sulfate > Predicted Sulfate	80
3.4.5 Application to Other Datasets	
3.4.6 Subsurface Redox Architecture in Small and Large Watersheds	85
3.5 Conclusions	86
3.6 Figures	
3.7 References	97
changes in temperature, precipitation, runoff, and erosion?	101
Abstract	101
4.1 Introduction	103
4.2 Methods	107
4.2.1 Watershed Selection and Data Acquisition	107
4.2.2 Climate Data	109
4.2.2 Sediment Yields	110
4.2.4 Weathering Calculations	112
4.3 Results and Discussion	114
4.3.1 Site Information	114
4.3.2 HI for Shale	
$4.3.3 \operatorname{SiO}_2$ Concentrations	
$4.3.4 \operatorname{SiO}_2$ Fluxes	101
4.3.5 Climate Controls on Weathering: Dry Watersheds	121
4.3.6 Climate Controls on Weathering: Wet Watersheds	
4.3./ Evaluation of Weathering Regimes in the United States	
4.3./ Evaluation of Weathering Regimes in the United States 4.4 Conclusions	121 122 127 129 132
 4.3./ Evaluation of Weathering Regimes in the United States 4.4 Conclusions	
 4.3./ Evaluation of Weathering Regimes in the United States	
 4.3./ Evaluation of Weathering Regimes in the United States	

A.1 NMF Model	151
A.2 Calculations	152
A.2.1 Solute Fluxes	152
A.2.2 Using Stream Chemistry to Calculate CO ₂ Drawdown or Release	153
A.2.3 Using Rock Chemistry to Calculate CO ₂ Drawdown or Release	158
A.2.4 Lag-time Calculation	162
A.2.5 Mineral-derived Solute Concentrations	163
A.3 Seasonality of Pyrite-sulfate Fluxes	164
A.4 Rain-correction	164
A.5 Supplemental Tables	165
A.6 Supplemental Figures	171
A.7 Supplemental References	175
Appendix B Supplemental Information for Chapter 3	176
B.1 Oxidation Model Derivation	176
B.2 Logistic Regression for Coal	179
B.3 Supplemental Tables	181
B.4 Supplemental Figures	
Appendix C Supplemental Information for Chapter 4	189
C.1 Sensitivity Analysis	189
C.2 Shale Age	190
C.3 Supplemental Tables	192
C.4 Supplemental Figures	198

LIST OF FIGURES

Figure 1-1: Schematic diagrams showing kinetic limited (A, B) and erosive transport limited (C, D) weathering regimes in both a 1-D soil profile (A, D) and 3-D watershed (B, C). Blue lines in B and C represent subsurface flowpaths in each weathering regime. Note that KL weathering only features shallow flowpaths through the reaction front; whereas ETL weathering features deeper flowpaths. This is because KL watersheds tend to be small and ETL watersheds tend to be large; thus, rivers in ETL watersheds sample deeper regional groundwater flow	.23
Figure 1-2: Schematic diagram showing the different concentration-discharge (C-q) relationships across Event (A), Seasonal (B), Interannual (C), and Inter-site (D) timescales. For explanations of equations shown for the respective C-q curves refer to Section 1.1.3. Annotation on the C-q curves represent the potential weathering regimes that feature the specific C-q relationships shown. Weathering regimes include Advective Transport Limited (ATL), Saturation Limited (SL), Equilibrium Limited (EL), Kinetic Limited (KL), Runoff Limited (RL), and Erosive Transport Limited (ETL).	.24
Figure 1-3: Schematic diagram showing weathering equations and expected plots for four spatiotemporal scales. For explanations on the equations shown for each scale, refer to section 1.1.4. In general, blue colors represent solute chemistry and brown colors represent solid-phase chemistry.	.25
Figure 2-1: Schematic summarizing the reactions, timescales, and net CO ₂ release to or uptake from the atmosphere accompanying weathering of silicate and carbonate minerals. Uptake or release depends upon timescale, as shown, and as discussed in text. CaSiO ₃ is used as a generic silicate mineral.	.55
Figure 2-2: Schematic diagram showing the differences between a traditional mixing model and our machine learning mixing model (A). Notably, in the machine learning mixing model, endmember chemistry is not assigned <i>a priori</i> , but rather derived from patterns in the data. Results from using our machine learning mixing model (i.e., NMF) on a synthetic dataset of known endmember chemistry and mixing proportions (i.e., α) are shown in B and C. Using only the synthesized stream sample chemistries, the model adequately recovered the correct mixing proportions (B) and endmember chemistries (C). The axes in (C) are the true concentration ratios of the endmembers and the NMF-derived concentration ratios of the endmembers.	.56
Figure 2-3: Schematic cross section of Shale Hills showing the depths (labelled lines) where oxidation of pyrite, and dissolution of carbonate, chlorite, and illite initiate	

where oxidation of pyrite, and dissolution of carbonate, chlorite, and illite initiate (modified after Brantley et al., 2013a). Illite and chlorite dissolve at all depths above the labelled lines, but reactions of carbonate minerals and pyrite only occur in a narrow one-meter wide depth zone under the ridge that widens to several meters toward the valley. Specifically, pyrite oxidation is complete under both ridge and valley at the depths where chlorite dissolution initiates. Carbonate dissolution is

- Figure 2-4: Sulfur isotope composition plotted versus concentration for sulfate in the subset of stream or groundwater samples at Shale Hills where S isotopes were measured (symbols; Jin et al., 2014). Dot-dashed lines represent the average sulfur isotope range for acid rain in USA (3-5‰; Bailey et al., 2004) and dashed lines represent the average sulfur isotope range of pyrite calculated from NMF results (-9.5% to -7.2%). Sulfur isotopes in pyrite at Shale Hills were previously constrained to lie in the range of -1‰ to -15‰ (Jin et al., 2014). (B) Plot showing the calcite saturation index (log $\Omega_{calcite}$) vs. concentration of pyrite-derived sulfate (calculated through NMF) in surface and groundwater samples at Shale Hills where alkalinity was measured. Here Ω_{calcite} (= ion activity product / equilibrium constant for calcite dissolution) is <1 the water is undersaturated with respect to calcite, and when Ω_{calcite} is >1, the water is oversaturated. Black line represents water-calcite equilibrium. Some samples in B differ from those in A because more samples were collected for alkalinity than sulfur isotopes. In both A and B, color shading represents the fraction of total sulfate derived from pyrite calculated by NMF (i.e., α_{deep}). (C) Time series plot showing the flux of sulfate in Pennsylvania NADP site PA42 (2.8 km from Shale Hills) from wet and dry deposition (see Appendix A.2.4). Black bar shows the NMF results for the export flux of sulfate derived from acid rain for Shale Hills during our sampling period, and the rationale for the inferred 19 y lag between input

Figure 3-7: Map showing the selected sites in the Western United States (A). Boxplots for natural (i.e., contains no coal) watersheds showing how $C_{sulf}^{max,obs}$ (B) and Da (C) change across spatial scale
Figure 3-8 : Schematic plot showing the three characteristic concentration-discharge patterns observed in watersheds in the northeastern and western US. By studying catchments within the SRB and western US, we observed that pyrite oxidation is always limited by transport of the oxidant to the mineral everywhere except where coal has exhumed at the land surface. For the latter catchments, oxidation is kinetic (or mineral interface-) limited
Figure 4-1: Map showing the coverage of shale lithology and the sampling locations (n = 142) for shale watersheds
Figure 4-2 : Holdridge classification triangle showing the climate classifications for our shale watersheds. Note that the potential evapotranspiration ratio is the inverse of HI (i.e., PET/MAP)
Figure 4-3: (A) Histogram (bars) and kernel density (solid black line) showing the distribution of HI values across the United States with shale as the outcropping lithology. (B) Plot showing HI vs. the between-group variance ($\sigma_{between}^2$) using the Otsu method for threshold determination for the same dataset in panel A. (C) Plot showing HI vs. SiO ₂ Flux, i.e., F_{SiO_2} , for all shale watersheds (n = 142). In all three plots (A-C), the vertical dashed line represents the threshold HI value determined using its respective method. 138
Figure 4-4: Flow weighted SiO ₂ concentrations as a function of MAT (A), MAP (B), Runoff (C), and Sediment Yield (D)
Figure 4-5: Activity diagrams of the chlorite-smectite-kaolinite-gibbsite system for Mg-SiO ₂ . (A) General stability zones for each of the minerals at T ₀ (i.e., 8.2°C). (B) Flow-weighted average river composition for of the 139 watersheds. The 3 missing watersheds had an insufficient number of Mg and pH measurements to calculate the average river chemistry. Error bars in (B) denote the interannual variability for the average composition. Plot (C) shows every sample (n = 11,291) for the 82 watersheds with HI < 0.55, and plot (D) shows every sample (n = 9,991) for the 60 watersheds with HI > 0.55. In both (C) and (D) data are only shown where concentrations of SiO ₂ , Mg ²⁺ , and pH were measured in the same water sample
Figure 4-6 : SiO ₂ Fluxes (<i>F</i> _{SiO₂}) as a function of MAT (A), MAP (B), Runoff (C), and Sediment Yield (D)
Figure 4-7 : Plots showing how [SiO ₂] (A), [Mg ²⁺] (B), and pH (C) vary with MAT for sites with HI < 0.55. Sites in equilibrium with amorphous SiO ₂ were removed because their equilibrium is not consistent with eqs. 4-10 and 4-11
Figure 4-8 : Activity product (Q) for the kaolinite-smectite equilibrium as a function of MAT (A) and MAP (B). In both plots dashed line represents the equilibrium

constant (K_{eq}) for the transformation of kaolinite to smectite, which was calculated using the thermo.tdat database in GWB 2022 Community Edition	143
Figure 4-9: Plot showing the calculated pCO_2 concentrations using eq. 4-18 vs. HI. Sites shown are watersheds with HI < 0.55. Sites in equilibrium with amorphous SiO ₂ were removed because their equilibrium is not consistent with eqs. 4-12 and 4-14	144
Figure 4-10 : Location of weathering regimes for HUC12 watersheds in the United States based on the intersections of shale lithology, climate, and topography	145

LIST OF TABLES

Table 1-1: Common abbreviations found in this dissertation	22
Table 2-1 : Fluxes of SO_4^{2-} , Cations, and CO_2	54
Table 4-1: Temperature sensitivity for silica fluxes in watersheds from this study and from published literature.	135

ACKNOWLEDGEMENTS

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Chapter 1

Motivation and Outline

1.1 Motivation

1.1.1 Introduction

Watersheds act as chemical reactors integrating complex interactions between the hydrosphere, biosphere, lithosphere, and atmosphere (Aufdenkampe et al., 2011; Grathwohl et al., 2013; Li, 2019; Li et al., 2022). As water flows through these reactors, minerals dissolve releasing solutes, which are exported by the stream. Mineral weathering is important because of its control on modern water quality and long-term climate. For example, minerals have been shown to release heavy metals into groundwater, impacting water quality (e.g., Smedley and Kinniburgh, 2013). Moreover, underlying lithology is considered a major control on river chemistry (e.g., Bluth and Kump, 1994). With respect to long-term climate, weathering of silicate minerals removes CO₂ from the atmosphere (e.g., Walker et al., 1981; Berner, 2004), and weathering of carbonate (coupled to pyrite oxidation) releases CO₂ to the atmosphere (e.g., Torres et al., 2014; Kölling et al., 2019; Kemeny et al., 2021).

Geologists investigate landscapes and Earth processes through direct observation. Mineral weathering, however, largely occurs below our feet along subsurface flowpaths that define landscapes we cannot see. These landscapes consist of depth-dependent distributions of minerals that control and are controlled by the evolution of groundwater chemistry. The subsurface architecture of most watersheds remains largely uncharacterized, hindering our abilities to predict water quality and mineral weathering across scales (Edmunds et al., 2003; Brantley et al., 2017).

In this dissertation I analyze river chemistry and relate it to the mineralogical structure of watersheds. I link variations in concentration and discharge (C-q; full list of abbreviations can be found in Table **1-1**) to subsurface flowpaths and mineral distributions. The new information gleaned from this work increases our knowledge of watershed processes and weathering dynamics. Future work could integrate the results herein into hydrologic and geochemical models.

1.1.2. Modalities of Weathering

Weathering dynamics in watersheds depend on many factors including -- but not limited to -- climate (e.g., White and Blum, 1995; Gaillardet et al., 1999), hydrology (e.g., Maher, K. 2010; Pacheco and Van der Weijden, 2012; Maher and Chamberlain, 2014), erosion (e.g., Stallard and Edmond, 1983; Calmels et al., 2007), lithology (e.g., Bluth and Kump, 1994), land use (e.g., Perrin et al., 2008), and vegetation (e.g., Nezat et al., 2004; Egli et al., 2008; Molina et al., 2019). In any given location, we often assume that there is a rate limiting step that controls weathering. We classify watersheds into "weathering regimes" based on their rate liming step. In this dissertation, I consider three endmember weathering regimes defined over long timescales: Erosive Transport Limited (ETL), Kinetic Limited (KL), and Runoff Limited (RL). When erosion rates are low, weathering is limited by the supply of fresh minerals (Stallard and Edmond, 1987; Stallard, 1988; West et al., 2005; Gabet and Mudd, 2009; Dixon and von Blanckenburg, 2012; Lebedeva et al., 2010). These watersheds are considered ETL, because weathering rates linearly increase with erosion (i.e., removal of weathered material and exhumation of fresh material). Using geochemical models, Lebedeva et al. (2010) have hypothesized that in ETL soils, reactive minerals are absent from the land surface (Figure **1-1C**) because they dissolved faster than they were physically removed from the system. When a mineral is absent in a soil profile at land surface, but present in the subsurface at some depth, we refer to the weathering profile as "completely developed" (Figure **1-1D**; Brantley et al., 2008). The depth interval across which the mineral is actively weathering is called a "reaction front" (Brantley et al., 2008). In some watersheds, erosion rates are fast enough that the reactive mineral does not completely dissolve before it is physically removed by erosion. In this situation, weathering rates are limited by interfacial reaction kinetics rather than erosion rates; therefore, these soil profiles are considered KL. In this dissertation, I follow a recent approach (Brantley et al., in review) and hypothesize that watersheds characterized by incompletely developed soil profiles across the landscape can be considered KL watersheds. In KL watersheds, the reactive mineral -- and its reaction front -- is present at land surface at ridgelines and in valleys (Figure **1-1B**), and we refer to this type of weathering profile as "incompletely developed" (Brantley et al., 2008; Figure **1-1A**).

Given the weathering profile framework for ETL and KL watersheds described above, we still must consider the subsurface mineral distributions because they are important in determining how weathering rates will respond to climate and erosion. For example, when reaction fronts for reactive minerals are situated beneath the land surface (i.e., ETL), soils shield them from the effects of climate (e.g., Edmond et al., 1995; Boeglin and Probst, 1998) and, thus, their weathering rates may become independent of temperature and precipitation. On the other hand, when reactive minerals are shallow so that reaction fronts are exposed at land surface (i.e., KL), weathering rates might increase exponentially with temperature and linearly with precipitation as has been shown by some workers (White and Blum, 1995). This simple view is made more complicated by several circumstances.

The first complication is that there are many different minerals that weather in a single watershed; some form completely developed profiles and others form incompletely developed profiles. Brantley et al. (2014) describe how this scenario results in "nested reaction fronts" (e.g., Brantley et al., 2014; Wan et al., 2019; Gu et al., 2020). In some watersheds, minerals that form completely developed profiles and minerals that form incompletely developed profiles release common solutes during weathering (e.g., SiO₂, Ca²⁺, Mg²⁺), which can lead to complex weathering dynamics as recorded by the stream chemistry and also can cause coupling between reaction kinetics. To more easily interpret these different weathering reactions, geochemists and hydrologists "unmix" the river chemistry using either forward (e.g., Garrels and MacKenzie, 1967; Moon et al. 2007) or inverse (e.g., Hooper et al., 1990; Gaillardet et al., 1999; Torres et al., 2016) modeling approaches. There are many unanswered issues surrounding interpreting weathering reactions from river chemistry, including: how can we identify unknown sources (e.g., Valder et al., 2012; Popp et al., 2019; Xu Fei and Harman, 2022) and how do we account for time lags in transport (e.g., DeWalle et al., 2016). While many geochemical papers have long treated questions of unmixing, new data-driven models are now allowing new approaches (e.g., Xu Fei and Harman, 2022). I address several aspects of these questions in Chapter 2 of this dissertation (see section 1.2.1).

The second complication is that watersheds are not 1-dimensional soil profiles and can integrate several different weathering regimes. For example, transitional or mixed regime (i.e., TR) weathering has been described for soils (Ferrier et al., 2016), hillslopes (Lebedeva and Brantley, 2013), and watersheds (Brantley et al., in review). TR describes weathering fluxes that are partly ETL and partly KL. Large watersheds can integrate both highland (potentially KL) and lowland (potentially ETL) topography (West et al., 2005; Dixon and von Blanckenburg, 2012); thus, weathering in large watersheds could be considered TR. To account for this issue, many weathering studies focus on small headwater catchments (e.g., White and Blum, 1995); however, global weathering budgets typically utilize chemistry from the world's largest rivers (Gaillardet et al., 1999). I evaluate weathering dynamics in small and large watersheds in Chapter 3 to consider

this issue (see Section 1.2.2). Additionally, I investigate weathering dependencies in TR watersheds in Chapter 4 (see Section 1.2.3).

The third complication is that an incompletely developed weathering profile does not always indicate that the weathering flux of that particular mineral is KL. In dry landscapes where potential evapotranspiration (PET) is much larger than mean annual precipitation (MAP), a third long-term weathering regime has been hypothesized (Rasmussen et al., 2011), and recently termed runoff limited weathering (RL) (Brantley et al., in review). In these watersheds, high PET causes weathering products to become concentrated in porefluids, leading to high solute concentrations in streams (Li et al., 2022) that in some cases have been observed to be constant across a wide range of discharge (Godsey et al., 2019). In these systems, water throughput limits the reaction rate; therefore, weathering rates linearly increase with runoff in RL watersheds (Brantley et al., in review). Like KL, soil profiles in RL landscapes have been hypothesized to typically form incomplete weathering profiles (Rasmussen et al., 2011; Brantley et al., in review). These profiles do not form because the timescale of weathering is longer than the timescale of erosion, but rather because of the lack of water, which in some cases results in formation of secondary minerals that retain some weathering products from the primary minerals even at the land surface (e.g., Folkoff and Meentemeyer, 1985). I investigate the different long term weathering modalities (ETL, KL, RL) for silicate weathering in shale watersheds in chapter 4 (see Section 1.2.3).

In addition to long-term weathering regimes (timescales relevant to the residence time of soils), there are also short-term weathering regimes (timescales relevant to the residence time of groundwater). For example, advection of meteoric water to the subsurface reaction fronts can bring fresh reagents (e.g., CO₂, O₂) other than H₂O needed for weathering reactions to progress. In these situations, the groundwater might not come to equilibrium, but rather approach a steady state concentration when all of the weathering reagent is consumed. When advection of reagent is

limited, the weathering regime has been called "Advective Transport Limited" (ATL) weathering (e.g., Yu and Hunt, 2017). Lastly, short term weathering (e.g., solute production in streams) can also be KL. In these systems, fast erosion does not cause the kinetic limitation but the cause, rather, is fast water throughput. Water advection is faster than mineral dissolution, resulting in KL weathering. Whether or not a watershed experiences ATL or KL (short-term) is related to the length of the groundwater flowpaths and the depths of the reactive minerals in the subsurface. I explore ATL and short-term KL in chapter 3 of this dissertation (see section 1.2.2).

1.1.3. Modalities of Concentration-Discharge Relationships

To investigate weathering dynamics, scientists often utilize concentration-discharge (C-q) relationships. Precipitation falls on a watershed, infiltrates through the soils and enters the groundwater. Groundwater then flows through the bedrock and enters the stream, dissolving minerals and releasing solutes along subsurface flowpaths. How the concentrations of these solutes change with discharge reveals information about weathering reactions (Ibarra et al., 2016), groundwater flowpaths (Hoagland et al., 2017), storage (Duffy and Cusumano, 1998), solute transport (Rose et al., 2018), among others. Additionally, C-q dynamics can reflect short-and long-term weathering regimes depending on the timescale of the C-q relationship. For example, C-q relationships can be classified at "event", "seasonal", "interannual", and "inter-site" scales (Godsey et al., 2009; Godsey et al., 2019; Figure **1-2**). Each of these classifications relates to different timescales and integrates different processes.

The shortest timescale is event-based C-q dynamics. These studies reflect C-q dynamics that typically track how concentration changes over the course of a single flood pulse or multiple such pulses. Event-scale C-q dynamics feature complex patterns such as hysteresis loops, which means that concentration varies with discharge in one way during the rising limb of the flood

pulse, and then it varies in a different way on the falling limb of the flood pulse (see Figure **1**-**2A**). This cyclic C-q relationship (i.e., hysteresis) is thought to be dependent on mixing (Evans and Davies, 1998; Bouchez et al., 2017; Neira et al., 2020), deep and shallow groundwater connectivity (Rose et al., 2018; Pohle et al., 2021), and the relative timescales of dissolution to advection (Hornberger et al., 2002). Most often, weathering products exhibit a clockwise hysteresis pattern with respect to concentration (y-axis) and discharge (x-axis) (Rose et al., 2018), which is schematically depicted in Figure **1-2A**. Event-scale C-q dynamics can be modeled using the following equation (Minaudo et al., 2017; Musolff et al., 2021):

$$C = aq^b + g\frac{dq}{dt} \tag{1-1}$$

Here, *C* is the concentration of weathering product in the stream, *q* is the instantaneous discharge during the flood pulse, $\frac{dq}{dt}$ is the derivative of the discharge that differentiates the rising and falling limbs, and *a*, *b*, and *g* are fitting parameters for the model. *b* is referred to as the power-law slope.

The next timescale is seasonal-based C-q dynamics. These dynamics typically describe how concentration varies with discharge across the wet to dry seasons. At the seasonal scale, concentration varies non-linearly with discharge. At low q, C tends to be high and constant with increasing q; whereas, at high q, C tends to be low and decreases with increasing q (Figure 1-2B). When concentration is constant with varying discharge, we refer to the C-q relationship as "chemostatic", and when concentration decreases with increasing discharge, we refer to the C-q relationship as "dilution behavior" (Godsey et al., 2009). There is a third C-q classification, which is when concentration increases with increasing discharge, which is referred to as "flushing behavior". Flushing behavior, uncommon for weathering products, is more often associated with dissolved organic carbon and nutrients in soils (e.g., Boyer et al., 1997; Zarnetske et al., 2018). The general shape of the seasonal C-q curve has been described by several different models (e.g., Langbein and Dawdy, 1964; Johnson et al., 1969; Berner, 1978; Kump et al., 2000). Recently, Maher and Chamberlain (2014) developed the "solute production model", which describes this seasonal behavior (where some terms have been re-named following Ibarra et al., 2016):

$$C = \frac{C_0}{1 + \frac{Dw}{q}} + \frac{C_{max}\frac{Dw}{q}}{1 + \frac{Dw}{q}}$$
(1-2)

Here, C_0 is the initial concentration of the solute for the water entering the system (i.e., rainwater; mg/l), C_{max} is the empirical maximum concentration of the solute (which may be an equilibrium concentration in some cases or a steady state in others; mg/l), and Dw is the Damköhler coefficient (m yr⁻¹). Dw is a function of the Damköhler number (Da; Da = Dw/q), which is the characteristic timescale of the reaction divided by the characteristic timescale of advection. If the initial concentration is zero or the sources of solutes are separated (see Section 1.1.2), then eq. 1-2 can be simplified to:

$$C = \frac{C_{max}Dw}{Dw+q} \tag{1-3}$$

The mathematical function expressed in Eq. 1-3 produces a C-q curve such as depicted in Figure 1-2B. We can investigate seasonal C-q dynamics to learn about the weathering regimes discussed in Section 1.1.2. For example, assuming that one mineral produces the target solute during a weathering reaction, when the C-q curve is chemostatic (i.e., low q), the flowpaths that are integrated by the stream are long and come to equilibrium (or steady state) with respect to the mineral reacting in the bedrock, such that *C* approaches C_{max} . This means that weathering at low q is controlled by equilibrium (SL or EL) or supply of reagent (ATL). Weathering at high q is controlled by reaction kinetics (KL) because water advection rates are faster than dissolution rates. Given this framework, at seasonal scales, chemostasis indicates ATL and dilution indicates KL. Over the course of a year, a stream intermittently switches between chemostatic and dilution (depending on wet and dry conditions); thus, the rate limiting step also changes. There are several outstanding questions surrounding seasonal C-q dynamics such as: How do we interpret

or predict C_{max} (Ibarra et al., 2016), at what q does a watershed switch from chemostatic to dilution, and how can we utilize seasonal C-q to predict where reaction fronts are located in the subsurface? I explore these questions in Chapter 3 of this dissertation (see Section 1.2.2).

The next C-q timescale is interannual dynamics. Unlike seasonal C-q dynamics, interannual C-q document the year-to-year variability in the flow-weight mean concentrations (C_m) and the mean annual discharge $(q_m; \text{Godsey et al., 2019})$:

$$C_m = aq_m^b \tag{1-4}$$

This equation is similar to the event-based C-q, but does not include the hysteresis term (i.e., $g \frac{dq}{dt}$). Again, *b* is the power law exponent, which tells us if the watershed is chemostatic (*b* = 0) or dilution (*b* = 1). The definitions of chemostatic and dilution are idealized endmembers, and, in reality, 0 > b > -1 is common. This can be explained by mixing and concentration contrasts between shallow and deep flowpaths (Zhi et al., 2019; Zhi and Li, 2020; Botter et al., 2020). For this reason, we often define ranges for chemostatic (i.e., 0.1 > b > -0.1) and dilution (*b* < -0.1) (Herndon et al., 2015). Over interannual timescales, C-q behavior does not change depending on whether q is high or low (like seasonal dynamics), but rather represents the long-term average of C-q behavior in a catchment. This means that, for weathering products, a watershed is generally classified as only chemostatic or only dilution (Figure 1-2C). Again, chemostasis indicates ATL and dilution indicates KL over this timescale. I explore interannual C-q dynamics for a series of watersheds in the Northeastern United States in Chapter 3 (see Section 1.2.2).

Lastly, the longest timescale is the inter-site comparison. Unlike the previous three timescales that look at C-q dynamics as a function of timescale, inter-site timescales treat C-q dynamics as a function of spatial variables. In other words, all timescales up to this point have referred to a single watershed, whereas inter-site timescales refer to multiple watersheds. Although short timescale C-q dynamics have been extensively studied, inter-site C-q dynamics have been far less frequently investigated (e.g., Godsey et al., 2019, Li et al., 2022) and remain a rich avenue for future work. Similar to interannual C-q, inter-site C-q is expressed in terms of flow-weight mean concentrations and the mean annual discharge:

$$C_m = Aq_m^B \tag{1-5}$$

Although eq. 1-4 and 1-5 are functionally identical, the preexponential (A) and the power law exponent (B) were defined differently in eq. 1-5 (see Li et al., 2022). Here, A is the bulk rate of the reaction, which is dependent on parameters such as the rate constant, surface area, temperature and soil moisture averaged over an entire watershed. B is the ratio of the rate dependence on water content to the discharge dependence on water content, which quantifies concentration sensitivity to variations in mean discharge (Li et al., 2022). Because inter-site C-q dynamics represent comparisons of multiple watersheds, they also reflect the longest timescales, and their C-q modalities are hypothesized to correspond more directly to the long timescale weathering regimes (i.e., ETL, KL, RL). As discussed in section 1.1.2, concentrations in RL watersheds are constant over long timescales because high PET concentrates weathering products until they reach equilibrium or steady state with respect to minerals in the bedrock. RL weathering fluxes at watershed scale are hypothesized, therefore, to exhibit chemostatic behavior at the inter-site scale (Brantley et al., in review). This has been observed in arid watersheds (Godsey et al., 2019). In contrast, ETL fluxes at the inter-site scale are more complicated to interpret. Intuitively, we might expect KL watersheds to exhibit dilution behavior because KL fluxes for watersheds at the seasonal and interannual scales exhibit dilution behavior. ETL fluxes for watersheds tend to be observed for larger watersheds; therefore, they might have long flowpaths and exhibit chemostasis at the interannual timescales. It is not obvious how inter-site C-q dynamics would behave for ETL watersheds. In general, we can conceptualize the long-term flux of weathering products as $Flux = C_m Q_m$. But for KL and ETL fluxes for watersheds, longterm weathering rates have been observed to depend on temperature and erosion rate, respectively (see Brantley et al., in review), but not on Q_m . Therefore, if Q_m increases or decreases, internal feedbacks must drive the system back to a constant $C_m Q_m$ at constant temperatures and erosion rates. This would be consistent with KL and ETL both exhibiting dilution behavior at inter-site timescales. Inter-site dilution behavior was observed for weathering products in humid watersheds (Godsey et al., 2019; Li et al., 2022), which supports our hypothesis for KL and ETL watersheds. Inter-site C-q dynamics have not been extensively studied, and many complicating factors such as land use and lithology make their interpretation difficult (Hartmann et al., 2010; Jansen et al., 2010; Godsey et al., 2019). I explore interannual C-q dynamics for a series of shale watersheds in the United States in Chapter 4 (see Section 1.2.3).

1.1.4. Weathering Across Space and Time

As seen in Section 1.1.3, C-q dynamics depend on temporal scales, which generally implies that they depend also on spatial scales. As spatial scales get larger, temporal scales also tend to increase. Weathering rates change as a function of spatial scale because of variations in techniques for estimating mineral surface area (Navarre-Sitchler and Brantley, 2007). Discrepancies in weathering dynamics have also been observed between different spatial and temporal scales (e.g., West et al., 2005; Dixon and von Blanckenburg, 2012; Larsen et al., 2014). Different methods for investigating weathering integrate different spatial and temporal scales, but it is not well understood how weathering dynamics change across these scales. Here we describe the materials, methods, and equations needed to investigate weathering across four spaciotemporal scales (Figure **1-3**).

To describe these scales for a given weathering reaction, I label them using the notation of space-time. There are two spatial scales (small and large) and two temporal scales (short and long), resulting in four permutations of space-time. In each case, the actual temporal or spatial dimension is defined by the characteristic timescale of equilibration for a weathering reaction or the characteristic length scale over which a flowing packet of water equilibrates. The first scale described here is the small-short scale. To study small-short scale weathering, scientists typically measure the chemistry of pore fluids in soils (Stonestrom et al., 1998). The pore fluids integrate weathering products from reactions happening today (i.e., short) and the soil profiles are points in space (i.e., small). For example, the rate for small-short weathering (i.e., $\Omega_{small-short}$, mol m⁻² yr⁻¹) can be described following (White, 2002):

$$\Omega_{small-short} = 1000 \frac{\phi S}{A\eta} \left(\frac{\nu}{b_p} \right) \tag{1-6}$$

Here, ϕ is the regolith porosity (m³ m⁻³), *S* is the pore fluid saturation (m³ m⁻³), η is the stoichiometric coefficient describing the solute release from mineral weathering, v is the solute advection velocity (m yr⁻¹), *A* is the mineral surface area (m² m⁻³), and *b_p* is the slope of the solute gradient in the soil profile (m l mol⁻¹). Using eq. 1-6, small-short weathering is assessed by the vertical gradient of solutes in the soil pore fluid.

We can also use the solid-phase chemistry of the soils to investigate weathering rate. I classify this as small-long weathering because soil chemistry changes over long timescales compared to solute chemistry. White (2002) describes the weathering rate for small-long weathering (i.e., $\Omega_{small-long}$, mol m⁻² yr⁻¹) as:

$$\Omega_{small-long} = 1000 \frac{\rho_{\rm w}}{A\eta} \left(\frac{\omega}{b_p}\right) \tag{1-6}$$

Here, ρ_w is the regolith specific density (g cm³) and ω is the solid-state weathering velocity (m yr⁻¹). Using eq. 1-6, small-short weathering is assessed by the vertical depletion of cations in the regolith. An alternative definition for $\Omega_{small-long}$ comes from Riebe et al. (2004):

$$\Omega_{small-long} = D[X]_{rock} CDF_x \tag{1-7}$$

where

$$CDF_{x} = \left(\frac{[X]_{rock}[Zr]_{soil}}{[X]_{soil}[Zr]_{rock}} - 1\right)$$
(1-8)

Here, D is the total denudation rate (kg m⁻² yr⁻¹), $[X]_{rock}$ is the concentration of element X (mol kg⁻¹) in the bedrock, and CDF_x is the fraction of X that has been chemically weathered. CDF_x is calculated by comparing the concentration of mobile element X in the soil ($[X]_{soil}$) and bedrock ($[X]_{rock}$) to the concentration of immobile element Zr in the soil ($[Zr]_{soil}$) and bedrock ($[Zr]_{rock}$) (eq. 1-8). CDF_x is calculated over different depth intervals, and the depth interval for the CDF_x used in eq. 1-8 is typically the depth where cosmic rays penetrate in the soil (e.g., Riebe et al., 2005).

Solid phase chemistry can also be used to assess long-large weathering. As erosion removes weathered material from hillslopes, sediments are transported to rivers and exported from the watershed. The flux of sediment out of watersheds is called sediment yield (S_y , kg m² yr⁻¹). By measuring the chemistry of exported sediments, we can calculate the rate for large-long weathering (i.e., $\Omega_{large-long}$, mol m⁻² yr⁻¹) because watersheds integrate large spatial scales and sediment chemistry integrates long temporal scales.

$$\Omega_{large-long} = S_{\gamma}[X]_{rock} CDF_{\chi} \tag{1-9}$$

One problem with this approach is defining the parent composition (i.e., $[X]_{rock}$ and $[Zr]_{rock}$), which is difficult when the bedrock composition is spatially variable. Recently, Deng et al. (2022) compiled sediment chemistry globally and assessed weathering utilizing the chemical index of alteration (CIA):

$$CIA = \frac{Al_2O_3}{Al_2O_3 + CaO + Na_2O + K_2O} \times 100$$
(1-10)

where Al_2O_3 , CaO, Na₂O, and K₂O are the weight percent oxides measured in suspended and bed sediments in rivers. Deng et al. (2022) compile sediment chemistry for global rivers. Using the

stoichiometry of feldspar dissolution and transformation to kaolinite, the fraction of feldspar dissolved (f_{diss}) can be calculated from CIA.

$$f_{diss} = -\frac{100}{CIA} + 2 \tag{1-11}$$

For feldspar, eq. 1-9 can be rewritten using eq. 1-11:

$$\Omega_{large-long} = S_y f_{diss} X_f \tag{1-12}$$

where X_f is the concentration of feldspar in the bedrock (mol kg⁻¹). X_f can easily be estimated for a particular rock type (Lerman and Wu, 2008).

The last spatiotemporal weathering scale is the short-large scale. For this scale, we utilize solute chemistry in rivers. As described for the short-small and long-large scales, solute chemistry reflects modern weathering (hence short timescales) and rivers integrate weathering over their entire drainage basin (hence the large spatial scale). We calculate the rate for large-short weathering (i.e., $\Omega_{large-short}$, mol m⁻² yr⁻¹) following (Moatar et al., 2013):

$$\Omega_{large-short} = \frac{\sum_{i} c_{i} Q_{i}}{\sum_{i} Q_{i}} \bar{Q} A^{-1}$$
(1-13)

Here, \bar{Q} is the mean annual discharge (l yr⁻¹), and $\frac{\sum_i C_i Q_i}{\sum_i Q_i}$ is the flow-weighted average concentration (mol l⁻¹) where C_i and Q_i are the instantaneous concentration and discharge measured at timepoint *i*. As seen in eq. 1-13, short-large weathering is dictated by river concentrations and discharge, which, as discussed in section 1.1.3, can vary dependent or independent of each other based on the weathering regime of the watershed. One complicating factor is the large variability in watershed size within the short-large weathering category. For example, small headwater catchments can be < 1km², and large HUC2 watersheds can be > 1,000,000 km². This variability reflects that the four categories of weathering dynamics are endmember categories.

Each spaciotemporal category has its own benefits and drawbacks with respect to understanding weathering dynamics. For example, large spatial scales give insights into globally relevant processes, but interpreting their site-to-site variability can be difficult because of highly heterogeneous watershed characteristics. Long temporal scales provide information about weathering relevant to earth history and the rock record, but climate variability over the residence time of soils can lead to confounding results or under-constrained models. Many questions remain unanswered with respect to scaling such as: how do we apply site-specific studies regionally or globally, how do weathering dynamics change across spatial scales, and are modern and long-term weathering rates consistent? In Chapter 2, I compare large-short to small-long weathering dynamics in three watersheds (see Section 1.2.1), in Chapter 3 I evaluate how large-short dynamics change across watershed size (see Section 1.2.2), and in Chapter 4 I investigate how spatial scale influences the long-term weathering regime across watersheds (See Section 1.2.3).

1.1.5. Connecting Mineral Distributions to Weathering Dynamics

As discussed throughout this chapter, where minerals are located in the subsurface impacts watershed processes and dictates weathering regimes. Connecting river chemistry with vertical mineral distributions remains difficult, however, because of the lack of subsurface observations in most watersheds. Typically, to assess reaction fronts and mineral depletion, geologists drill boreholes and measure the solid phase chemistry with depth (e.g., Jin et al., 2010; Brantley et al., 2014; Gu et al., 2020; Liao et al., 2022). These 1-dimensional weathering profiles cannot fully describe the complexity of the subsurface because they are spatially limited. Recently, intensive application of geophysical techniques have yielded 2-dimensional (e.g., Befus et al., 2011; Holbrook et al., 2014; Gu et al., 2020; Ma et al., 2021) and 3-dimensional (e.g., Keifer et al., 2019; Wang et al., 2021) views of subsurface weathering patterns.

An alternative approach to investigating the subsurface is through analyzing river chemistry. How river chemistry changes with time and space reveals information about subsurface flowpaths and mineral distributions. In this chapter, I have reviewed the importance of weathering dynamics in watersheds and how they relate to the mineralogical architecture of a watershed. I highlighted several unknowns in the field related to rate limiting step, concentration discharge dynamics, and spaciotemporal scaling. Although this dissertation cannot address all outstanding questions posed here, we do analyze several aspects of these issues, specifically related to weathering of carbonate minerals, silicate minerals, and pyrite in shale and mixed lithology watersheds. This dissertation is a culmination of comparing chemical analyses from more than 120,000 river samples from >600 watersheds across the United States that are available in publicly-available databases, many maintained by the U.S. Geological Survey. What follows are brief outlines of each of the chapters contained within this dissertation.

1.2 Chapter Summaries

1.2.1 Summary of Chapter 2

In this chapter, we investigate the weathering dynamics of pyrite, carbonate, and silicate minerals by analyzing variations in river chemistry. Typically, to understand weathering reactions in watersheds, scientists measure the chemistry in rivers because they integrate weathering processes over their entire drainage area. Solutes in streams, however, come from many different sources; therefore, we must "unmix" the river chemistry to apportion solutes to various dissolving minerals. This process is difficult because endmembers chemistries of various sources are often unknown or under constrained.

Based on the analysis of subsurface mineral distributions in boreholes (e.g., Jin et al., 2010; Brantley et al., 2013; Wan et al., 2019; Gu et al., 2020), we know that reactive minerals such as pyrite and carbonate weather deep in the subsurface and less reactive silicate minerals

weather shallow in the subsurface. We hypothesize that different minerals dissolve along different groundwater flowpaths because of the presence of these shallow and deep reaction zones. As waters follow these flowpaths to the stream, they produce distinct patterns in the river chemistry. We developed a machine-learning based mixing model to detect these patterns and "unmix" their signals. This model does not make assumptions about the sources *a priori*, instead it derives the optimal source chemistries and mixing fractions simultaneously. The identity of these sources must be interpreted by the scientists using domain knowledge of the system.

We developed this model at the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO), an extensively studied watershed in central Pennsylvania (Brantley et al., 2018). We then applied our model to two other watersheds: East River in Colorado (Hubbard et al., 2018) and Hubbard Brook in New Hampshire (Holmes and Likens, 2016). These sites were selected to test the efficacy of our model across different climates and lithologies. After unmixing the weathering signals in these streams, we determined weather CO₂ was being sequestered or released in these watersheds. Lastly, we compared the results of our river chemistry to long-term weathering patterns as recorded in the rock and soil chemistry of these sites.

In this chapter, we found that watersheds intermittently switch between sequestering and releasing CO₂ depending on the predominant flowpath sampled by the stream. When flow is deep, pyrite oxidation coupled to carbonate dissolution results in release of CO₂, and CO₂ sequestration via silicate weathering is dominant in shallow flowpaths. We also found that acid rain competes with CO₂ as a weathering agent, which reduces the capacity of a watershed to sequester CO₂. Through comparing soil chemistry to river chemistry, we determined that watersheds have recently begun to recover from the impacts of acid rain. Long-term CO₂ dynamics recorded by soil profiles is roughly consistent with short-term CO₂ dynamics as recorded by stream chemistry.

In this chapter I worked collaboratively with Dr. Susan Brantley, Dr. Xin Gu, and Dr. Tao Wen to design, execute, and ultimately publish the chapter in *Hydrology and Earth System*

Sciences (Shaughnessy et al., 2021). Drs. Brantley and Gu assisted with the design of the study and the analysis of the results, and Dr. Wen assisted in methodology development. I was responsible for conceptualizing, analyzing, coding, and writing the publication.

1.2.2 Summary of Chapter 3

In this chapter we investigated how the depth of pyrite in the subsurface changes across spatial scale through analysis of concentration-discharge relationships. We couple our machine learning-based mixing model from Chapter 2 to a physically-based oxidation model that describes how concentrations of sulfate change as a function of discharge. In essence, our oxidation model represents the balance between solute production and dilution processes. We first develop this model in Shale Hills and then expand to Shaver's Creek, the larger HUC10 watershed that encompasses Shale Hills (Brantley et al., 2018). In Shaver's Creek, we assess where pyrite is present or absent at land surface by sampling outcropping bedrock along the streambed downstream. After that assessment, we apply our oxidation model to the Juniata River Basin (which encompasses Shaver's Creek) and the Susquehanna River Basin (encompasses Juniata River Basin). In all, we investigate a series of 15 sites within a series of 4 nested watersheds in the northeastern United States. Finally, we expand our analysis to ~300 watersheds in the western United States to compare results from the northeast and to test how coal mining impacts concentration-discharge dynamics.

In this Chapter, we found that variations in pyrite-derived could be described through a simple oxidation model that is a function of discharge. Using this model at Shale Hills, We found that the seasonality of sulfate production was consistent with the seasonality of dissolved oxygen (DO) consumption in groundwater. At low flow conditions, sulfate concentrations were high in the stream and DO was low in groundwater. When flow was high, sulfate concentrations were

low in the stream and DO was high in groundwater. Across all of the northeastern sites, the maximum sulfate concentrations observed in the streams were lower than would be predicted by DO in equilibrium with the atmosphere for small watersheds. Large watersheds featured sulfate concentrations much higher than would be predicted by the advection of dissolved oxygen. In the northeastern United States, large watersheds have extensive coal mining in their catchments, which has exhumed pyrite to land surface. Concentration-discharge (C-q) dynamics in the east coast are consistent with ATL weathering for watersheds without coal and KL for watersheds with coal. In the Western United States, we found that C-q relationships are consistent the pyrite reaction front becoming shallower as drainage area increases for watersheds without coal. Overall, this work has implications for predicting the fate and transport of redox sensitive contaminants.

In this chapter I worked collaboratively with Dr. Susan Brantley, Michael Forgeng, Dr. Xin Gu, Dr. Jordon Hemmingway, and Dr. Tao Wen to design, execute, and write the chapter (and submit it to *Water Resources Research*). Drs. Brantley and Gu assisted with the design of the study and the analysis of the results. Dr. Wen assisted in methodology development. Michael Forgeng assisted with coordinating and executing field work. Dr. Hemmingway was responsible for analyzing sulfur isotopes and assisting in the interpretation of these data. I was responsible for conceptualizing, data acquisition, lab work, data analysis, coding, and writing the publication. Brantley also participated in writing of the paper.

1.2.3 Summary of Chapter 4

In this chapter we investigate how the presence or absence of reactive minerals at Earth's surface impact weathering dynamics in watersheds. For example, when reactive minerals are depleted at land surface (i.e., completely developed weathering profile), weathering is limited by
the supply of fresh minerals via physical erosion. Alternatively, when reactive minerals are present at land surface (i.e., incompletely developed profile), weathering is limited by interfacial reaction kinetics. Here, we calculate silicate weathering rates as SiO₂ fluxes in 142 watersheds underlain by shale. Shale is important because it is covers a significant portion of Earth's continents (estimated at 34.4 % (Meybeck, 1987), 12.6 % (Gibbs and Kump, 1994), 25.4% (Amiotte Suchet et al., 2003), 6.6% (Hartmann and Moosdorf, 2012)), but weathering in shale watersheds has been under-characterized when compared to other lithologies such as granite and basalt. We then aggregate datasets of climate (i.e., precipitation, temperature, potential evapotranspiration), hydrology (i.e., runoff), and geomorphology (i.e., basin area, relief, elevation, slope) for each of these watersheds. We first define a criterion to separate dry watersheds and wet watersheds based on mean annual precipitation (MAP) and potential evapotranspiration (PET). We then investigate what controls variations in SiO₂ fluxes in dry watersheds. Next, we apply a weathering model to our wet watersheds to determine the sensitivity of weathering to temperature, precipitation, and erosion. Lastly, determine which wet watersheds experience only kinetic-limited silicate weathering and which experience only erosive transport limited weathering.

In this chapter, we found that silica weathering fluxes vary by several orders of magnitude between sites. When PET/MAP (referred to as humidity index or HI) is less than 0.55, then fluxes increase linearly with runoff. We hypothesize that silica fluxes in these sites are RL. In these watersheds, we observe that stream chemistry is consistent with an equilibrium between smectite and kaolinite. The weathering fluxes in these sites, show an inverse relationship with temperature, which is consistent with the ΔH_r for the smectite-kaolite equilibrium. When HI > 0.55, we observe a temperature dependence (when fit to the Arrhenius equation) of 56 kJ mol⁻¹. We hypothesize that, as a whole, these sites are TR, and a subset of these sites are likely KL and ETL. For sites with HI > 0.55 and a mean catchment slope > 10°, the apparent activation energy

is 92 kJ mol⁻¹, which is consistent with the experimental activation energy for chlorite dissolution, a major mineral present in shale rocks. We hypothesize that silica fluxes in these sites are KL. For sites with HI > 0.55 and a mean catchment slope < 5°, weathering fluxes predominantly depend on erosion rate. We hypothesize that silica fluxes in these sites are ETL. Overall, we found that 48%, 37%, and 7% of silicate weathering in US Shales is limited by runoff, erosion, and reaction kinetics, respectively

In this chapter I worked collaboratively with Dr. Susan Brantley to design, execute, and analyze the data. Aspects of the analysis in this chapter was incorporated into a submission to *Science* that is first authored by Dr. Brantley. Other co-authors on that manuscript include Dr. Marina Lebedeva and Dr. Viktor Balashov, both of whom were involved in contributing to the submission to *Science* but not to the data, analysis, and writing presented in chapter 4. Although part of this chapter was included in Dr. Brantley's manuscript, the writing and analysis presented here are my own and extend beyond the information previously submitted.

1.3 Tables

Table 1-1: Common abbreviations found in this dissertation

Abbreviation	Variable Name
ATL	Advective Transport Limited
CHELSA	Climatologies at High resolution for the Earth Land Surface Areas
C-q	Concentration-Discharge
DIC	Dissolved Inorganic Carbon
DO	Dissolved Oxygen
EDS	Energy Dispersive X-ray Spectroscopy
EMMA	Endmember Mixing Analysis
ETL	Erosive Transport Limited
HI	Humidity Index
HUC	Hydrologic Unit Code
KL	Kinetic Limited
MAP	Mean Annual Precipitation
MAT	Mean Annual Temperature
mbls	Meters Below Land Surface
NMF	Non-negative Matrix Factorization
NWIS	National Water Information System
PAL	Present Atmospheric Level
PCA	Principal Component Analysis
PET	Potential Evapotranspiration
p-sulfate	Pyrite-derived Sulfate
RL	Runoff Limited
SEM	Scanning Electron Microscopy
SGMC	State Geologic Map Compilation
SRB	Susquehanna River Basin
SSHCZO	Susquehanna Shale Hills Critical Zone Observatory
TR	Transition Regime
US	United States
USGS	United States Geological Survey
WQP	Water Quality Portal
yr	Year

1.4 Figures



Figure 1-1: Schematic diagrams showing schematic representations of hypothetically kinetic limited (A, B) and erosive transport limited (C, D) weathering regimes for a given geochemical reaction in both a 1-D soil profile (A, D) and 3-D watershed (B, C). Blue lines in B and C represent subsurface flowpaths in each weathering regime. Note that KL weathering only features shallow flowpaths through the reaction front; whereas ETL weathering features deeper flowpaths. This is because KL watersheds tend to be small and ETL watersheds tend to be large; thus, rivers in ETL watersheds sample deeper regional groundwater flow.



Figure 1-2: Schematic diagram showing different concentration-discharge (C-q) relationships across Event (A), Seasonal (B), Interannual (C), and Inter-site (D) timescales as discussed in chapter 1 of this dissertation. For explanations of equations shown for the respective C-q curves refer to Section 1.1.3. Annotations on the C-q curves represent one version of how to define weathering regimes that feature the specific C-q relationships shown as described in chapter 1. Names for weathering regimes used here include Advective Transport Limited (ATL), Kinetic Limited (KL), Runoff Limited (RL), and Erosive Transport Limited (ETL). While explicit definition of Cq behavior with respect to weathering regimes is not well-established, this figure is one conceptualization of such definition.



Figure 1-3: Schematic diagram showing equations and characteristic plots for four spatiotemporal scales of assessment of weathering. For explanations on the equations shown for each scale, refer to section 1.1.4. In general, blue colors represent solute chemistry and brown colors represent solid-phase chemistry.

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Chapter 2

Machine Learning Deciphers CO₂ Sequestration and Subsurface Flowpaths from Stream Chemistry

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Abstract

Endmember mixing analysis (EMMA) is often used by hydrogeochemists to interpret the sources of stream solutes, but variations in stream concentrations and discharges remain difficult to explain. We discovered that machine learning can be used to highlight patterns in stream chemistry that reveal information about sources of solutes and subsurface groundwater flowpaths. The investigation has implications, in turn, for the balance of CO_2 in the atmosphere. For example, CO_2 -driven weathering of silicate minerals removes carbon from the atmosphere over ~10⁶-yr timescales. Weathering of another common mineral, pyrite, releases sulfuric acid that in turn causes dissolution of carbonates. In that process, however, CO_2 is released instead of sequestered from the atmosphere. Thus, to understand long-term global CO_2 sequestration by weathering requires quantification of CO_2 - versus H_2SO_4 -driven reactions. Most researchers estimate such weathering fluxes from stream chemistry but interpreting the reactant minerals and acids dissolved in streams has been fraught with difficulty. We apply a machine learning technique to EMMA in three watersheds to determine the extent of mineral dissolution by each acid, without pre-defining the endmembers. The results show that the watersheds continuously or intermittently sequester CO_2 but the extent of CO_2 drawdown is diminished in areas heavily affected by acid rain. Prior to applying the new algorithm, CO_2 drawdown was overestimated. The new technique, which elucidates the importance of different subsurface flowpaths and longtimescale changes in the watersheds, should have utility as a new EMMA for investigating water resources worldwide.

2.1 Introduction

We need to understand the long-term controls on atmospheric CO_2 because of the impact of this greenhouse gas on global climate. This is important because humans are increasingly burning fossil fuels and releasing long-sequestered carbon to the atmosphere (Kasting and Walker, 1992). This new C flux upsets the natural long-term balance in the atmosphere between volcanic degassing and weathering-induced drawdown of CO_2 over millennial timescales. Chemical weathering of the most common rock-forming minerals, silicates and carbonates, removes CO_2 from the atmosphere by forming dissolved inorganic carbon that is carried in rivers

to the ocean (DIC; Figure 2-1). Over $10^5 - 10^6$ yr timescales, this DIC is precipitated as marine calcite, releasing half or all of the atmospherically derived CO₂ back to the atmosphere for silicates and carbonates, respectively (Figure 2-1). Thus, over this timescale, CO_2 -driven weathering (CO₂-weathering) of silicates sequesters CO₂ out of the atmosphere while CO₂weathering of carbonates neither removes nor releases CO_2 to the atmosphere (Figure 2-1). Some researchers also emphasize that this simple picture neglects weathering of another ubiquitous mineral, pyrite (Lerman et al., 2007). When pyrite weathers, it produces sulfuric acid that also dissolves silicates and carbonates, i.e., H₂SO₄-weathering. When DIC generated through H₂SO₄weathering of carbonates is carried to the ocean, marine calcite precipitates and releases CO_2 , increasing atmosphere concentrations (Spence and Telmer, 2005; Calmels et al., 2011; Torres et al., 2014; Kölling et al., 2019). Thus, determination of the weathering contributions of silicates, carbonates, and pyrite is essential toward understanding long-term dynamics of CO₂. In this paper we describe a powerful machine learning technique to interpret the sources of stream solutes to understand problems such as weathering. While we show the importance of applying this machine learning technique to the weathering question, we also emphasize how machine learning can teach hydrogeochemists about subsurface flow paths and other characteristics of stream systems.

The most common way hydrogeochemists interpret the fluxes of weathering are to investigate stream and river chemistry. Determining the endmembers for streams is important because streams integrate the byproducts of weathering reactions over drainage basins, allowing assessment of regional to global understanding of fluxes – but only if minerals weathered by different acid sources can be deconvoluted (Li et al., 2008; Calmels et al., 2011; Torres et al., 2016; Winnick et al., 2017; Burke et al., 2018; Killingsworth et al., 2018). In small-scale studies in the laboratory or soil profiles, mineral reactions can be documented, but this information cannot be scaled up easily (Navarre-Sitchler and Brantley 2007). Here we show that machine learning can decipher the balance of fluxes of CO₂- versus H_2SO_4 -weathering as recorded in stream chemistry. We discovered that catchments partition water into subsurface flowpaths that can be i) deciphered with respect to the extent of pyrite, silicate, and carbonate weathering in different lithologies, and ii) interpreted with respect to whether weathering is driven by CO₂ or H_2SO_4 . We emphasize the long-term effects (over $10^5 - 10^6$ yr) on the CO₂ balance in the atmosphere.

Although geochemists commonly use stream chemistry to determine mineral sources of solutes via weathering reactions over large aerial extents (Gaillardet et al., 1999) and hydrologists commonly use endmember mixing analysis (EMMA) to determine the sources of solutes in a stream (Christophersen et al., 1990), stream datasets remain difficult to interpret because of spatial and temporal variations in endmember composition. For example, sulfur isotopes in stream solutes can distinguish pyrite-derived from rain-derived sulfate because pyrite typically is depleted in ³⁴S (Burke et al., 2018; Killingsworth et al., 2018). But this attribution is difficult, more expensive, and often ambiguous because pyrite δ^{34} S varies between formations (Gautier, 1986) or within a single catchment (Bailey et al., 2004). Likewise, inputs of sulfate to watersheds, such as acid rain, can swamp out the signal from mineral reactions, and can change significantly over time (e.g., because of changing acid rain deposition) (Lynch et al., 2000; Lehmann et al., 2007). These factors make it difficult to determine sources releasing sulfate to varying stream chemistries over time.

Several so-called "inverse models" have been used successfully to partition sulfate into endmember sources for streams and rivers. These include the two prominent modeling approaches by Torres et al. (2016) and Burke et al. (2018). However, because the chemistry of acid rain has varied over the past decades, utilizing the full range of rain chemistry in those models results in unrealistic contributions of acid rain (i.e., > 100%) or models that fail to converge. This is at least partly because the chemistry of acid rain has been so variable that it spans the entire measured range of stream samples. Additionally, utilizing the approach of Burke et al. (2018), based on the approach of Gaillardet et al. (1999), requires a priori assignment of accurate endmember chemistries. Often, the researcher must rely on a few samples to characterize endmembers, resulting in large uncertainties in endmember chemistry and in source apportioning. Since the inception of EMMA, many researchers have aimed to improve analysis through a more accurate determination of unknown or under-constrained endmember chemistries (Hooper, 2003; Carrera et al., 2004; Valder et al., 2012). But these efforts all use some a priori determination of endmembers. Our machine learning model adds to the growing effort to improve EMMA by applying blind source separation. The machine-learning approach we describe here de-convolves sources of stream chemistry without pre-defining the endmembers. We demonstrate this first with a synthetic dataset and then with data from three well-studied watersheds with different characteristics. The new method discovers the endmember chemistries and, as a result, documents new findings of importance previously undiscovered with the other methods.

For the target watersheds, we focus first on Shale Hills, an acid rain-impacted shale watershed in central Pennsylvania, USA with extensive data for water/rock chemistry (Jin et al., 2010; Brantley et al., 2013a; Sullivan et al., 2016). This watershed allows the most complete understanding of solute sources. Although we do not show this here, if we use either of the two previously used models for source attribution, stream chemistry data for Shale Hills either does not separate acid rain and pyrite as a sulfate source (if we use the model of Torres et al., 2016) or yields a proportion for acid rain which is larger than 100% (if we use the model of Burke et al., 2018). As shown below, the Non-negative Matrix Factorization (NMF) model easily defines endmembers and proportions.

We then show the utility of the machine learning method for watersheds where less water/rock chemistry has been published: we investigate East River and Hubbard Brook catchments. Like Shale Hills, East River is shale-hosted, but it receives little acid rain (Winnick et al., 2017). In contrast, Hubbard Brook has been extensively impacted by acid rain but is underlain by glacial till over schist (Likens et al., 2002). In both cases, NMF successfully determines endmembers and source proportions.

2.2 Methods

2.2.1 Study Sites

Where previous deconvolutions of stream chemistry into endmembers were generally based on assumptions of the chemistry of dissolving minerals alone, data for watersheds show that the flowpath of the water also affects this chemistry (e.g., Brantley et al 2017). We demonstrate this with data from three well-studied watersheds with different characteristics. We focus first on Shale Hills, a small (0.08 km²), acid-rain impacted forested watershed underlain by Rose Hill shale located in central Pennsylvania, USA (Brantley et al., 2018). The Rose Hill Formation shale contains ~0.14 wt% S as pyrite (FeS₂) (Gu et al., 2020a).

We then show utility of the method in East River (shale-hosted but it receives little acid rain) and Hubbard Brook (extensively impacted by acid rain but is underlain by schist and glacial till) catchments. Specifically, East River is a large (85 km²), mountainous watershed underlain by Mancos Shale that is located near Gothic, Colorado USA within the Gunnison River basin (Winnick et al., 2017). The Mancos is a black shale that contains ~1.6 wt% S as pyrite (Wan et al., 2019). Both of these shale-hosted watersheds contain carbonate minerals that vary in composition and abundance in the subsurface. Lastly, Hubbard Brook (Nezat et al., 2004), located in the White Mountains of New Hampshire USA, consists of a series of nine small (0.14-0.77 km²), forested watersheds underlain by Rangeley Formation metamorphosed shale and sandstone (schist) generally covered by glacial till derived mostly from the Kinsman granodiorite. The schist bedrock contains ~0.2-0.9 wt% S and till contains ~0.1-0.2 wt% S. Again, almost all S is present as iron sulfide (pyrite or pyrrhotite). Both bedrock and till are largely carbonate-free.

2.2.2 Data Acquisition

For Shale Hills, daily stream chemistry has been reported from 2008-2010 (Brantley et al., 2013b; Brantley et al., 2013c; Brantley et al., 2013d). Additional samples were measured in other time intervals for sulfur isotopes and alkalinity (Jin et al., 2014). All samples were filtered through a 0.45 μm Nylon filter and aliquots for cation analysis were acidified with nitric acid. Cations were measured on a Leeman Labs PS3000UV (Teledyne Leeman Labs, Hudson, NH) inductively coupled plasma–optical emission spectrometer (ICP-OES), and anions were measured on a Dionex Ion Chromatograph (Sunnyvale, CA). Alkalinity was measured by titration with 0.16 M H₂SO₄. Discharge data are available online (http://www.czo.psu.edu/data_time_series.html).

All published data from East River were used in analysis (Winnick et al., 2017), except for two samples with extremely high values of chloride (246 and 854 μ M) because they differed significantly from the remaining sample chemistry (average Cl concentration = 21 μ M). Hubbard Brook weekly chemistry from 2000-2017 was downloaded for the sub-catchments (3, 6, 7, 8, 9) that were not experimentally manipulated (Bernhardt et al., 2019). Stream discharge data for each sub-catchment are from USDA Forest Service (USDA, 2019).

2.2.3 Machine Learning Model

To assign the proportion of sulfate in streams to sources, we first bootstrapped a training dataset and then used a method of blind source separation (Alexandrov and Vesselinov, 2014; Vesselinov et al., 2018) called non-negative matrix factorization (NMF). NMF is unique from

previously used methods in that it allows calculation of endmember compositions and mixing proportions simultaneously and does not rely on measurements or assumptions of endmembers a priori (Figure 2-2A; see Appendix A.1). Specifically, NMF decomposes the $n \ge m$ matrix, V, into two matrices W and H:

$$V = WH \tag{2-1}$$

Here, cell entries of V are molar solute concentration ratios, [X]/[Y], for stream samples. Indicator *n* refers to the sampling date, *m* refers to different solutes $X (= Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-})$, and brackets refer to concentrations. W is the $n \ge p$ matrix whose cell entries are proportions, α , for each endmember in each stream sample. Again, *n* refers to sampling dates, but *p* is the number of sources of solutes (referred to as endmembers). The proportions refer to the fractions of sulfate in each sample that derive from an individual endmember, where the sum of proportions must equal 1 ± 0.05 for each sample. To derive the mixing proportions of sulfate specifically, we set up the NMF approach by normalizing each analyte concentration by sulfate concentration ($Y = SO_4^{2-1}$)), the target solute. After running the algorithm for each of the three watersheds, we then inferred by inspection (see discussion below) that the endmembers represent different flowpaths in the subsurface. Therefore, these proportions of sulfate are referred to here as shallow, moderately shallow, and deep flowpaths, i.e. $\alpha_{shallow}$, $\alpha_{moderate}$, and α_{deep} respectively (only one of our target watersheds revealed the moderate-depth flowpath). H is the $p \ge m$ matrix whose cell entries are the concentration ratios that define the chemical signature of each of the p endmembers. The key to NMF is that these concentration ratios are not determined prior to apportionment but rather are determined from the data itself. In addition, the chemical signatures of each endmember can vary temporally around central tendencies. Because the solution to eq. 2-1 is non-unique, we run the model 20,000 times, apply a filter to the models, and then calculate the mean and standard deviation of the remaining models for trend and error analysis (Appendix A.1; Eq. A-1).

The only hyperparameter that must be defined to run NMF a priori is the number of endmembers, *p*. We used principal component analysis (PCA) to determine the minimum number of components needed to explain >90% of the variance in stream solute ratios, and trained NMF to the bootstrapped data while assuming that number of endmembers. Machine learning determined the compositions defining the endmembers and the mixing proportions of each endmember in each sample. After running NMF, we interpreted each endmember composition based on geological and watershed knowledge.

Based on the outputs of the NMF model, we calculated the weathering rates of sulfide, carbonate, and silicate minerals in the watersheds. Additionally, we calculated the relative contributions of sulfuric and carbonic acid driving those weathering reactions. For details on the weathering calculations see Appendix A.2.

2.2.4 Synthetic Dataset

NMF is an algorithm that has been used for many applications (e.g., spectral analysis, email surveillance, cluster analysis; Berry et al., 2007) but has only recently been applied to stream chemistry (e.g., Xu and Harman, 2020). To exemplify the validity of our modeling approach, we generated a dataset of synthetic stream chemistry versus time and ran it through our NMF model. First, we defined two known endmember compositions, which are shown in Table **A-1** in Appendix A.5. Next, we randomly generated 300 synthetic stream samples that were each calculated as a mixture of the two endmembers. Lastly, we ran NMF on the synthetic stream chemistry to determine the mixing proportions (α) and endmember compositions ($[X]/[SO4^{2-}]$), for all *X*.

2.3.1 Synthetic Data Model

After generating the synthetic dataset of stream samples, we utilized NMF to determine the mixing proportions and endmember compositions. We then filtered out the poor fitting models (see Appendix A.1 eq. A-1). As described more fully in Appendix A.1, this left an average number of valid models of 62 (range: 42-77). The average variance between valid models was <10%. Without any prior information about the system, NMF accurately determined the correct mixing proportions (RMSE = 0.04; $R^2 = 0.98$; p < 0.001; Figure 2-2B) and endmember compositions (RMSE = 0.21; $R^2 = 0.99$; p < 0.001; Figure 2-2C). In effect, the model was able to use patterns in the data to deconvolve sample chemistry into endmembers and proportions.

2.3.2 Application to Shale Hills

While clay minerals in shale-underlain watersheds in rainy climates are found at all depths because of their low chemical reactivity, pyrite and carbonate minerals are often chemically removed from upper layers and only found in unweathered shale at depth (Figure 2-3; Brantley et al., 2013a; Wan et al., 2019; Gu et al., 2020a). For example, at Shale Hills, pyrite and carbonate minerals are only observed deeper than at least 15 meters below land surface (mbls) under the ridges and 2 mbls under the valley. In these deeper zones, calcite (CaCO₃), ankerite (Ca(Fe_{0.34}Mg_{0.62}Mn_{0.04})(CO₃)₂), and pyrite (FeS₂) dissolve in regional groundwaters that flow to the stream (Brantley et al., 2013a; Gu et al., 2020a). These groundwaters thus contribute DIC, Ca²⁺, Mg²⁺, and SO₄²⁻ into the stream.

Like many catchments, water also flows to the stream in Shale Hills along a much shallower near-surface flowpath, which we call interflow (Figure **2-3**). Interflow is thought to

occur along a transiently perched water table that lies within the upper 5-8 mbls. The most abundant mineral, illite ($K_{0.69}$ (Si_{3.24}Al_{0.76})(Al_{1.69}Fe³⁺_{0.10}Fe²⁺_{0.16}Mg_{0.19})O₁₀(OH)₂), dissolves in interflow where it flows through the soil, with minimal illite dissolution in underlying weathered rock. Illite dissolution releases DIC and Mg²⁺ and K⁺ to interflow waters and causes precipitation of clays and iron oxides. Interflow derives ultimately from local precipitation that also contains Na⁺, Cl⁻, and SO₄²⁻. Interflow and deep groundwater flowlines converge under the catchment outlet where the stream, on average, is 90% interflow and 10% deep groundwater (Sullivan et al., 2016; Li et al., 2017).

Only one mineral, chlorite ($(Fe^{2+}_{0.40}Mg_{0.15}Al_{0.35})_6(Si0_{.76}Al_{0.24})_4O_{10}(OH)_8$), is observed to begin to weather in the deep groundwater and continue weathering all the way to the surface (Figure 2-3; Gu et al., 2020a). Chlorite thus dissolves to release Mg²⁺ to both interflow and deep groundwater. While most water entering the catchment leaves as interflow without entering deep groundwater, the wide reaction zone observed for chlorite is consistent with a small fraction of water infiltrating vertically to the deeper zone (Brantley et al., 2017).

PCA for stream chemistry (2008-2010) at Shale Hills revealed two sources of sulfate, and this was used to set up NMF, i.e., p = 2 (Table A-2 in Appendix A.5). By comparing the compositions from matrix H (Table A-2 in Appendix A.5) determined by NMF to our knowledge of the subsurface (Figure 2-3), we interpreted the two endmembers as deep and shallow weathering along the two flowpaths, i.e. groundwater and interflow (Figure 2-3), respectively (Jin et al., 2014; Sullivan et al., 2016). The endmember with high $[Ca^{2+}]/[SO4^{2-}]$ and $[Mg^{2+}]/[SO4^{2-}]$ was attributed to deep weathering because Ca- and Mg-containing minerals (i.e., calcite and ankerite) only dissolve at depth (Figure 2-3; Jin et al., 2014; Gu et al., 2020a). The high $[Cl^{-}]/[SO4^{2-}]$ endmember was attributed to shallow interflow because it is dominated by Cl-containing acid rain. This attribution revealed, consistent with other studies of the acid rain-impacted northeastern United States, that precipitation accounts for the majority of sulfate flux (i.e., 77%) at Shale Hills between 2008 and 2010.

Many lines of evidence back up these endmember attributions. The sulfate in the shallow endmember derives from interflow well above the pyrite oxidation front through pyrite-depleted rock and is thus attributed to acid rain, while the sulfate in the deep endmember is attributed mostly to pyrite oxidation. Some sulfate from acid rain may infiltrate to the regional groundwater, but the fraction is small. At Shale Hills, acid rain always contains Cl⁻ and pyrite oxidation always preferentially dissolves carbonate minerals, giving each flowpath endmember a unique signature.

To test the NMF deconvolution, we compared these attributions to isotopic data. The value of δ^{34} S in dissolved sulfate is observed to correlate with increasing concentrations of pyritederived sulfate determined by NMF (Figure 2-4A), consistent with depleted δ^{34} S signatures in pyrite (e.g., -20‰; Killingsworth et al., 2018). In contrast, acid rain shows δ^{34} S values around +3-5‰ (Bailey et al., 2004), and low sulfate concentrations in stream samples are characterized by δ^{34} S values within this range. Also, as pyrite oxidizes, the concentration of sulfate increases and the δ^{34} S values decrease to reflect the inferred composition of pyrite, -9.5‰ to -7.2‰ (Figure 2-4A). Finally, Gu et al. (2020b) showed that pyrite oxidation drives the carbonate dissolution at Shale Hills. NMF results show that stream water was near calcite equilibrium (i.e., $\Omega_{calcite} = 1$; log $\Omega_{calcite} = 0$) and had the highest pyrite-derived sulfate concentrations when the stream was fed by groundwater (Figure 2-4B).

However, the annual flux of acid rain-derived sulfate from 2008-2010 in the shallow endmember determined from NMF at Shale Hills (Table **2-1**) far exceeds the wet deposition of sulfate during the sampling period (Figure **2-4C**). Such inconsistencies have been noted elsewhere and attributed to travel-time delays over decades between acid rain input and stream output (Cosby et al., 1985; Prechtel et al., 2001; Mörth et al., 2005; Rice et al., 2014).

Figure **2-4C** thus allows us to estimate a ~19-31-year lag time between input and export of sulfate from the temporally changing acid rain (see Appendix A.2.4).

Weathering profiles at Shale Hills, the chemistry of the composition (*H*) matrix, sulfur isotopes, calcite saturation, and lag in acid rain export all support our interpretation that the two components in the NMF model are shallow and deep flowpaths and that sulfate largely derives from acid rain and pyrite respectively. The dissolution of different minerals along these flowpaths lead to patterns in stream chemistry that our NMF model discerns and separates. If mineral reaction fronts are not separated in the subsurface, different flowpaths might not be separated by NMF; however, Brantley et al. (2017) and Gu et al. (2020a) have shown that separation of reaction fronts is common.

2.3.3 Rates of Weathering and CO₂ Sequestration at Shale Hills

With these calculations we can use NMF results to elucidate the effect of sequestration or release of CO_2 at Shale Hills. We emphasize fluxes of importance over 10^5 – 10^6 yr timescales. CO_2 -driven weathering of the silicate minerals chlorite and illite removes carbon from the atmosphere and carries it as DIC in rivers to the ocean where it is buried as carbonate minerals (akin to reaction 2 in Figure 2-1, Table A-3 in Appendix A.5). In contrast, calcite and ankerite weathering coupled to pyrite oxidation instead releases CO_2 to the atmosphere over those timescales (reaction 7 in Figure 2-1) and carbonate mineral weathering is neutral over those timescales (reaction 4 in Figure 2-1). Additionally, acid rain can interact with silicate minerals but not carbonate minerals at Shale Hills (because these are not present in the shallow subsurface (Figure 2-3)). Thus H₂SO₄-dissolution caused by acid rain competes with CO₂-dissolution for silicates. This competition lowers the CO₂ consumption from silicate weathering, which been observed in other watersheds (e.g., Suchet et al., 1995).

To summarize the effect of weathering on CO₂ considered at the timescale of 10^5-10^6 yr as shown in Figure 2-1, we propose a new parameter, the stream CO₂ sequestration coefficient, k_{stream} (see Appendix A.2.2 for full derivation). This coefficient is defined as mol CO₂/[Σ^+]_{total} where [Σ^+]_{total} is the sum of the equivalents of base cations in a sample. Here, equivalents refer to molar concentration multiplied by charge for an ion. Positive k_{stream} implies the stream acts as a source and negative implies it acts as net sink of CO₂ and the values are calculated for an individual sample or integrated over some time period of stream sampling. The product of k_{stream} times [Σ^+]_{total} in a sample equals the moles of CO₂ sequestered or released during weathering as represented in that sample (but the accounting is calculated for the reactions considered for the 10⁵-10⁶ y timescale in Figure 2-1). Quantitatively this parameter reveals the moles of CO₂ sequestered or released during weathering per cation equivalent in a given stream sample:

$$\kappa_{stream} = \frac{1}{2} \left(-1 + \gamma_{stream} + \zeta_{stream} \right) \tag{2-2}$$

Here, γ_{stream} is the proportion of cation equivalents in the stream derived from carbonate weathering per $[\Sigma^+]_{total}$, and ζ_{stream} is the ratio of sulfate equivalents from sulfuric acid per total base cation equivalents. We calculate γ_{stream} for a sample by multiplying the pyrite-derived sulfate concentration (i.e., α_{deep} multiplied by total sulfate concentration) by the $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]$ and $[\text{Mg}^{2+}]/[\text{SO}_4^{2-}]$ ratios in the sample calculated by NMF to have derived from the deep weathering endmember and then dividing by $[\Sigma^+]_{total}$. Likewise, ζ_{stream} is calculated by multiplying the fraction of sulfate from pyrite + acid rain (e.g., $\alpha_{\text{deep}} + \alpha_{\text{shallow}}$) by the total sulfate concentration and dividing that by $[\Sigma^+]_{total}$. This calculation shows that seasonally, Shale Hills switches between net source and net sink of CO₂ (Figure **2-5D**). Using the weathering reactions described in Appendix A.2.2, we also calculated the actual associated CO₂ fluxes; annual CO₂ dynamics are net-neutral at Shale Hills when considered over timescales of 10^5 – 10^6 yr (Table **2-1**; Figure **A-4** in Appendix A.6). The switch in systems from operating as a source or a sink is attributed to seasonality in the dominant flowpath: CO_2 -weathering of silicates occurs year-round, but H₂SO₄-weathering is more important in the wet season and is dominated by acid from rain. Specifically, in the dry season when water tables are low, the stream water is often dominated by deeper groundwater flow that interacts with the deep pyrite reaction front and has little contribution of acid rain. However, even though this dry season is characterized by higher proportions of pyrite-derived sulfate, the watershed acts predominantly as a sink of CO_2 during this time of the year because the drawdown of CO_2 from CO_2 -weathering of silicates is larger than the efflux of CO_2 from pyrite-driven H₂SO₄-weathering of carbonate (Figure **2-5D**). In the wet season when water tables are high, however, the stream is dominated by shallow interflow that does not interact with pyrite but has a large contribution of H₂SO₄ from rain. Kanzaki et al. (2020) also previously showed that the separation of reaction fronts (Figure **2-3**) can cause such important effects on CO_2 fluxes, although that previous treatment focused strictly on simple model systems unaffected by acid rain.

To test the accuracy of these inferences based on NMF, we compare to previous results for Shale Hills. Based on soil pore-water chemistry and rain fluxes at Shale Hills, Jin et al. (2014) estimated the CO₂ drawdown from silicate weathering to be 44 mmol m⁻² yr⁻¹. We find that if we assume all silicate weathering is CO₂-driven, then the silicate weathering drawdown is 38 mmol m⁻² yr⁻¹, which is consistent with the estimate of Jin et al (2014). But 44 mmol m⁻² yr⁻¹ is an overestimate because it does not consider H₂SO₄-weathering of silicates or carbonates.

2.3.4 East River

Shale Hills is unique in that it is a monolithologic catchment and the data volume to constrain endmember apportionment is large. But NMF also works well for watersheds in which

the subsurface flow and reactions are less constrained partly due to the more complex subsurface geology. The weathering profile at East River (underlain by black shale) shows that pyrite and carbonate are depleted in upper layers but start dissolving at ~2-4mbls (Wan et al., 2019). PCA shows that the number of components is 2. The composition of the endmembers for East River are similar to Shale Hills (Table **A-2** in Appendix A.5); however, the endmember composition indicates a higher proportion of H₂SO₄-weathering of carbonates (see Appendix A.2).

Based on NMF for East River, pyrite contributes 62% of the annual sulfate flux (Table 2-1). Sulfuric acid drives 29% to 69% of carbonate dissolution depending on the season, and this compares well with previous estimates of 35-75% (Winnick et al., 2017). Unlike Shale Hills, pyrite oxidation at East River is the dominant source of sulfate because acid rain is less important, and the black shale is pyrite-rich (Figure 2-5B).

Although East River is like Shale Hills in that it intermittently switches between acting as a source or sink of CO₂ (Figure **2-5**), the seasonality of the switch between Shale Hills and East River is reversed. During baseflow (i.e., between periods of precipitation), Shale Hills is predominantly a sink of CO₂, and it sometimes switches to a source of CO₂ in the wet season because acid rain competes with CO₂ and reduces CO₂ consumption from silicate weathering. Without the large acid rain influx, East River instead acts as a sink of CO₂ during the wet season of snowmelt and then switches to a source during baseflow. Our results are consistent with previous interpretations (Winnick et al., 2017) suggesting CO₂ efflux rates are highest in baseflow-dominated and lowest in snowmelt-dominated flow regimes.

2.3.5 Hubbard Brook

Monolithologic shale watersheds are not the only target chemistries that can be deconvoluted with NMF: we now consider Hubbard Brook, a catchment on crystalline rock.

Large variations in the δ^{34} S composition of the bedrock at Hubbard Brook (Bailey et al., 2004) mean that sulfur isotopes in stream water cannot be used to unambiguously apportion sulfate sources. Weathering fluxes from sulfide minerals are therefore difficult to constrain (Mitchell et al., 2001).

At Hubbard Brook, PCA shows three endmember sources of sulfate. As described below, we attribute these to three inferred flow lines, two in till and one at depth: waters flowing through i) shallow soil developed from till, ii) moderately-deep, less-weathered till, and iii) weathering bedrock. A three-layered weathering profile has been observed in other till-covered areas of New Hampshire as well (Goldthwait and Kruger, 1938). We used these ideas to identify endmembers as described below.

Concentrations of sulfate in acid rain have declined over time in northeastern USA (Lynch et al., 2000; Lehmann et al., 2007). Of the three NMF-determined endmembers at Hubbard Brook, two of them show declining sulfate concentrations with time. We therefore attributed the first and second endmembers to acid rain (Figure **A-1** in Appendix A.6).

Only one endmember showed little to no decline in sulfate concentration over time, and we therefore attributed that endmember to deep weathering in water interacting with the underlying bedrock. The composition of the deep weathering endmember shows a strong correlation between $[Mg^{2+}]/[SO_4^{2-}]$ and $[K^+]/[SO_4^{2-}]$. This chemical signature is similar to previous observations of weathering of metasedimentary rock piles where silicates (biotite and chlorite) are the first minerals to dissolve when sulfides oxidize (Moncur et al., 2009). Specifically, biotite (K(Si_3Al)Mg_2FeO_{10}(OH)_2) is known to release Mg²⁺ and K⁺ while chlorite releases Mg²⁺ upon weathering. Moreover, the metamorphic conditions that produce pyrrhotite also produce biotite and chlorite, and those three minerals tend to be located together in schist foliations (Carpenter, 1974). We thus infer that pyrrhotite oxidation at Hubbard Brook apparently causes dissolution of biotite \pm chlorite because these are the most susceptible minerals in close proximity to the sulfide. Thus, several lines of evidence underlie our interpretation that component 3 is the deep weathering source of sulfate.

From the NMF results summarized in Table **2-1**, pyrrhotite can account for 30% of the total sulfate flux at Hubbard Brook. The schist and till contain essentially no carbonate; therefore, weathering is always a net sink for CO_2 . In this watershed, however, the story is complicated by the dissolution of silicate minerals by sulfuric acid from pyrrhotite oxidation and acid rain. If we had assumed all of the base cations detected in Hubbard Brook were caused by CO_2 -weathering, we would have overestimated the net drawdown of CO_2 out of the atmosphere (Figure **2-1**).

2.3.6 Predicting CO₂ release or drawdown from rock chemistry

From the stream chemistry, we found that Shale Hills and East River are net neutral with respect to CO_2 , and Hubbard Brook is a net sink (Table 2-1; Figure 2-5). In Table 2-1, the weathering fluxes are summarized as CO_2 fluxes (see Appendix A.2.2; Figure A-4 in Appendix A.6), but the NMF results can also be used to calculate weathering losses for each mineral as described in Appendix A.2.5 (Table A-5 in Appendix A.5). Although we do not explicitly discuss each of these mineral-related fluxes learned from NMF, they have resulted in differences in composition of soil versus protolith and we can use soil chemistry therefore as an additional test of κ_{stream} : specifically, we compare κ_{stream} to the CO_2 flux recorded in the weathered profile as solid-phase chemistry. To do this, we calculate a CO_2 sequestration coefficient analogous to κ_{stream} but instead based on rock chemistry, κ_{rock} , by assessing soil and taking into account the fraction of base cations weathered, the fraction of base cations from carbonates, and the capacity of the bedrock to produce H₂SO₄:

$$\kappa_{rock} = \frac{1}{2} \left(\tau + \gamma_{rock} + \zeta_{rock} \right) \tag{2-3}$$

In effect, κ_{rock} is the time-integrated CO₂ sequestration coefficient recorded as the solid phase weathering products in units of mol CO₂/eq base cation. In eq. 2-3, τ is the mass transfer coefficient for base cations at the land surface (where $1-\tau$ equals the fraction of total base cations originally present in parent rock that remain in topsoil at land surface), γ_{rock} is the proportion of base cations in the bedrock associated with carbonate minerals, and ζ_{rock} is the acid generation capacity of the rock. The derivation of eq. 2-3 and description of each variable is more fully summarized in Appendix A.2.3. Briefly, γ_{rock} expresses the proportion of base cations in the parent rock that are associated with carbonate minerals (varies from 0 to 1 for 100% silicate protolith to 100% carbonate protolith). $\zeta_{\rm rock}$ expresses the relative amount of (acid-generating) pyrite to base cations in the protolith (varies from 0 to 1.5 for catchments where 100% of weathering is CO_2 -driven to catchments where 100% of weathering is H_2SO_4 -driven, respectively). τ expresses the fraction of cations that have not dissolved away upon exposure at the land surface (varies from -1 to 0 for 0% cations remaining at land surface to 100% cations remaining, respectively). Negative κ_{rock} describes a lithology that has been net sequestering CO₂ over the duration of weathering, whereas positive κ_{rock} has been net releasing CO₂. Based on the chemistry of the bedrock and topsoil at each watershed, κ_{rock} is -0.08 ± 0.11, 0.08 ± 0.17, and - 0.19 ± 0.11 for Shale Hills, East River, and Hubbard Brook, respectively (Table 2-1 and Table A-**4** in Appendix A.5). Based on these values from observations of the solid weathering phases, Shale Hills and East River on net are CO_2 neutral (i.e., within error of 0), but Hubbard Brook has acted as a long-term CO₂ sink.

If the streams at each site today are acting just like the weathering recorded over the last tens of thousands of years in the solid-phase material and our assumptions about CO₂- versus H₂SO₄-weathering are correct, κ_{rock} should equal κ_{stream} . Here, we find that κ_{stream} (discharge-weighted average) for Shale Hills, East River, and Hubbard Brook are 0.01 ± 0.03 , -0.02 ± 0.02 ,

and -0.14 \pm 0.01 respectively (Table 2-1, Figure 2-5). For all sites, the stream chemistry shows similar values of CO₂ sequestration coefficient for the modern (stream timescale) compared to the time-integrated (soil timescale), i.e., $\kappa_{stream} \approx \kappa_{rock}$, consistent with Shale Hills and East River acting as CO₂ net neutral but Hubbard Brook as a CO₂ sink. In addition, at Hubbard Brook, it can be seen that acid rain has competed with CO₂ in weathering minerals, lowering the capacity of the rock to sequester atmospheric CO₂. Because our calculation of κ_{rock} does not include acid rain, we would expect acid rain would increase κ_{stream} relative to κ_{rock} , which is what we observe at Hubbard Brook. Hubbard Brook has only moved back to equivalency between the rock and stream record in recent years (2013-2016; Figure 2-5F) as the system has recovered from acid rain. These comparisons also suggest that rock chemistry, which is much easier to analyze, can sometimes predict stream fluxes adequately.

2.4 Conclusions

By not requiring a priori assignments of endmembers, our machine learning model not only successfully reproduced source apportionments made in more traditional endmember analysis for streams, but also revealed new information about how watersheds work. At the same time, the method also solved some issues related to source apportionment for streams with time variations of large acid rain inputs. The approach documented that two carbonate-containing shale watersheds (Shale Hills, East River) are intermittent sources or sinks of CO₂ to the atmosphere but on net are neutral with respect to CO₂. In contrast, because it has no carbonate minerals, Hubbard Brook is a constant sink for CO₂ (Figure **2-5** and Figure **A-5** in Appendix A.6). These observations were compared and confirmed by comparing stream chemistry to rock chemistry. NMF also emphasized the importance of different water flowpaths in determining endmembers: the endmembers were not strictly defined by mineralogy but by patterns of subsurface flow that can be related to subsurface reaction zones. These flowpaths lead to patterns in stream water chemistry that were easily deciphered by our newly developed machine learningbased mixing model. In particular, for three streams, signals in the chemical variations were observed to reveal dissolution of the most reactive mineral in proximity to sulfide oxidation. Many watersheds have flowpaths distinguished by geochemical signatures from mineral reactions (Brantley et al., 2017) but we do not know these paths a priori when we investigate stream chemistry. Machine learning will be useful to model mineral reactions on broader spatial scales and will help constrain global weathering-related CO₂ dynamics because it can delineate endmembers without a priori assumptions.

Beyond these attributes, the machine learning approach also revealed other new attributes of weathering. In Shale Hills, we discovered that sulfate inputs from acid rain may not be exported completely for two decades, which impacts mass balance and weathering-related CO₂ dynamics. Although not discussed explicitly here, this decadal time-lag was also observed at Hubbard Brook. NMF also showed that Hubbard Brook, recovering from the impacts of acid rain, is only recently returning to its full potential as a CO₂-sequestering rock system. In other words, prior to acid rain, Hubbard Brook sequestered more CO₂ per mole of weathered bedrock than it does today. But acid rain dissolved some of the silicates with H₂SO₄, lowering the CO₂ sequestration capability of the watershed. NMF led us to discover this new attribute of acid rain, namely that it diminishes the capacity of a rock to sequester CO₂ at millennial timescales (Figure **2-1**) by replacement of CO₂ by H₂SO₄ as a weathering agent. Regardless of the net CO₂ dynamic, we discovered that without considering sulfide oxidation or acid rain, the CO₂ weathering sink considered over 10⁵ to 10⁶ yr timescales is always overestimated.

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Data availability.

Data used in analysis of this work can be found online for Shale Hills (https://doi.org/10.1594/IEDA/100241, https://doi.org/10.1594/IEDA/100242, https://doi.org/10.1594/IEDA/100243, Brantley et al., 2013b, c, d), the Hubbard Brook data catalog (https://doi.org/10.6073/pasta/4022d829f3a1fa4057b63b5db8b1a1, Bernhardt et al., 2019), and in Wan et al. (2019) and in Winnick et al. (2017).

	Shale Hills	East River	Hubbard Brook	
	Base Cation Fluxes (meq $m^{-2} yr^{-1}$) ^a			
Total base cation flux	336 ± 13	1540 ± 30	84.6 ± 0.8	
Base cation flux from CO ₂ -weathering of silicates	12.6 ± 21.1	315 ± 58	24.1 ± 0.8	
Base cation flux from CO ₂ -weathering of carbonates	216 ± 16	587 ± 48	NA ^c	
Base cation flux from H ₂ SO ₄ -weathering of silicates	62.4 ± 1.0	152 ± 4	60.5 ± 0.2	
Base cation flux from H ₂ SO ₄ -weathering of carbonates	44.8 ± 1.9	488 ± 9	NA ^c	
	Fluxes (mmol $m^{-2} yr^{-1})^b$			
Total sulfate flux	50.3 ± 0.3	198 ± 1	30.3 ± 0.1	
Sulfide-derived sulfate flux	11.2 ± 0.9	122 ± 4	9.1 ± 0.1	
Rain-derived sulfate flux	38.9 ± 1.0	76.0 ± 4.2	21.2 ± 0.6	
CO ₂ sequestration or release	4.9 ± 10.7	-35.6 ± 30.4	-12.1 ± 0.4	
	CO ₂ Sequestration Coefficients			
$\kappa_{stream}^{d,e}$	0.01 ± 0.03	-0.02 ± 0.02	-0.14 ± 0.01	
K _{rock}	-0.08 ± 0.11	0.08 ± 0.17	-0.19 ± 0.11	

Table **2-1**: Fluxes of SO₄²⁻, Cations, and CO₂

^aWeathering fluxes calculated following procedure in Appendix A.2.2

^bNegative O_2 flux indicates sequestration and positive indicates release to atmosphere as considered over 10^5 – 10^6 yr timescales (see Figure 2-1)

°No carbonate cation fluxes reported because the bedrock contains no carbonate

^dStream CO₂ sequestration coefficient integrated over the period of record for each site

^eRock and stream CO₂ sequestration coefficients show that Shale Hills and East River are within error of net-neutral with respect to CO₂ and Hubbard Brook sequesters CO₂.

2.6 Figures

Reaction Number	CO ₂ -Weathering of Silicates	Net Effect on Atmospheric CO ₂ Timescale (mol CO ₂ /mol Mineral) (yr)	
1	$\begin{array}{l} \text{CaSiO}_{3\ (s)} + \textbf{2CO}_{2\ (g)} + \text{H}_2\text{O} \rightarrow \text{Ca}_{(aq)}^{2+} + 2\text{HCO}_{3\ (aq)}^{-} + \text{SiO}_{2\ (aq)} \\ \text{Silicate Dissolution} \rightarrow \text{Riverine DIC} \end{array}$	-2 CO ₂	<104
2	$\begin{aligned} & \text{CaSiO}_{3(\text{s})} + \textbf{2CO}_{2(\text{g})} + \text{H}_2\text{O} \rightarrow \text{CaCO}_{3(\text{s})} + \textbf{CO}_{2(\text{g})} + \text{H}_2\text{O} + \text{SiO}_{2(\text{aq})} \\ & \text{Silicate Dissolution} \rightarrow \text{Marine Carbonate Precipitation} \end{aligned}$	-1 CO ₂	10 ⁵ -10 ⁶
	CO ₂ - Weathering of Carbonates		
3	$CaCO_{3 (s)} + CO_{2 (g)} + H_2O \rightarrow Ca^{2+}_{(aq)} + 2HCO^{-}_{3 (aq)}$ Terrestrial Carbonate Dissolution \rightarrow Riverine DIC	-1 CO ₂	<104
4	$CaCO_{3}(s) + CO_{2}(g) + H_{2}O \rightarrow CaCO_{3}(s) + CO_{2}(g) + H_{2}O$ Terrestrial Carbonate Dissolution \rightarrow Marine Carbonate Precipitation	0 CO ₂	10 ⁵ -10 ⁶
	H ₂ SO ₄ -Weathering of Silicates		
5	$\begin{array}{c} \text{CaSiO}_{3(s)} + \frac{1}{2}\text{FeS}_{2(s)} + \frac{15}{8}\text{ O}_{2(g)} + \frac{3}{4}\text{H}_2\text{O} \rightarrow \text{Ca}^{2+}_{(aq)} + \text{SO}^{2-}_{4(aq)} + \text{SiO}_{2(aq)} + \frac{1}{2}\text{Fe(OH)}_{3(s)}\\ \text{Silicate Dissolution} \rightarrow \text{Riverine Sulfate} \end{array}$	0 CO ₂	10 ⁵ -10 ⁶
	H ₂ SO ₄ -Weathering of Carbonates		
6	$\begin{aligned} CaCO_{3(s)} + \frac{1}{4}FeS_{2(s)} + \frac{15}{16}O_{2(g)} + \frac{7}{8}H_2O \to Ca_{(\mathrm{aq})}^{2+} + HCO_{3(\mathrm{aq})}^- + \frac{1}{2}SO_{4(\mathrm{aq})}^2 + \frac{1}{4}Fe(OH)_{3(s)} \\ \text{Terrestrial Carbonate Dissolution} \to Riverine DIC \end{aligned}$	0 CO ₂	<104
7	$CaCO_{3(s)} + \frac{1}{4}FeS_{2(s)} + \frac{15}{16}O_{2(g)} + \frac{3}{8}H_{2}O \rightarrow \frac{1}{2}CaCO_{3(s)} + \frac{1}{2}CO_{2(g)} + \frac{1}{2}SO_{4(aq)}^{2} + \frac{1}{2}Ca_{(aq)}^{2+} + \frac{1}{4}Fe(OH)$ Terrestrial Carbonate Dissolution \rightarrow Marine Carbonate Precipitation	$\left +\frac{1}{2}CO_2\right $	10 ⁵ -10 ⁶

Figure 2-1: Schematic summarizing the reactions, timescales, and net CO_2 release to or uptake from the atmosphere accompanying weathering of silicate and carbonate minerals. Uptake or release depends upon timescale, as shown, and as discussed in text. $CaSiO_3$ is used as a generic silicate mineral.


Figure 2-2: Schematic diagram showing the differences between a traditional mixing model and our machine learning mixing model (A). Notably, in the machine learning mixing model, endmember chemistry is not assigned *a priori*, but rather derived from patterns in the data. Results from using our machine learning mixing model (i.e., NMF) on a synthetic dataset of known endmember chemistry and mixing proportions (i.e., α) are shown in B and C. Using only the synthesized stream sample chemistries, the model adequately recovered the correct mixing proportions (B) and endmember chemistries (C). The axes in (C) are the true concentration ratios of the endmembers.



Figure 2-3: Schematic cross section of Shale Hills showing the depths (labelled lines) where oxidation of pyrite, and dissolution of carbonate, chlorite, and illite initiate (modified after Brantley et al., 2013a). Illite and chlorite dissolve at all depths above the labelled lines, but reactions of carbonate minerals and pyrite only occur in a narrow one-meter wide depth zone under the ridge that widens to several meters toward the valley. Specifically, pyrite oxidation is complete under both ridge and valley at the depths where chlorite dissolution initiates. Carbonate dissolution is complete at the depth where pyrite oxidation is complete under the ridge but at ~4 m above the pyrite front under the valley. These reaction fronts are estimated and extrapolated from bulk chemistry measured in samples from boreholes located at the ridge and valley (Jin et al., 2010; Brantley et al., 2013a; Gu et al., 2020b).



Figure 2-4: Sulfur isotope composition plotted versus concentration for sulfate in the subset of stream or groundwater samples at Shale Hills where S isotopes were measured (symbols; Jin et al., 2014). Dot-dashed lines represent the average sulfur isotope range for acid rain in USA (3-5%; Bailey et al., 2004) and dashed lines represent the average sulfur isotope range of pyrite calculated from NMF results (-9.5‰ to -7.2‰). Sulfur isotopes in pyrite at Shale Hills were previously constrained to lie in the range of -1‰ to -15‰ (Jin et al., 2014). (B) Plot showing the calcite saturation index (log $\Omega_{calcite}$) vs. concentration of pyrite-derived sulfate (calculated through NMF) in surface and groundwater samples at Shale Hills where alkalinity was measured. Here Ω_{calcite} (= ion activity product / equilibrium constant for calcite dissolution) is <1 the water is undersaturated with respect to calcite, and when Ω_{calcite} is >1, the water is oversaturated. Black line represents water-calcite equilibrium. Some samples in B differ from those in A because more samples were collected for alkalinity than sulfur isotopes. In both A and B, color shading represents the fraction of total sulfate derived from pyrite calculated by NMF (i.e., α_{deep}). (C) Time series plot showing the flux of sulfate in Pennsylvania NADP site PA42 (2.8 km from Shale Hills) from wet and dry deposition (see Appendix A.2.4). Black bar shows the NMF results for the export flux of sulfate derived from acid rain for Shale Hills during our sampling period, and the rationale for the inferred 19 y lag between input and output.



Figure 2-5: Concentration of total sulfate (black line), rain-derived sulfate (NMF-calculated; gray) and sulfide-derived sulfate (NMF-calculated; yellow) in stream water plotted versus time at Shale Hills (A), East River (B), and Hubbard Brook (W-3 sub-catchment) (C). Shale Hills and East River temporally switch between being a source and sink of CO₂, while Hubbard Brook is always a sink over the timescales studied, as shown by the CO₂ sequestration coefficient (κ_{stream}) for Shale Hills (D), East River, (E), and Hubbard Brook (F). Gray error bars in D, E and F represent 1s.d. from the calculated κ_{stream} for that sample. The range (mean + 1s.d.) indicated in red to the right of D, E, and F represent κ_{rock} , the time integrated CO₂ sequestration coefficient calculated from the rock chemistry (see text). Here, $\kappa_{stream} > 0$ or <0 indicates stream is a source or sink of CO₂ respectively when considering weathering reactions over 10⁵ to 10⁶ yr timescales (see Figure 2-1). The long record at Hubbard Brook shows that κ_{stream} is approaching κ_{rock} as the watershed recovers from acid rain. Gaps in the time series for Shale Hills occur when the autosampler tubing or stream froze.

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Chapter 3

Linking Stream Chemistry to Subsurface Redox Architecture

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Abstract

As drinking-water scarcity grows worldwide, we need to improve predictions of the quantity and quality of our water resources. An overarching problem for model improvement is that we do not know geological structure of aquifers in sufficient detail. We discovered that mineral-water reactions imprint structure in the subsurface that impacts flow and transport of some chemical species. Specifically, pyrite, a ubiquitous mineral, commonly oxidizes and depletes in the upper layers of most watersheds, only remaining at tens of meters of depth. Variations in sulfate concentrations released into rivers from oxidizing pyrite reflect the rate

limiting step of oxidation and the relationship between the land surface and pyrite-oxidizing layers. Although coal mining changes the natural dynamics, patterns in stream chemistry as a function of discharge are consistent with deep and shallow pyrite oxidation zones in small and large watersheds respectively. Understanding the subsurface patterns of mineral reactions and how they affect the architecture of aquifers will elucidate patterns of changing river chemistry and our ability to manage water resources.

3.1 Introduction

Geologists investigate the evolution of the land surface through direct observation. In contrast, below the land surface, water dissolves and precipitates minerals in localized zones called reaction fronts that define landscapes we cannot see (Brantley et al., 2014). These subsurface landscapes have both a physical and chemical structure that impact many processes such as groundwater flow and storage and contaminant fate and transport. Of particular interest is the redox architecture of a watershed, a term we use to refer to the zones of oxidized and unoxidized bedrock (Gu et al., 2020a), which includes both minerals and organic matter. Understanding the redox architecture of a watershed is important because the fate and transport of many environmental contaminants depend on redox processes along subsurface flowpaths (Borch et al., 2010). For example, nitrate leaching into groundwater from excess fertilizer application is one of the major threats to environmental and public health worldwide (Galaviz-Villa et al., 2010). Although conservation efforts have reduced nitrate runoff from farms, stream nitrate concentrations have remained high due to the persistence of legacy nitrate in groundwater (Van Meter et al., 2017; Van Meter et al., 2018). Whether or not a watershed is susceptible to legacy contamination may depend on its underlying redox architecture (Tesoriero et al., 2013; Tesoriero et al., 2015). Several studies have aimed to predict redox conditions in groundwater using

measurements of dissolved oxygen, watershed characteristics (e.g., lithology, land use, and soil properties), and statistical analysis (e.g., Tesoriero et al., 2015; Close et al., 2016; Tesoriero et al., 2017; Friedel et al., 2020), but interpreting these results with respect to watershed function and contaminant transport remains difficult – especially at large spatial scales – because of landscape heterogeneity.

While we do not focus on the nitrate system here, we nonetheless explore the redox architecture of the subsurface by investigating pyrite oxidation. Pyrite, a ubiquitous but trace iron sulfide mineral, is generally depleted through oxidation in the upper layers of near-surface rock through interaction with oxygenated water (Gu et al., 2020a, and citations therein). In fact, only rarely are detrital pyrite-containing sediments found in the rock record since atmospheric oxygen levels increased above 10^{-5} PAL (present atmospheric level), because pyrite in these particles oxidizes so rapidly near Earth's surface (Johnson et al., 2019). Gu et al. (2020a) showed that many rocks are unaffected by oxidation at depths of tens of meters below land surface but are completely pyrite-free at the land surface. They also identified a depth interval of oxidation (a reaction front) that somewhat parallels the land surface under headwater catchments. In some watersheds where the front remained sub-parallel to the land surface, pyrite-containing rock was observed to never reach the land surface but in other watersheds, river incision exposes pyrite in the channel. We hypothesized that the pyrite oxidation front might indicate the transition from oxic to anoxic groundwater in a watershed and might control sulfate dynamics. Understanding the vertical distribution of pyrite in the subsurface (i.e., the depth of the reaction front) might eventually enhance predictions of transport for redox-active contaminants such as nitrate or organic compounds.

Here we join a machine learning based mixing model with a physically based oxidation model to explore what concentration-discharge relationships can teach us about the subsurface redox architecture of a watershed across spatial scales, and we apply it to watersheds in the United States (US) using publicly accessible water quality databases. This investigation is important because, although it is known that outcropping rock type is a major control on river chemistry (Meybeck, 1987), few studies have linked subsurface distributions of minerals (e.g., pyrite) to changes in stream concentrations at basin scale. If such linkages could be made, our ability to predict water quality and legacy contamination would greatly improve.

3.2 Methods

3.2.1 Data Acquisition

For this study, we first aggregated datasets of stream concentration and discharge measurements in a series of four increasingly larger, nested watersheds that range from zeroth order to 7th order (HUC16 to HUC4) (Figure **3-1**; Table **B-3** in Appendix B.3). For the smallest watershed of Shale Hills (HUC16; Figure **3-1A**), we utilized data collected from 2008-2010 (Brantley et al., 2013a-c). For the next larger watershed of Shaver's Creek (HUC10; Figure **3-1B**), we utilized datasets from three locations for samples collected from 2014-2020 (Brantley et al., 2018a,b, this study). This HUC-10 watershed comprises the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO) (Brantley et al., 2018c). Lastly, data were downloaded for two sites in the Juniata River Basin (HUC8; Figure **3-1C**) and nine sites in the Susquehanna River Basin (SRB) (HUC4; Figure **3-1D**) from the Water Quality Portal (WQP; Read et al., 2017), a national repository for water quality data. These sites were selected based on the following criteria: 1) they were located along the main stem of the river, and, 2) they provided >15 samples where aqueous Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, NO₃⁻, and SO₄²⁻, were all measured between 2014 and 2020. All data from the WQP were accessed and downloaded using dataRetrieval, an R package developed by the United States Geological Survey (USGS; De Cicco et al., 2018). To disentangle effects related to watershed scale from those related to presence/absence of coal, we retrieved data from watersheds in the western US. For these watersheds, we do not apply the machine learning model (see Section 3.2.3) to separate the sources of sulfate due to computational limitations. Instead, we target watersheds where pyrite would be the predominant source of sulfate by querying for watersheds that meet the following five criteria: 1) west of longitude -104° to minimize the effects of acid rain (longitude determined using acid deposition maps from the National Atmospheric Deposition Program); 2) <5% agricultural land use to minimize the effects of fertilizers; 3) without evaporites (i.e., gypsum); 4) with a positive water balance (precipitation/potential evapotranspiration >1) to minimize the effects of evaporation; 5) with >15 concentration-discharge (*C-q*) measurements for analysis. We identified 291 watersheds that met these criteria.

3.2.2 Water Sampling and Analysis

Although much of the Shaver's Creek data has been published as referenced above, some waters were also sampled in this study using identical sampling approaches. For routine sampling, we collected stream water and split the sample into two subsamples. For cation analysis, we filtered the sample through a 0.45 μ m filter and field-acidified to pH < 2 using 10% nitric acid. For anion analysis, we filtered the sample through a 0.45 μ m filter and left the sample unacidified. All samples were stored at temperatures 5°C before analysis. Cation concentrations were measured on an Thermo Scientific iCAP 7400 Inductively Coupled Atomic Emissions Spectrometer and anion concentrations were measured on an Dionex Ion Chromatograph.

Additionally, an optical sensor (Campbell Scientific CS511) was deployed 20mbls in a well (CZMW11) at Shale Hills to measure dissolved oxygen concentrations over time from 2019-2020. A stage sensor (MeterGroup Hydros 21) was also deployed to monitor water level depth

during the same time interval. Measurements were taken every 15 minutes and stage measurements were corrected to account for instrumental drift (Shaughnessy et al., 2019). All data for these sensors can be found on the SSHCZO website

(http://www.czo.psu.edu/data_time_series.html).

On two sampling campaigns, surface water and groundwater were collected over the course of two days throughout the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO; Shale Hills, Cole Farm, Garner Run, Shaver's Creek; see Brantley et al. (2018c) for site details) for sulfur isotope compositions of sulfate (i.e., δ^{34} S; **Table B-2** in Appendix B.3). These samples were vacuum filtered through a 0.2 µm filter in the laboratory. Then, samples were dripped through an ion exchange column packed with 5 g of Cl⁻ type Bio Rad 1-X8 anion exchange resin. Before introducing each sample, ion exchange columns were pre-cleaned by triple rinsing with 3 M hydrochloric acid and then triple rinsing with deionized water. Once loaded, sulfate from each sample was eluted with 45 mL of 0.8 M hydrochloric acid as described in Le Gendre et al. (2017). This approach isolates sulfate and removes potential contamination by other anions (e.g., nitrate). Once eluted, sulfate was precipitated as barite (BaSO₄) by adding 5 mL of saturated BaCl₂ in deionized water. Barite was then centrifuged and rinsed 3x with deionized water and dried for isotope analysis.

For isotope analysis, ~0.3 to 0.4 mg of barite were weighed into a tin boat along with an excess (~5x) of vanadium pentoxide (V₂O₅) to ensure consistent ¹⁸O abundance in resulting SO₂ analyte gas, as ³²S¹⁸O¹⁶O will isobarically interfere with ³⁴S¹⁶O¹⁶O (e.g., Fry et al. 2002). Samples were dried at least overnight in a vacuum oven prior to analysis on a Thermo Flash EA coupled to a Thermo Delta V isotope ratio mass spectrometer operated in continuous flow mode. Results are reported on the Vienna Canyon Diablo Troilite (VCDT) scale by analyzing a 3-point suite of international reference standards between every 10 samples (IAEA SO-5, $\delta^{34}S = +0.5 \%$; IAEA SO-6, $\delta^{34}S = -34.1 \%$; NIST NBS127, $\delta^{34}S = +20.3 \%$). Samples were analyzed in duplicate, and

uncertainty is reported as the difference between duplicate measurements; long-term precision of standard reference materials was always better than $\pm 0.3 \%$ (± 1 std. dev.).

3.2.3. Rock Sampling and Analysis

In addition to water samples, in-place bedrock was sampled from outcrops within the streambed at various locations within Shaver's Creek catchment (Figure **B-1** in Appendix B.4; Table **B-4** in Appendix B.3). These samples were either collected from the surface using a rock hammer or recovered using a Shaw Portable Core Drill. The pulverized samples ($<150 \mu m$) were analyzed for the concentration of total sulfur (Gu et al., 2020a) and the values were compared to unweathered bedrock to estimate the extend of pyrite oxidation by assuming pyrite is the main sulfur-bearing mineral. A few thin sections were made by cutting across the center of the rocks and were checked under scanning electron microscopy (SEM). The elemental compositions of spots within the thin section were determined by energy dispersive X-ray spectroscopy (EDS). Based on the bulk analysis of total sulfur and microscopic observations from SEM and EDS, the samples were classified as either fully oxidized, partially oxidized, or unoxidized with respect to pyrite (Figure **B-1** in Appendix B.4).

3.2.4 Machine Learning Model

To separate the sources of sulfate we utilize a machine learning-based mixing model called Non-negative Matrix Factorization (NMF) (Shaughnessy et al., 2021). In short, NMF is unique among mixing models because it determines the chemistry of the endmembers and the mixing proportions simultaneously. As a "blind source separation", the user does not stipulate an endmember chemistry *a priori*; rather, NMF identifies endmember water chemistries and then

geochemists must interpret the identity of the endmember based on understanding of the system. NMF decomposes a matrix of stream chemistry, *V* (dimensions = $n \ge m$), into the product of two matrices, *W* and *H*. The *m* columns of *V* are concentration ratios $[X]/[SO_4^2]$, where brackets denote molar concentration and $X = Ca^{2+}$, Mg^{2+} , Na^+ , K^+ , Cl^- , and NO_3 . The *n* rows of *V* are samples taken at different sampling dates. *W* has the dimensions $n \ge p$, where *n* is the number sampling dates and *p* is the number of endmembers. The cell entries of *W* are the mixing proportions of the endmembers. The row sum of each entry in *W* is 1.00 ± 0.05 , meaning that the stream chemistry is completely described (± 0.05) as a combination of endmembers. This is referred to as a unity constraint. *H* has the dimensions *p* $\ge m$ and its cell entries represent the chemical signature of each of the endmembers. The only parameter that needs to be set before the model is run is *p* – the number of endmembers. To determine *p*, we utilize principal component analysis (PCA) to determine the number of components that are needed to explain >90% of the variation in the stream ratio data. We set *p* equal to this number of components. As used here, NMF is governed by a series of mass balance equations.

The solution for NMF is non-unique; therefore, we run the model 10,000 times to account for variability in the derived endmember compositions and mixing proportions. We filter out any models that do not fulfill the unity constraint. Additionally, following Shaughnessy et al. (2021), we filter out poor-fitting models and retain only the 5th percentile of best-fitting models. These are averaged and reported here.

The validity of the NMF modeling was investigated in Shaughnessy et al. (2021). In our previous study, we created a synthetic dataset where the mixing proportions and the endmember chemistries (H) were known, but not input into the model. We found that NMF successfully derived the correct endmember chemistries and mixing proportions for the synthetic dataset. Additionally, we compared sulfur isotopes and calcite saturation indices to the modeling results for samples from Shale Hills. We found that when pyrite-derived sulfate concentrations were high

(as determined by NMF), sulfur isotopes showed a depleted signature that is consistent with pyrite at Shale Hills, and the water was saturated with respect to calcite, which is consistent with sulfuric acid driving dissolution of the ubiquitous mineral, calcite, at depth. Both of these observations are consistent with pyrite oxidation, which supports that our model identifies the pyrite-sulfate signal in the stream chemistry and separates pyrite-sulfate from other sulfate sources such as acid rain or fertilizer.

3.2.5 Data Analysis

First, stream samples from Shaver's Creek were utilized in the NMF model (Section 2.3; eq. 1) to separate the sources of sulfate. Sources for Shaver's Creek were determined using sulfur isotopes and the *H* matrix from the NMF decomposition. After developing the Shaver's Creek model, we constructed models for the Juniata and Susquehanna River sites (Figures **3-1C,D**).

After NMF, we utilized the pyrite-derived sulfate concentrations in an oxidation model for each site (see Section 3.4.1; eq. 3-3). Following a published approach (i.e., Ibarra et al., 2016), we fit the oxidation model to the concentration and discharge data using a non-linear least squares model. All model calculations were performed in R using the nls2 package.

3.3 Results

3.3.1 Sources of Sulfate

Following our previous approach for Shale Hills where two components (i.e., pyrite oxidation and acid rain) were observed to explain stream sulfate concentrations (Shaughnessy et al., 2021), we investigated pyrite oxidation in the larger, encompassing HUC-10 watershed of

Shaver's Creek. For that dataset, principal component analysis (PCA) revealed three components were needed to explain >90% of the variance in stream chemistry. Given that Shaver's Creek has agricultural land use, we anticipated that the three sources of sulfate would be the two identified at Shale Hills (acid rain, pyrite) and an additional sulfate source, fertilizer.

Sulfur isotopic measurements are also consistent with three inferred sources of sulfate in Shaver's Creek (Figure **3-3**). In particular, the isotopic signature of dissolved sulfate in Shaver's Creek water falls in between the inferred compositions of three sources inferred to be acid rain, pyrite, and fertilizer. For example, the δ^{34} S values in shallow groundwater near a farm field are consistent with measurements of fertilizer sulfate as reported elsewhere (Zhang et al. 2015). In contrast, the δ^{34} S values in groundwater in a subcatchment within the SSHCZO that is underlain by sandstone (i.e., Garner Run) are consistent with acid rain. A third sulfate source is inferred from the δ^{34} S values in deep groundwater at Shale Hills: these are very depleted, ranging from - 15‰ to 0‰, consistent with pyrite oxidation (Jin et al., 2014). The isotopic signature of dissolved sulfate in Shaver's Creek water falls in between the inferred compositions of acid rain, pyrite, and fertilizer, as expected if these three endmembers contribute sulfate to Shaver's Creek (Figure **3-3**).

Based on the PCA and the isotope data, we set the number of endmembers (i.e., p) in the NMF model to 3. After running the model, the derived geochemical signatures for each of the three endmembers are distinct (Table **B-1** in Appendix B.4). We use geochemical knowledge to identify these sources. Comparing results from Shaver's Creek to non-agricultural headwater Shale Hills, we identify the first two sulfate sources in Shaver's Creek as pyrite oxidation and acid rain (Shaughnessy et al. 2021). Pyrite oxidation can be identified because oxidation releases sulfuric acid which, in almost all sedimentary rock, causes dissolution of (Ca, Mg) carbonate minerals at depth, releasing Ca²⁺ and Mg²⁺ to ground waters. Therefore, the source with the highest ratios of $[Ca^{2+}]/[SO_4^{2-}]$ and $[Mg^{2+}]/[SO_4^{2-}]$ is identified as pyrite oxidation. To identify the

acid rain endmember, we note that rain retains the Na/Cl ratio of ocean water, 0.86 (Möller, 1990; Neal and Kirchner, 2000), very close to that of endmember 2, 0.89 (Table **B-1** in Appendix B.4). The third endmember in the Shaver's Creek model has the highest $[NO_3^-]/[SO_4^{2-}]$ ratio, which we infer to represent fertilizer application in the watershed.

3.3.2 Dissolved Oxygen Dynamics

The reactant driving pyrite oxidation is dissolved oxygen at the reaction front. Here, we show the concentration of DO in groundwater, C_{DO} , measured from 2020-2021 in a ridgetop borehole (CZMW11) located towards the outlet of the watershed at Shale Hills (Figure **3-5B**). The DO probe was placed at 20 meters below land surface (mbls) within the reaction front, the depth of which was determined via solid phase analysis of drill cuttings (Gu et al., 2020a). Although sampled in different years, the seasonal trends of pyrite-derived sulfate in the stream, C_{sulf} (sampled 2008-2010), and groundwater C_{DO} (sampled 2020-2021) are opposite. C_{sulf} is high in the dry season and low in the wet season, while C_{DO} is high in the wet season and low in the

3.3.3 Streambed Pyrite in Shaver's Creek

In addition to water chemistry, the extent of pyrite oxidation in the stream bed varied downstream in Shaver's Creek. In the samples where thin sections were made, euhedral or framboidal pyrite was observed in unoxidized samples via SEM. Where oxidation had occurred, we observed iron oxide pseudomorphs after pyrite. The elemental compositions of the framboids were determined by EDS and the pseudomorphs were found to contain no sulfur. We found that in some samples, pyrite framboids and iron oxide pseudomorphs were both present, which we refer to as partially oxidized samples. In the upper part of the watershed, pyrite in outcrops within the streambed was predominantly fully or partially oxidized, whereas pyrite in downstream outcrops was predominantly unoxidized (Figure **B-1** in Appendix B.4).

3.3.4 Concentrations Across Watershed Scale

The average sulfate concentration in the streams increases as the size of the drainage basin increases (Figure 3-4A). At the outlets of Shale Hills, Shaver's Creek, the Juniata River, and the Susquehanna Rivers, for example, the average sulfate concentrations are 95 ± 17 , 114 ± 23 , 160 ± 37 , and $223 \pm 57 \mu$ M, respectively. All sites show similar seasonal trends in stream sulfate concentrations, where sulfate concentrations are highest in the summer and fall and lowest in the winter and spring.

The relative proportions of pyrite, acid rain, and fertilizer derived sulfate change both temporally (seasonally) and with increasing spatial scale. The proportions of acid rain sulfate are larger in small watersheds, and as the watershed size increases, the proportions of pyrite and fertilizer both increase (Figure **3-4C**). In all watersheds, we observe the highest proportion of pyrite-derived sulfate in the summer and fall and the highest proportion of acid rain in the winter and spring (Figure **3-4B**). We observe no significant temporal trend in fertilizer-derived sulfate.

3.4 Discussion

3.4.1 Oxidation Model

To explore river and groundwater sulfate dynamics, we propose a simple model that describes pyrite oxidation along a flowpath as recorded in variations in stream chemistry. There are many oxidation reactions that remove O_2 from groundwater. Some of the electron donors in these reactions include soil organic carbon, petrogenic organic carbon, and redox sensitive minerals such as pyrite and chlorite. We assume that oxidation of the modern organic matter occurs strictly in the soil and sediment, affecting the initial DO concentrations entering the underlying rock (as described below). In contrast, petrogenic organic matter can oxidize in the rock or in the soil. In general, however, pyrite is usually observed to be the first mineral to oxidize in bedrock. For example, observations document that pyrite tends to be depleted by oxidation before all the petrogenic organic carbon is oxidized (Petsch et al., 2000; Bolton et al.,2006; Hemingway et al. 2018). For this reason, we focus on pyrite oxidation because it is likely the deepest oxidation occurring in the bedrock.

Following other simple weathering model treatments (e.g., Berner, 1978; Kump et al., 2000) the change of pyrite-derived sulfate concentrations, C_{sulf} (mol m⁻³), in stream waters over time, *t*, is a balance between dilution and *R*, the rate of pyrite oxidation (mol sulfate m⁻³ yr⁻¹):

$$\frac{\partial C_{sulf}}{\partial t} = R - C_{sulf} \frac{Q}{V}$$
(3-1)

For simplicity, we abbreviate pyrite-generated sulfate as p-sulfate. In eq. 3-1, Q is the volumetric flow rate of water through the system (m³ yr⁻¹), and V is the volume of water stored in the watershed (m³). Ultimately, solving eq. 3-1 for steady state with respect to p-sulfate concentrations and defining Dw as the Damköhler coefficient (m yr⁻¹) (Maher and Chamberlain, 2014) results in the following equation (see Appendix B.1):

$$C_{sulf} = \frac{c_{sulf}^{max,obs} Dw}{Dw+q}$$
(3-2)

Here, $C_{sulf}^{max,obs}$ is the empirical maximum concentration of p-sulfate, and q is the runoff (m yr⁻¹). *Dw* equals the advective Damköhler number, *Da*, multiplied by q for the watershed. *Da* is the characteristic time scale of advection divided by that of pyrite oxidation. Although derived differently, eqn. 3-2 is mathematically equivalent to the equation previously proposed (Maher and

Chamberlain, 2014) that has been used by several authors to fit *C-q* data for silicate weathering (Ibarra et al., 2016; Wymore et al., 2017), carbonate weathering (Zhong et al., 2020), and global weathering patterns (Maher and Chamberlain, 2014, Ibarra et al., 2017); however, this study is the first time that the model is linked to the subsurface distribution of minerals. We determined $C_{sulf}^{max,obs}$ and Dw for each watershed here by fitting measurements of C_{sulf} versus q to eqn. 3-2 using non-linear least squares regression.

The flux of p-sulfate, F_{pyrite} , is manifested in stream chemistry as the product of C_{sulf} and q and thus, using eq. 3-2, we can write

$$F_{pyrite} = qC_{sulf} = \frac{qC_{sulf}^{max,obs}Dw}{Dw+q}$$
(3-3)

When q is very small, $F_{pyrite} = qC_{sulf}^{max,obs}$ and $C_{sulf} = C_{sulf}^{max,obs}$ (eqs. 3-2- and 3-3), which means that p-sulfate concentrations are constant, and the rate of pyrite oxidation linearly increases with runoff. This behavior is interpreted as pyrite oxidation limited by transport of DO into or sulfate out of the system (transport-limited oxidation). When q is very large, $F_{pyrite} = C_{sulf}^{max,obs}Dw$ and $C_{sulf} = \frac{C_{sulf}^{max,obs}Dw}{q}$ (eqs. 3-2- and 3-3), which means that p-sulfate concentrations are inversely proportional to runoff and pyrite oxidation rate is constant. Here, the rate of oxidation cannot keep up with the rate of dilution (kinetic-limited oxidation).

Next, we interpreted our oxidation model with respect to the subsurface redox architecture across small and large watersheds. First, we define a new term, $C_{sulf}^{max,pred}$, as the maximum concentration of p-sulfate in groundwater predicted after complete consumption of DO. We assume water at 10°C (i.e., the average temperature of groundwater at Shale Hills) is equilibrated with atmospheric oxygen (i.e., DO = 11.3 mg/l or 353 µM) and reacts with pyrite

until DO reaches zero. Given these assumptions, $C_{sulf}^{max,pred}$ equals 188 µM. Although $C_{sulf}^{max,pred}$ varies slightly with temperature, we assume that $C_{sulf}^{max,pred} = 188$ µM everywhere for simplicity.

We suggest four reasons why $C_{sulf}^{max,obs}$ could be less than $C_{sulf}^{max,pred}$. First, groundwater could be in equilibrium with soil gases rather than atmospheric gases. At Shale Hills, soil gas O_2 concentrations are 75% of PAL; therefore, groundwater in equilibrium with soils would have DO concentrations of 260 μ M (8.3 mg/l) (Gu et al., 2020b). Second, other redox sensitive species in the bedrock (e.g., petrogenic organic matter, chlorite, biotite) could consume DO before the oxygen reaches pyrite. The relative importance of each electron donor in removing DO is determined by the vertical distribution, concentration, and oxidation kinetics of each species in the bedrock. Third, there could be too little pyrite in the bedrock to completely deplete the DO for a given packet of water and a given flowpath. In this situation, then the groundwater will remain oxic, and groundwater entering the stream will still contain DO. Lastly, the depth of groundwater flow might be less than the depth of the pyrite reaction front. A typical weathering profile from Shale Hills and other shale-underlain watersheds (Gu et al., 2020a) for pyrite is shown in Figure **3-2A**. Based on this weathering profile structure, three generalized types of flowpath are possible (Figure 3-2B): 1) above the reaction front such that water does not interact with pyrite and $C_{sulf} = 0$; 2) through part of the reaction front such that pyrite oxidation affects the water but does not deplete all DO, resulting in $C_{sulf} < C_{sulf}^{max,pred}$, and 3) completely through a reaction front that has enough pyrite to deplete the DO, such that $C_{sulf} = C_{sulf}^{max,pred}$ (Figure 3-2B). Flowpaths 1 and 2 result in $C_{sulf}^{max,obs} < C_{sulf}^{max,pred}$.

Given the four explanations for understanding $C_{sulf}^{max,obs}$, only the last explanation (i.e., differing flowpaths) has any implicit scaling relationship. In other words, the length and depth of flowpaths can change as a function of drainage area, but it is unlikely that relative importance of

different redox reactions (explanations 1 and 2) or the concentration of pyrite in the bedrock (explanation 3) systematically varies with watershed size. For this reason, we infer that $C_{sulf}^{max,obs}$ can give clues to the average flowpath and its position with respect to the reaction front.

Another way to understand the chemistry of each packet of water along a flowpath is to consider the average length of flow of the packet through the reaction front, l, normalized by the length of the total flowpath from the land surface to the stream (L). Those two quantities can be used to approximate the advective Damköhler number, Da, for a reaction under some circumstances (Brantley and Lebedeva, 2021):

$$Da = \frac{L}{l} \tag{4}$$

In defining this Damköhler number, the watershed is likened to a packed-bed chemical reactor where *L* is the length of the reactor and *l* is the length of the reaction zone. For Da > 1 (*L* > *l*), the system is transport-limited, and for Da = 1 (*L*=*l*), the system is kinetic limited (the derivation for this treatment does not allow Da < 1 because *L* cannot be smaller than *l*). We can determine the relative flowpath length through the reaction front by converting *Dw* from our oxidation model to *Da* (i.e., Da = Dw/q).

3.4.2 Oxidation Model for Shale Hills

As discussed in Shaughnessy et al. (2021), there are two sources of sulfate at Shale Hills: pyrite oxidation and acid rain, and the NMF model successfully separates contributions in each stream sample from each source. Using the oxidation model (eq. 3-2) and our NMF decomposition, we aimed to describe how the concentration of pyrite-derived sulfate (C_{sulf}) in the stream at Shale Hills changes as a function of runoff (q). We found that at low q, C_{sulf} is relatively constant, consistent with pyrite oxidation limited by the transport of DO to the reaction front (i.e., transport limited). At high q, C_{sulf} is diluted to lower values, consistent with pyrite oxidation limited by reaction kinetics (i.e., kinetic-limited). For Shale Hills, we observe both transport- and kinetic-limited oxidation as evident in the C-q curve shown in Figure **3-5A**. Fitting eq. 3-2 to C_{sulf} and q, we find $C_{sulf}^{max,obs} = 54 \pm 2 \,\mu\text{M}$ and $Dw = 0.4 \pm 0.05 \,\text{m yr}^{-1}$ (p < 0.01; Figure **3-5A**).

At Shale Hills, $C_{sulf}^{max,obs} < C_{sulf}^{max,pred}$, regardless of whether we use soil O₂ or

atmospheric O₂ to define $C_{sulf}^{max,pred}$. Using the conceptual model in Figure 3-2, we interpret this to mean that the stream mostly integrates flowpaths above and partially through the reaction front with little contribution of completely oxygen-depleted water that travels in flowpaths completely through the reaction front. However, we know that some groundwater flowpaths at Shale Hills travel across the pyrite reaction front. For example, Sullivan et al. (2016) collected groundwater samples from a ridgetop borehole (i.e., CZMW8) below the pyrite oxidation front as determined based on mineralogical analysis of borehole cuttings at depth. They found that the average sulfate concentration in the groundwater from this well at 30.1 mbls was $182 \pm 38.7 \,\mu\text{M}$ (n = 9), which is consistent with $C_{sulf}^{max,pred} = 188 \,\mu\text{M}$. This flowpath might not make it to the stream; therefore, it is not detected by our oxidation model, which relies on flowpaths that return to the stream.

The seasonality of C_{sulf} and C_{DO} is consistent with consumption of DO via pyrite oxidation at Shale Hills. We observe that C_{DO} increases seasonally (in CZMW11) as the water level in the borehole increases, i.e., as the water table rises (Figure **3-5B**). This is consistent with advection of groundwater with high dissolved oxygen to the reaction front – perhaps through interconnected fractures (Gu et al., 2020b; Sullivan et al., 2016) – during the wet season. As the water level lowers, C_{DO} decreases sharply, likely due to pyrite oxidation removing dissolved oxygen from the groundwater (Figure **3-5B**). Because these measurements are taken 20 mbls and are within the pyrite reaction front, it is unlikely that the removal of oxygen from the groundwater in this location is due to oxidation of other materials (e.g., organic matter).

3.4.3 C-q Analysis

Similar to Shale Hills (see Section 3.4.2), we calculated Dw and $C_{sulf}^{max,obs}$ for sites across Shaver's Creek, the Juniata River, and the Susquehanna River using the oxidation model. The oxidation model successfully described the *C-q* behavior for all the sampling points (watersheds) in the study, except for S9, the most upstream site in the SRB. For S9, we observe an increase in C_{sulf} as *q* increases, which cannot be described by our model. The fit of the model to the *C-q* data (for all sampling locations except for S9) can be seen in Figure **3-6**. Generally, $C_{sulf}^{max,obs}$ increases with increasing drainage area and Dw decreases. Small watersheds tend to show $C_{sulf}^{max,obs} < C_{sulf}^{max,obs}$ and large watersheds tend to show $C_{sulf}^{max,obs} > C_{sulf}^{max,obs}$. As explained previously, values of $C_{sulf}^{max,obs} < C_{sulf}^{max,ops} > C_{sulf}^{max,obs}$. We explore this trend further in Section 3.4.4.

3.4.4 Explanations for Observed Sulfate > Predicted Sulfate

3.4.4.1 Two hypotheses

To explain why most large watersheds show $C_{sulf}^{max,obs} > C_{sulf}^{max,pred}$ in the SRB, we hypothesized that a different oxidant is present for the pyrite in larger watersheds. Fe³⁺ is a known oxidant for pyrite (Silverman, 1967), but ultimately, O₂ is needed to transform Fe²⁺ (produced during pyrite oxidation by Fe³⁺) back to Fe³⁺ (i.e., regeneration of oxidant) and ferric iron concentrations are low at circumneutral pH; therefore, ferric iron cannot be the missing oxidant. Some studies have suggested that NO₃⁻ can oxidize pyrite (Jørgensen et al., 2009; Torrentó et al., 2011); however, this reaction must be microbially mediated. Pore throats in the pyrite-containing zone of the shale at Shale Hills are too small for microorganisms to access the pyrite; therefore, pyrite oxidation in these locations is abiotic (Gu et al., 2020b). Although other watersheds might have larger pores, it is unlikely that pore size depends on watershed size; therefore, NO_3^{-} -dependent pyrite oxidation is unlikely to explain the overall trends. We therefore concluded that an alternate oxidant is unlikely to explain our findings.

This led us to hypothesize that transport of O₂ to the mineral surface differed in large and small watersheds. If this is the explanation, it is likely related to the importance of coal mining in impacting riverine sulfate dynamics in the SRB over the last many decades (Raymond and Oh, 2009). For example, coal mining in parts of the SRB has exhumed pyrite and exposed it at the surface, which allows direct interaction of pyrite with gaseous O₂. The easy influx of O₂ in air could explain riverine concentrations of C_{sulf} and $C_{sulf}^{max,obs}$ greater than $C_{sulf}^{max,pred}$. We infer that as drainage area in the SRB increases, the probability that the watershed is impacted by coal mining increases (Figure **B-2B** in Appendix B.4). After mining coal in the larger watersheds, oxidation of pyrite becomes kinetic- rather than transport-limited. For example, studies investigating pyrite oxidation in mine tailings have documented that oxidation is limited by reaction kinetics (Elberling et al., 1994). In effect, as transport of O₂ changes from advection of oxygenated water in small watersheds to transport in air in large watersheds with mining-exposed pyrite, the overall rate limiting step changes from transport- to kinetic-limited.

To test this hypothesis, we used a geospatial dataset of coalbed lithology (East, 2013) (Figure **B-2A** in Appendix B.4) and classified each watershed as "coal containing" (>0% of watershed area occupied by coal mining) or "non-coal containing" (0% coal mining). Using these classifications, watersheds with coal show $C_{sulf}^{max,obs} > C_{sulf}^{max,pred}$, and those without show $C_{sulf}^{max,obs} < C_{sulf}^{max,pred}$ (Figure **B-3A** in Appendix B.4). We quantified this further by utilizing a logistic regression model. Logistic regression models work by fitting explanatory variables (i.e., drainage area) to binary responses (i.e., a watershed contains coal or does not). The model is fully described in the supplementary material. We analyzed 335 watersheds within the SRB and found that any watershed > 1,355 km² has >50% chance of integrating coalbed lithology. We conclude that in the SRB, stream chemistry yields evidence for a change in rate limiting step at larger spatial scales, and this is likely because larger subbasins within the SRB contain coal.

One issue in the SRB, however, is that spatial scale and coal-containing lithology covary; therefore, we cannot disentangle the effects of coal mining from spatial scale. Thus, an alternate hypothesis might be that $C_{sulf}^{max,obs}$ increases above $C_{sulf}^{max,pred}$ simply because the watersheds are larger. As a first test of the scaling hypothesis, we identified two additional sites slightly north of the SRB that are large and contain no coal: the Hudson (USGS site 01358000; drainage area: 20,981 km²) and the Mohawk Rivers (USGS site 01357500; drainage area: 8,950 km²). Water quality data were accessed as for the SRB (see materials and methods). $C_{sulf}^{max,obs}$ values for these two watersheds equal 97 μ M and 108 μ M, respectively. These values are both below $C_{sulf}^{max,pred}$. This suggests that coal is a better explanation than watershed size for why $C_{sulf}^{max,obs} > C_{sulf}^{max,pred}$ in large subwatersheds of the SRB.

These arguments are consistent with a change in rate-limiting step as watersheds become large enough to be coal-containing. In the next two sections, we provide additional evidence for the presence of coal in watersheds as the important variable (rather than scaling). First, we look at the power-law exponent in C-q behavior, and then we look at watersheds in other parts of the USA. This latter investigation also allows us to determine if the behavior we document in the SRB is particular to just this one region or more general.

3.4.4.2 Sulfate Concentration-Discharge Relationship

Many researchers have documented a power-law relationship between stream concentration, C, and discharge, q (Godsey et al., 2009) and have interpreted the power law exponent, b, in terms of physical processes:

$$C = aq^b \tag{3-5}$$

In addition to increases in $C_{sulf}^{max,obs}$, we therefore tested how coal mining impacts the power-law relationship between sulfate concentration and discharge. If DO is the oxidant source, then there is a fixed amount of oxidant available within any packet of water (i.e., the amount of O_2 that can be dissolved in water). In such systems where the source of the oxygen is dissolved in groundwater, we might expect chemostatic or dilution C-q behavior (i.e., b = 0 or b < 0) depending on if the rate of advection is faster or slower than the rate of oxidation (i.e., transport or kinetic-limited, respectively). In contrast, if gaseous O_2 is the oxidant source, we might only expect dilution behavior (i.e., b < 0) because in such systems oxidation is usually kinetic-limited (Elberling et al., 1994). We tested this using 92 watersheds throughout the SRB. For these sites, we did not separate the sources using our machine learning model due to limited concentration data availability, but rather calculated the C-q power law slope for total sulfate concentrations. We found that 71% of coal-containing watersheds show dilution C-q behavior (b = -0.2 ± 0.2 , n = 56), and 72% of non-coal containing watersheds show chemostatic C-q behavior (b = 0.0 ± 0.1 , n = 36) (Figure **B-3B** in Appendix B.4). This shows that the C-q may indicate the relative importance of different oxidants and supports our hypothesis that we observe a change in the rate limiting step of oxidation as a result of coal mining.

3.4.5 Application to Other Datasets

To further investigate the effects of coal and watershed size on pyrite oxidation at the same time as exploring new climate and lithologic effects, we queried data within the WQP for the western US. In this region, we were able to investigate large watersheds on several lithologies in different climate regimes that do not contain coal. We identified 293 watersheds that fulfill the criteria outlined in materials and methods (109 with and 184 without coal-lithology) (Figure **3**-**7A**). Using this dataset, we were able to test how pyrite oxidation changes as a function of drainage area of a watershed regardless of whether it contained coal. Using the total sulfate concentration and discharge, we calculated Dw and C_{sulf}^{max} for each watershed as described above (eq. 3-2).

Analogous to the eastern US results, watersheds with coal show $C_{sulf}^{max,obs} > C_{sulf}^{max,pred}$ and watersheds without coal tend to show $C_{sulf}^{max,obs} < C_{sulf}^{max,pred}$ (Figure **B-4** in Appendix B.4). In addition, for watersheds without coal, as spatial scale increases, $C_{sulf}^{max,obs}$ approaches $C_{sulf}^{max,pred}$ (=188 uM) (Figure **3-7B**) rather than increasing above $C_{sulf}^{max,pred}$ as observed in the SRB. Once again, this corroborates the findings from the SRB that $C_{sulf}^{max,obs} > C_{sulf}^{max,pred}$ is only observed in the presence of coal.

To explain why $C_{sulf}^{max,obs}$ increases with watershed size in the western dataset, we turn back to observations at Shale Hills and Shaver's Creek. Explanations might include that the predominant flowpath type changes and/or that the depth of the oxidation front changes relative to land surface as a function of spatial scale. In small headwater watersheds (like Shale Hills) flowpaths above and within the pyrite reaction front contribute dominantly to the stream. In other words, the reaction front is relatively deep (Figure 3-2B), consistent with $C_{sulf}^{max,obs} < C_{sulf}^{max,pred}$ (Figure 3-8). In larger watersheds, flowpaths through the pyrite reaction front are dominant, as evident by $C_{sulf}^{max,obs} = C_{sulf}^{max,pred}$. In addition, if watersheds are like Shaver's Creek, the pyrite reaction front is likely to become increasingly shallow as the stream incises into bedrock (Figure **3-2B**), leading to $C_{sulf}^{max,obs} = C_{sulf}^{max,pred}$ (Figure **3-8**).

In addition to $C_{sulf}^{max,obs}$, we found that Dw (and Da) also change with scale. In particular, as watersheds get larger, Da \rightarrow 1. In relationship to eqn. (3-4), this can be conceptualized as $l \rightarrow$ L as watersheds get larger.

3.4.6 Subsurface Redox Architecture in Small and Large Watersheds

To recap the observations, in watersheds without coal, we found that $C_{sulf}^{max,obs} \rightarrow C_{sulf}^{max,pred}$ and Da \rightarrow 1 as watersheds become larger (Figure 3-7). Both observations are consistent with $l \rightarrow L$ (see eq. 3-4). We propose two ways to interpret this observation. The first explanation is that as watersheds get larger, their streams integrate water from deeper flowpaths where water is more likely to have traveled completely through the reaction front, depleting DO completely (i.e., flowpath 3; Figure 3-2B). The second explanation is that streams incise into the pyrite reaction zones in increasingly larger watersheds.

Explanation 1 implies that flow length and depth of flow both increase as drainage area increases. However, tributaries also enter the mainstem of large rivers contributing significantly to streamflow. Instead of integrating deeper flowpaths, therefore, large rivers might simply be manifesting the influence of their tributaries (i.e., higher order streams are a summation of lower order streams) (Shaman et al., 2004; Hrachowitz et al., 2010). For example, runoff in watersheds in the Neversink River watershed in New York become similar after watersheds exceed 21 km² (Shaman et al., 2004). This suggests that water from deeper flowpaths only significantly increase streamflow in moderately small watersheds. Moreover, mean transit times of water in streams

converge to the same value at increasingly large watershed scale, and large watersheds show no major change of dominant flow paths (Hrachowitz et al., 2010). Given these findings, variations in flow length and depth likely describe some of the differences between small in large watersheds, but they cannot solely account for all the trends in our data.

We therefore favor explanation two: reaction fronts shallow as watershed size increases. Instead of flowpaths becoming deeper, allowing stream waters to have interacted with pyrite for longer, the reaction front instead shallows such that shallow flowpaths are within the reaction front rather than above it (i.e., flowpath type 1 disappears in favor of flowpath type 2; Figure 3-**2B**). This explanation is also consistent with our observation of unoxidized pyrite outcropping along sections of Shaver's Creek and in other locations (Gu et al., 2020a). Headwater streams (i.e., zeroth or first order) may generally develop deep pyrite oxidation fronts at least partly because recharging water has high concentrations of DO. But as groundwater flows from the headwaters downstream to join higher order streams, it becomes depleted with respect to DO and in turn less reactive with pyrite; therefore, the reaction front shallows downstream (schematically depicted in Figure 3-2B). This idea is a corollary to hydrologic models which show local flowpaths contributing to flow in first order streams and significant regional groundwater flowpaths contributing to third order streams (Gleeson and Manning, 2008). Our data document changes in the subsurface redox architecture as a function of watershed size. Integrating subsurface mineral distributions into conceptual and hydrologic models will help improve water quality predictions.

3.5 Conclusions

Through a unique combination of machine learning and physically based modeling, we investigated the mechanism of pyrite oxidation through concentration-discharge relationships. We

found three characteristic concentration-discharge trends as depicted in Figure 3-8. In small watersheds without coal, we found that the maximum stream sulfate concentrations are less than predicted by equilibrium with pyrite ($C_{sulf}^{max,obs} < C_{sulf}^{max,pred}$), and the Damköhler number (Da) is greater than 1. In large watersheds without coal $C_{sulf}^{max,obs} = C_{sulf}^{max,pred}$ and Da = 1. This is partly because subsurface flowpaths get deeper and longer as spatial scale increases but especially because the pyrite reaction front tends to shallow downstream in larger watersheds. Nonetheless, across all spatial scales, the transport of dissolved oxygen to the reaction front limits pyrite oxidation in these watersheds (Figure 3-8). On the other hand, coal mining results in $C_{sulf}^{max,obs}$ > $C_{sulf}^{max,pred}$ across all-sized watersheds, which is consistent with kinetic-limited, rather than transport-limited, oxidation of exhumed pyrite (Figure **3-8**). We found that coal containing watersheds have steeper C-q power law slopes (i.e., b-values) than non-coal containing watersheds; therefore, C-q slopes might indicate the relative importance of kinetic- vs. transportlimited oxidation. Through analysis of C-q relationships, we were able to determine information about subsurface flowpaths, the subsurface redox architecture, and oxidant source dynamics, all of which will help to better interpret reaction mechanisms across spatial scales. Understanding the subsurface redox architecture of a watershed will help to improve our predictions of legacy contamination in the future.

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3.6 Figures



Figure **3-1**: Map showing the sampling locations and relationship of the four nested watersheds: Shale Hills (A), Shaver's Creek (B; SCAL, SCCF, and SCO), Juniata River (C; J1 and J2), and Susquehanna River (D; S1-S9). Shapes refer to river basin and intensity of shading indicates relative drainage area of the sub-catchments (light = smaller, dark = larger).



Figure 3-2: (A) Schematic representation of a weathering profile (on left) and expected depth profiles for sulfate and oxygen concentrations (i.e., C_{sulf} and C_{DO} , respectively) in the groundwater (on right) based on consumption of DO via pyrite oxidation across the pyrite reaction front. (B) 3-D cross-sectional view of a schematic watershed showing the subsurface pyrite oxidation zone (yellow) and subsurface flowpaths above (1), partially through (2), and through (3) the reaction front. In both A and B, the pyrite reaction front (yellow) is defined as the zone where oxidation is actively occurring. Above the oxidation zone (i.e., 100% pyrite-depleted; brown), pyrite has been completely oxidized to form secondary iron oxide minerals. Below the oxidation zone, no oxidation is occurring; therefore, this zone is fresh, pyrite-containing bedrock. Except for within a few isolated fracture sets (Gu et al., 2020), oxidation does not occur below the oxidation front (A). This means that groundwater above the reaction front is oxic and below the reaction front is anoxic.



Figure 3-3: Plot showing sulfur isotope values (i.e., $\delta^{34}S$) plotted vs. the reciprocal of sulfate concentration [SO₄²⁻] (µM) for surface and groundwater samples across the Shaver's Creek watershed. Sulfur isotope ranges (i.e., the y-axis) shown for fertilizer (green rectangle) are from a global compilation (Zhang et al., 2015), and the concentration range (i.e., the x-axis) is inferred from measurements of sulfate in groundwater near a farm field in Shaver's Creek (i.e., Cole Farm Well CFW4; see Forgeng (2021) for well location). Sulfur isotope and concentration ranges for pyrite oxidation are also shown (yellow rectangle) as inferred for pyrite oxidation at Shale Hills (Jin et al. 2014). The range of values for acid rain (blue rectangle) are based on measurements of rain chemistry at Hubbard Brook, a watershed ~600 km to the northeast (Alewell et al., 2019). Circle points are surface and groundwater samples from Shale Hills reported in Jin et al. (2014) and square points are surface and groundwater samples collected throughout the SSHCZO in this study


Figure **3-4**: Plot showing the average concentration (A) and mixing proportions (C) determined by NMF for sampling locations as a function of drainage area. (B) shows an example of the temporal series of sulfate concentrations broken down by source for site S4 in the SRB (see Figure **3-2D**).



Figure **3-5**: Concentration-discharge relationship for pyrite-derived sulfate concentrations measured in the outlet stream at Shale Hills (A) measured during 2008-2010. The solid line is the fit of eqn. 2 to the data, and the dashed line is the 95% confidence interval. (B) shows the monthly average DO concentration in groundwaters collected at 20 mbls in a ridgetop borehole near the outlet (CZMW11) at Shale Hills from 2020-2021 plotted vs the water table depth. Arrows in (B) indicate the general trend over time. First, DO is advected to the sensor in the wet season and then DO is depleted in the dry season.



Figure **3-6**: Plot showing the C-q relationships for all 14 sampling locations where symbols (NMF derived concentrations) are plotted on top of one another, and lines refer to model fits to each subwatershed.



Figure 3-7: Map showing the selected sites in the Western United States (A). Boxplots for natural (i.e., contains no coal) watersheds showing how $C_{sulf}^{max,obs}$ (B) and Da (C) change across spatial scale.



Figure **3-8**: Schematic plot showing the three characteristic concentration-discharge patterns observed in watersheds in the northeastern and western US. By studying catchments within the SRB and western US, we observed that pyrite oxidation is always limited by transport of the oxidant to the mineral everywhere except where coal has exhumed at the land surface. For the latter catchments, oxidation is kinetic (or mineral interface-) limited.

3.7 References

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Chapter 4

Silicate Weathering in Shale Watersheds: How do weathering rates respond to changes in temperature, precipitation, runoff, and erosion?

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Abstract

Mineral weathering is a major control on long term atmospheric CO₂. The sensitivity of weathering rates to changes in climate and erosion depends on the regime of weathering. For example, when reaction kinetics, supply of fresh mineral, or water throughput is limiting, weathering fluxes increase with temperature, erosion rate, and runoff, respectively. We call these three weathering regimes kinetic limited (KL), erosive transport limited (ETL), and runoff limited (RL). Watersheds can also exhibit complex weathering dependencies when they become large and integrate several different regimes. We refer to such behavior for larger watersheds as transition regime (TR). Another strong influence on weathering is lithology. However, although silicate weathering and CO₂ drawdown have been extensively studied for granitic and basaltic

watersheds, weathering dependencies in shale watersheds have not been fully characterized despite the observation that shale is one of the most widespread lithology exposed at land surface globally.

Here we identified and analyzed 142 shale watersheds across the United States, spanning a diverse range of climatic (mean annual temperature (MAT): 3-17 °C; mean annual precipitation (MAP): 220-1,975 mm yr⁻¹; potential evapotranspiration (PET): 908-2,059 mm yr⁻¹), topographic (mean catchment elevation: 78-2,346 m; mean catchment slope: 0.4-28°), and hydrologic (annual runoff (q): 0.002-1.3 m yr⁻¹) conditions. For these sites, we calculated silica fluxes (i.e., F_{SiO2}) using SiO_2 concentrations and river discharge measurements. We observed that when the humidity index (HI; MAP/PET) is less than 0.55, F_{SiO2} increases with MAP and q; however, when $HI > 0.55 F_{SiO2}$ does not increase with MAP or q. We posit that sites with HI < 0.55 are RL. The river chemistry for the RL sites is consistent with equilibrium between smectite and kaolinite. We find that the exponential temperature dependence (termed, here, apparent activation energy or Ea) for sites with HI < 0.55 is -89 kJ mol⁻¹. In this case the Ea is consistent with the negative ΔH_r for this equilibrium. Fitting the data for sites with HI > 0.55 to an exponential temperature dependence, we find that the sensitivity of weathering to temperature is 55 kJ mol⁻¹. Rather than defining this as the KL Ea, we also hypothesized that watersheds with steep slopes are more likely to be KL because of fast erosion. For sites with HI > 0.55 and slopes > 10° , we find a temperature dependence of 92 kJ mol⁻¹. This value is consistent with the Ea measured experimentally for the dissolution of chlorite, a clay mineral found in most shales. Using geospatial-based definitions defined in this study to classify watersheds across the United States, we find that 48%, 37%, 9%, and 7% of shale watersheds are RL, ETL, TR, and KL, respectively.

Shales cover a large fraction of land surface globally and have temperature sensitivities similar to granitic watersheds; therefore, they should be considered when evaluating global CO₂ dynamics.

4.1 Introduction

Silicate weathering is a major control on Earth's atmospheric CO_2 concentrations (e.g., Berner, 2004). When silicate minerals weather, they draw CO_2 out of the atmosphere, producing alkalinity, cations, and aqueous SiO₂ (eq. 4-1). Most of the alkalinity is dissolved inorganic carbon, which, over longer timescales encompassing riverine transport, is precipitated as calcium carbonate in the ocean and eventually subducted and returned to the atmosphere via volcanism on ~10⁶-year timescales (e.g., Doney and Schimel, 2007). A canonical model has suggested that Earth's long-term climate is stabilized by this reaction as a result of a negative feedback between CO_2 concentrations, temperature, and silicate weathering rates (e.g., Walker et al., 1981). According to this paradigm, as CO_2 concentrations increase in the atmosphere, global temperature also increases, which results in faster silicate weathering rates and thus faster rates of CO_2 removal. In this way, a negative feedback between silicate weathering and atmospheric CO_2 concentrations stabilize Earth's climate. Previous studies have characterized this feedback through determining mineral weathering dependencies on CO_2 and temperature (e.g., Velbel, 1993; Kump et al., 2000).

$$CaSiO_{3(s)} + 2CO_{2(g)} + H_2O \rightarrow Ca_{(aq)}^{2+} + 2HCO_{3(aq)}^{-} + SiO_{2(aq)} \rightarrow CaCO_{3(s)} + CO_{2(g)} + H_2O + SiO_{2(aq)}$$
(4-1)

Here, we write CaSiO₃ as a generic form for any cation-containing silicate mineral.

Although mineral weathering is sometimes controlled by dissolution kinetics, other factors are thought to play an important role in silicate weathering as well. For example, physical

erosion can affect silicate weathering rates by modulating the supply of fresh reactive minerals (Stallard et al., 1983; Calmels et al., 2007). Additionally, precipitation (and in turn runoff) has been shown to impact weathering rates (e.g., White and Blum, 1995). Thermodynamic limitations have also been explored as a control on global silicate weathering rates (Maher and Chamberlain, 2014, Winnick and Maher, 2018). Because all these factors can influence weathering, complex relationships between temperature, precipitation, erosion, and weathering rates have been observed (Kump et al., 2000; Riebe et al., 2004; West et al., 2005), making predicting trends across landscapes difficult.

Although many factors are important in controlling silicate weathering rates in any given location, we often assume there is one rate limiting step that dominates a given system and assume we can classify weathering regimes for a given mineral reaction and solute release rate in watersheds by the rate-limiting factor. Here we discuss three primary types of weathering regimes: runoff-limited (RL), erosive transport-limited (ETL), and kinetic-limited (KL).

In some watersheds, potential evapotranspiration can be larger than precipitation, which leads to a negative water balance (Budyko, 1974), which, for soils, has been described as "water-limited" (Rasmussen et al., 2011). In high PET watersheds, concentrations (C) of weathering products remain high in porefluids and in the stream despite large ranges in discharge (q) due to the high rates of evapotranspiration. It has been observed that, if concentrations are relatively constant because of high PET, weathering fluxes (C x q) are hypothetically only dependent on runoff (defined here as long-term average discharge and in other studies as mean annual precipitation minus potential evapotranspiration) (Brantley et al., in review). Here, following Brantley et al. (in review), we refer to this weathering regime as "runoff-limited" (i.e., RL). It is important to note that there are other mechanisms that cause constant concentrations of weathering products in streams. In watersheds with ample runoff but long timescales of groundwater flow relative to mineral reaction timescales, concentrations in streams can also be

constant. These situations have been referred to as "saturation-limited" or "equilibrium-limited" (White et al., 2001).. These terms, however, emphasize the addition of solutes from weathering until the water reaches equilibrium rather than the removal of water that concentrates the products of very little weathering (i.e., negative water balance). Moreover, these terms also describe short-term weathering dynamics (i.e., residence times of groundwater), rather than the long-term dynamics (i.e., residence times of soils). In addition, the first two of these terms imply a reason for the constant concentrations, rather than indicating the rate limiting step or factor. We argue that RL is a better name for this high PET regime at least partly because "equilibrium-limited" can imply a result of runoff limitation rather than a rate-limiting step and can point to a fundamentally different weathering regime. RL is the best descriptor for weathering in dry landscapes because it emphasizes the observation that weathering depends on runoff in this regime.

At low erosion rates, where reactive silicate minerals are completely depleted at land surface, weathering rates must eventually be limited by the supply of fresh minerals. This hypothetical endmember is referred to as "supply-limited" or "erosive transport limited" (West et al., 2005; Gabet and Mudd, 2009; Dixon and von Blanckenburg, 2012; Lebedeva et al., 2010). Here we classify this weathering regime as erosive transport limited (i.e., ETL) because weathering in soils of steady-state thickness are ultimately limited by the rate of erosion, which dictates the speed at which minerals pass through the weathering zone. One result of erosion can be that new mineral surface are "supplied" to the weathering zone, but other processes are encompassed in the term ETL. For example, after erosion and thinning of a soil, porewater chemistry can be more corrosive. Regardless of these subtleties, in a system that is ETL, we expect that weathering rates linearly increase with erosion rates and show little to no dependence on temperature or runoff. Using an advection-diffusion-reaction model, Lebedeva et al. (2010) shows that as erosion rates increase for a simple albite-quartz system, weathering rates and production of kaolinite increase until eventually, erosion rates become too large, and the weathering rate becomes constant. Under those conditions, the albite is not totally dissolved away from the soil, and it remains even at the land surface. For this theoretically explored regime where erosion rates are high and reactive silicate minerals are present at land surface, weathering rates are limited by interfacial reaction kinetics rather than erosion, which we refer to as kinetic limited (KL). In these watersheds, weathering rates are expected to increase exponentially with temperature according to the Arrhenius equation.

Although these are the three theoretical endmember weathering regimes we consider in this paper, observations and models also show that soils can integrate multiple weathering regimes into what has been referred to as the transition or mixed regime for soils (Ferrier et al., 2016) or hillslopes (Lebedeva et al., 2013). West et al. (2005) suggests variability in weathering rates observed in very large rivers (Gaillardet et al., 1999) could potentially be explained by integrating both KL and ETL landscapes. Most recently, Brantley et al. (in review) describes these types of watersheds as "Transition Regime" (TR), which can depend in complex ways on erosion, temperature, and precipitation.

Although variations in climate and erosion create regimes of weathering defined by ratelimiting steps, lithology is also a primary control on weathering rates that affects these regimes (e.g., Bluth and Kump, 1994). Many studies have investigated how climate and erosion impact silicate weathering in granitic (e.g., Velbel, 1993; White and Blum, 1995; White et al., 1999; Dalai et al., 2002; Oliva et al., 2003; West et al., 2005; Clow and Mast, 2010; Yadav and Chakrapani, 2011) and basaltic (e.g., Dessert et al., 2001; Dessert et al., 2003; Navarre-Sitchler and Brantley, 2007; Eiriksdottir et al., 2013; Li et al., 2016) watersheds. Although there are studies in mixed sedimentary watersheds (e.g., Gaillardet et al., 1999; Dalai et al., 2002; WolffBoenisch et al., 2009; Yadav and Chakrapani, 2011; Dixon and von Blanckenburg, 2012), few studies investigate these dependencies for shales and have largely been constrained to soils rather than watersheds (e.g., Dere et al., 2013; Gu et al., 2020). Shales cover a significant fraction of global land area (estimated at 34.4 % (Meybeck, 1987), 12.6 % (Gibbs and Kump, 1994), 25.4% (Amiotte Suchet et al., 2003), 6.6% (Hartmann and Moosdorf, 2012)) and constitute 51% of total mass of sediments worldwide (Lerman et al., 2007). Moreover, shales have been found to contribute significantly to global silicate weathering rates (Amiotte Suchet et al., 2003).

To more accurately predict global CO₂ consumption from weathering, we need a better understanding of silicate weathering in shale watersheds. Here, we present silica flux data from 142 shale watersheds from the United States that cover significant variability in climate and erosion. Although silica fluxes have previously been reported for a dataset targeting many US watersheds (e.g., Jansen et al., 2010), this chapter presents the first study to specifically isolate shale watersheds. Shale is of particular interest not only because of its importance as a common lithology, but also because it is one of the fastest eroding common lithologies. We aim to explore whether watersheds show characteristics that allow identification of their respective weathering regimes (i.e., RL, ETL, KL, TR), and determine how the weathering fluxes change with runoff, precipitation, temperature, and erosion for each regime through regression analysis.

4.2 Methods

4.2.1 Watershed Selection and Data Acquisition

For this study, we are interested in weathering fluxes in shale watersheds, and we focus our analysis on the United States because it has the highest number of waters chemistry sampling sites. First, we utilize the State Geologic Map Compilation (SGMC) geodatabase of the conterminous United States (Horton et al., 2017) to define shale lithology. The SGMC is a geographic database compiled by the United States Geological Survey (USGS) that maps outcropping lithology across the United States and classifies different lithologic units by their major and minor rock types. For the purposes of our study, we define shale as any formation/unit where the major rock type (i.e., MAJOR1 in the attributes table of the SGMC) is Shale, Mudstone, Siltstone, or Siltstone-mudstone. The geospatial coverage of shales, as defined by the criteria above, can be seen in Figure **4-1**.

After defining shale lithology, we identify watersheds with \geq 75% coverage by shale lithology (i.e., shales at land surface). We start by aggregating watershed shapefiles from the GAGESII (Falcone, 2011) and USGS Streamgage NHDPlus Version 1 Basins (USGS, 2011) datasets, which contain 20,163 unique watershed boundaries. We then calculate the percent areal coverage of shale in each of these watersheds using the tabulate intersection function from the Analysis Toolbox in ArcGIS Pro. Next, we remove any watersheds with <75% shale, leaving 1,033 remaining watersheds. For each of these watersheds, we query water quality data from the Water Quality Portal (WQP), a national repository managed by the USGS and United States Environmental Protection Agency (USEPA) (Read et al., 2017). Specifically, we downloaded silica (SiO_2) concentrations because SiO₂ is released during silicate weathering (eq. 4-1) and does not have many other sources (e.g., anthropogenic contamination) and typically is only present at low concentrations in precipitation. To download data, we utilized the dataRetrieval package in R (Hirsch and De Cicco, 2015). We found that 588 watersheds have measurements of SiO_2 . After, we filter out sites with an insufficient number of measurements. Specifically, we require that each site has at least four concentration measurements per year and at least three years of measurements. All measurements must also be located at the outlet of the watershed (i.e., mainstem sampling site and not tributaries). Based on this criterion, the number of watersheds is reduced to 187. Lastly, we query discharge measurements for the remaining sites from the

National Water Information System (NWIS). After matching concentrations measurements with discharge measurements, we again require that there are at least four concentration-discharge paired measurements per year for at least three years of measurements, which results in the final number of sites (watersheds) – 142 (Figure **4-1**). After identifying these 142 watersheds, we also downloaded Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and pH data following the same procedure for SiO₂ in order to make activity-activity diagrams (see Section 4.3.3).

4.2.2 Climate Data

To investigate the impacts of climate on weathering, we compiled the humidity index (HI), mean annual temperature (MAT), mean annual precipitation (MAP), potential evapotranspiration (PET), and runoff (q) for each of the 142 watersheds. Humidity index (sometimes called aridity index) is defined as the ratio of MAP to potential evapotranspiration (PET). When MAP > PET, then HI > 1 and there is a positive water balance in a watershed. When MAP < PET, then HI < 1 and we expect dry conditions.

Different methods of calculating PET yield different values for HI; therefore, we do not expect to see a transition from negative to positive water balance strictly at HI = 1. Furthermore, seasonality of dry and wet conditions can influence stream water quality and quantity, and the size of the watershed influences the water budget that controls stream discharge (because of groundwater). Instead, we utilize a consistent method of determining HI for each watershed and then look at the data to determine where runoff-limited conditions may exist. To compile HI and PET, we utilize the Global Aridity Index and Potential Evapo-Transpiration (ET0) Climate Database v2 (Trabucco and Zomer, 2018). For each watershed, we calculate the spatially averaged HI and PET values utilizing the Zonal Statistics function in the Image Analyst toolbox in ArcGIS Pro.

To compile MAT and MAP, we utilized the Climatologies at High resolution for the Earth Land Surface Areas (CHELSA) V2.1 dataset (Karger et al., 2017). CHELSA contains highresolution information on climatic conditions around the globe. MAT and MAP were calculated by averaging the annual temperature and precipitation datasets within CHELSA across the drainage area of each watershed using the same method described for HI and PET.

Lastly, we determined q, i.e., the runoff of a watershed. Runoff is related to MAP; however, some MAP is lost to interception by trees, evapotranspiration, or groundwater storage. Runoff accounts for these different processes. In some studies, q is calculated as MAP – PET. As noted earlier, in some watersheds, PET > MAP, which would yield negative or zero runoff. In reality, however, rivers still flow seasonally in dry watersheds during precipitation events or during snowmelt. We instead calculate q using measured discharge values. We first downloaded the average discharge in the stream for each year of recorded flow (m³ yr⁻¹) using the readNWISstat function from the dataRetrieval package. Then, we averaged the yearly data and divided by the drainage area (m²) to calculate q (m yr⁻¹). We take the average of the yearly averages to better account for interannual variability in q.

4.2.2 Sediment Yields

Erosion is an important process for weathering in watersheds in that it exhumes fresh minerals to interact with meteoric solutions (e.g., Millot et al., 2002; Stallard et al., 1983; Calmels et al., 2007) and thins soils to allow minerals to interact with more corrosive porewaters (Fletcher et al., 2006); thus, silicate weathering rates can depend upon erosion rate (Riebe et al., 2004; West et al., 2005; Millot et al 2002; Lebedeva et al. 2010). Here, we utilize sediment yield as a proxy for erosion rate. Sediment yield is flux of sediments leaving a watershed via the river and is typically calculated using measurements of suspended sediments and discharge. Suspended sediment measurements, however, are not regularly measured in many watersheds; therefore, we aim to model the sediment yield in watersheds using an empirical equation, i.e., the BQART model (Syvitski and Milliman, 2007).

$$S_{y} = wBQ^{0.31}A^{-0.5}rT (MAT \ge 2^{\circ}C)$$
(4-2)

$$S_y = 2wBQ^{0.31}A^{-0.5}r \ (MAT < 2^{\circ}C)$$
(4-3)

Here, S_y is the sediment yield (t km⁻² yr⁻¹) for a watershed, *w* is a coefficient (600 t yr⁻¹), *Q* is the annual discharge (km³ yr⁻¹), *A* is the drainage area (km²), *r* is the maximum relief of the watershed (km; i.e., maximum elevation minus minimum elevation), and *T* is the MAT (°C). *B* is an empirical term that accounts for geological and human impacts.

$$B = (1 + 9A_g)(1 - T_E)L_r E_h$$
(4-4)

Here, A_g is the areal fraction of ice and snow in a watershed, L_r is the rock erodibility index, T_e is the trapping efficiency, and E_h is the human-influenced soil erosion factor. None of our sampling locations are currently glaciated; therefore, A_g is 0. Following Deng et al. (2022), we set T_e to 0 and E_h to 1. E_h is set to 1 because the timescales of weathering are longer than the timescales of human impacts. It is true that T_e could be larger than 0, especially if a watershed contains dams; however, for simplicity we will ignore this term because of the large uncertainty surrounding it. Based on our assumptions, eq. 3 can be simplified to $B = L_r$. Although we use many assumptions here, it has been shown that when the entire *B* term is simply set to 1 (i.e., ignoring the effects of lithology and humans), the BQART model still accounts for 68% of between-river variations in sediment yields (Syvitski and Milliman, 2007). This model has been shown to give very good predictions of sediment yield when compared to measured sediment fluxes ($R^2 = 0.94$; Syvitski and Milliman, 2007).

To calculate S_y using eqs. 4-2 through 4-4, we integrate data from several different sources. The data sources and acquisition methods for *T* and *Q* were discussed in section 4.2.2. To calculate *B*, we use a global dataset of erodibility indices, L_r (Moosdorf et al., 2018), and calculated the spatial average L_r for each watershed following the same method described with MAP and MAT. Drainage area was downloaded from the USGS site metadata, which was accessed using the whatWQPsite function from the dataRetrieval package. To calculate the maximum relief of each watershed, *r*, we utilized a digital elevation model (DEM) for the conterminous United States (USGS, 2022). Because of the large size of the DEM, we utilized the terrain toolbox in Google Earth Engine (Gorelick et al., 2017) to extract the maximum and minimum elevations for each of the watersheds, which were used to calculate *r* (i.e., *r* = max elevation – min elevation). In addition to the minimum and maximum elevations, we

4.2.4 Weathering Calculations

To investigate how silicate weathering rates change as a function of climate, tectonic, and topographic conditions, we first calculate the release rate of silica in each watershed as defined by concentration and discharge. We define the release rate as the flux of dissolved silica (mass per time per unit area) as recorded in the stream at the outlet of the watershed. Streams integrate weathering across their entire drainage area (A (km²)); therefore, this flux represents the catchment-average release rate. The equation to calculate flux is as follows (modified from Moatar et al., 2013):

$$F_{SiO_2} = b \frac{\sum_i Q_i C_i}{\sum_i Q_i} \bar{Q} A^{-1}$$
(4-5)

113

Here, F_{SiO_2} is the flux of SiO₂ (t km⁻² yr⁻¹), *b* is a coefficient for unit conversion (10⁻⁶ t 1 m⁻³ mg⁻¹), Q_i and C_i are the instantaneous discharge (m³ s⁻¹) and SiO₂ concentration (mg l⁻¹) at timepoint *i*, and \bar{Q} is the annual average discharge (m² yr⁻¹). The term $\frac{\sum_i Q_i C_i}{\sum_i Q_i}$ is the flow weighted average SiO₂ concentration for a given river.

To compare F_{SiO_2} across watersheds and to incorporate dependence upon MAT (*T*), MAP (*P*), and erosion rate (*E*; sediment yield (t km⁻² yr⁻¹)), we fit F_{SiO_2} to a modified Arrhenius equation that has been previously used to model weathering of soils and watersheds (Riebe et al., 2004; West et al., 2005).

$$F_{SiO_2} = K \left(\frac{E}{E_0}\right)^{\alpha} \left(\frac{P}{P_0}\right)^{\beta} e^{\left(-\frac{Ea}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right)}$$
(4-6)

$$\ln\left(F_{SiO_2}\right) = \ln(K) + \alpha \ln\left(\frac{E}{E_0}\right) + \beta \ln\left(\frac{P}{P_0}\right) - \frac{Ea}{R} \left[\frac{1}{T} - \frac{1}{T_0}\right]$$
(4-7)

Here, α and β are fitting parameters that describe the non-linear dependance of F_{SiO_2} on *E* and *P*, respectively. *Ea* is the apparent activation energy (kJ mol⁻¹), which describes the sensitivity of weathering to changes in *T* (K), and R is the ideal gas constant (8.314 j mol⁻¹ K⁻¹). E₀, P₀, and T₀ are reference values for *E*, *P*, and *T*, respectively, that are set to the log-mean values for each of those parameters in the dataset (i.e., 60.3 t km⁻² yr⁻¹, 831 mm yr⁻¹, and 281 K). K is the flux of SiO₂ when *E*, *P*, and *T* are equal to their respective reference values. Eq. 4-7 is the linearized form of eq. 4-6. To determine *K*, α , β , and *Ea*, we fit F_{SiO_2} with a multiple regression using values of *E*, *P*, and *T* for each watershed (eq. 4-7). In some cases, fitting the full model can result in insignificant parameters. For a more robust analysis, we fit the regression using every combination of fitting parameters (i.e., α , β , and *Ea*). For example, in one model we include an erosion and precipitation dependence (i.e., α and β), but omit the temperature dependence. In another model, we only utilize the temperature dependence. In all, there are 7 parameter combinations. We also include an 8th model, which is a linear precipitation correction (i.e., $\beta = 1$) and no erosion correction (i.e., $\alpha = 0$). We include this model because this correction is common in weathering studies (e.g., White and Blum, 1995; Dere et al., 2013). For this analysis, we define a valid model as any model where all fitting parameters are significant (p < 0.05) and the correlation between the modeled F_{SiO_2} and the measured F_{SiO_2} is also significant (p < 0.05). The goodness of fit is determined by the R² value and the adjusted R² value. Note that the difference between the R² and adjusted R² values was <0.02; therefore, we only report the R² herein. We note that the input variables to the model (i.e., MAP, MAT, S_y) are largely uncorrelated in the dataset.

4.3 Results and Discussion

4.3.1 Site Information

The 142 shale watersheds span a wide range of geographic locations and are climatically, topographically, and hydrologically diverse. Geographically, the sampling locations range from latitude 33.3 to 48.9 and longitude -109 to -71.6 (Figure **4-1**), and the average drainage area is 3,400 km² (min = 2 km², max = 41,000 km²). Climatically, MAT, MAP, PET, and HI range from 3 to 17 °C, 220 to 1,975 mm yr⁻¹, 908 to 2,059 mm yr⁻¹, and 0.14 to 1.58, respectively. Topographically, mean catchment elevation, mean catchment slope, and S_y range from 78 to 2,346 m, 0.4 to 28°, and 8 to 405 t km⁻² yr⁻¹, respectively. Runoff (q) varies from 0.002 to 1.3 m

yr⁻¹. Based on the Holdridge classification system, our sites fall within the arid, semiarid, subhumid, and humid categories (Holdridge, 1947; Figure **4-2**).

4.3.2 Humidity Indices for Shale-underlain Watersheds

We follow the suggestion in the literature (Rasmussen et al., 2011) and hypothesize that the RL regime can be delineated from the relative magnitudes of MAP and PET (i.e., HI). When PET far exceeds MAP, only a small amount of water flows through the weathering minerals and the systems could become runoff-limited. In order to increase F_{SiO_2} , then, runoff needs to increase (i.e., MAP increases relative to PET). At some HI value, however, the flow through the system will be fast and weathering fluxes will no longer vary with runoff and in that case will, according to the paradigm presented here, become ETL or KL. Here we aim to determine the threshold HI value that defines the transition from RL to ETL or KL. When HI is less than the threshold, a watershed is RL, and when HI is greater than the threshold, a watershed is KL, ETL, or TR. We use four methods to determine the threshold: 1) the local valley method, 2) the Otsu method, 3) break point analysis, and 4) Holdridge classification system (Holdridge, 1947).

Across the United States, we observe that there are two distinct climates: one with high HI values and one with low HI values (HI varies from ~0.1 to 3; Figure 4-3A). When we plot the distribution of HI values from outcropping shale lithologies across the United States, we observe a bimodal distribution that is roughly the combination of two log-normal distributions (Figure 4-3A). Our first hypothesis is that one of the peaks in the bimodal distribution could represent dry climates (i.e., RL) and the other could represent wet climates (i.e., KL or ETL). The transition from dry to wet is therefore the minimum (i.e., valley) between the two bimodal peaks. This is called the local valley method of determining a threshold. To determine this minimum, we first estimate the distribution by fitting a kernel density to the histogram (density function from the

stats package in R; Figure 4-3A). Then, we determine the location of the valley between the two peaks based on the kernel density. We found that the threshold using this method is HI = 0.59.

Next, we use the same distribution data, but define the threshold using another method (i.e., method 2) called the Otsu method (Otsu, 1979). This method defines a threshold as a value that maximizes the between-group variance, $\sigma_{between}^2$.

$$\sigma_{between}^2 = n_A n_B (\mu_A - \mu_B)^2 \tag{4-8}$$

Here, n_A and n_B are the number of pixels in the HI raster above and below the threshold, respectively, and μ_A and μ_B are the mean HI values above and below the threshold, respectively. Using this method, we found that the maximum $\sigma_{between}^2$ occurs when the HI threshold is equal to 0.50 (Figure **4-3B**).

Recognizing that these first two estimates might reflect climate distributions but not necessarily weathering distributions, we also tried a third method to determine a threshold HI value based on measurements of F_{SiO_2} versus the HI for each watershed. We observe that F_{SiO_2} first increases with HI and then approximates a constant at higher HI values (Figure **4-3C**). There are three sites that are outliers to this trend and show low HI values but large F_{SiO_2} . These three sites are co-located in western Colorado and feature low MAP but high q. With this method, we argue that the break in slope observed in Figure **4-3C** defines the HI threshold. To statistically determine the break in slope, we utilized break point analysis with the mcp package in R (Lindeløv, 2020). The mcp package utilizes a Bayesian regression to identify the location for changes (i.e., break points) in trends. For our system, we define the model as two linear segments that are joined by a break point. Utilizing this method to determine the optimal break point, we found that the HI threshold (i.e., the break point) is 0.62 (Figure **4-3C**).

Lastly, we utilized the Holdridge climate classification system (Figure **4-2**) to define the threshold HI value (Holdridge, 1947). To do this, we simply noted that the threshold determined

from the first three methods roughly co-aligns with the transition from semiarid to subhumid climates. This climate transition occurs when the potential evapotranspiration ratio is 2, which is the same as HI = 0.50. Although this definition is more qualitative than quantitative, it is consistent with values from the other 3 methods and gives a conceptual definition rather than solely a statistical definition. Furthermore, the Holdridge classification is based not only climate variables but also on ecological observations.

For a best estimate, we take the average value from the four methods described above, i.e., HI = 0.55, and we now test if the weathering flux varies with runoff as expected for this hypothetical RL regime. We hypothesize that when HI < 0.55 watersheds are RL and when HI > 0.55, watersheds are KL, ETL, or TR. We do not define an HI value to separate KL from ETL because HI alone cannot describe the balance between chemical weathering and physical weathering needed to define these two categories. Based on this final definition, 82 watersheds are RL, and 60 watersheds are KL, ETL, or TR. For the rest of this analysis, we will separate these two groups as HI < 0.55 and HI > 0.55.

4.3.3 SiO₂ Concentrations

Flow weighted SiO₂ concentrations (herein denoted as [SiO₂]) for each watershed vary from 1.6 to 54.3 mg/l (Figure **4-4**). The average SiO₂ concentration across watersheds when HI < 0.55 is 16.9 ± 11.9 mg/l (min = 3.1 mg/l, max = 54.3 mg/l) and 6.1 ± 2.7 mg/l (min = 1.6 mg/l, max = 14.4 mg/l) when HI > 0.55. Overall, sites with HI < 0.55 have significantly higher concentrations than sites with HI > 0.55 (two-sided t-test; *p* << 0.01).

Variations in temperature can partly explain the variability in [SiO₂]. For example, if groundwater is in equilibrium with the surrounding minerals, then we expect [SiO₂] to vary with MAT because the equilibrium constant (K_{eq}) is dependent on temperature. We explore the possibility of weathering controls by temperature-dependent K_{eq} further in Section 4.3.5. Additionally, reaction rate increases with increasing temperature; therefore, if groundwater is not at equilibrium with surrounding minerals, increasing MAT might increase [SiO₂] by accelerating reaction kinetics and bringing the water closer to equilibrium. We observe that, when HI < 0.55, even though concentrations are relatively constant with discharge, there is no correlation between [SiO₂] and MAT (Figure **4-4A**). When HI > 0.55, [SiO₂] increases as MAT increases, until MAT = 10 °C. For MAT > 10 °C, [SiO₂] becomes constant at ~ 7 mg/l (Figure **4-4A**). For HI > 0.55, the trend in [SiO₂] vs. MAT is therefore consistent with the system approaching equilibrium from 5 °C to 10 °C, and then reaching equilibrium at 10 °C. Another explanation for such behavior might be that concentrations approach or reach a steady state (a balance between dissolution and precipitation) that is not a true equilibrium.

We can test whether the observed temperature dependence can be considered thermodynamic in nature by using activity-activity diagrams for appropriate mineral assemblages. We cannot explore the composition of all the shales for the watersheds, so we rely on the average compositions of shales: 60% clay minerals (predominantly chlorite, smectite, illite, kaolinite), 30% quartz, 4% feldspar, 4% carbonate, and 2% other (Rimstidt et al., 2017). Figure **4-5** shows activity-activity diagrams for the chlorite-smectite-kaolinite-gibbsite system (Figure **4-5**). These stability fields are calculated using the thermo.tdat database (i.e., Lawrence Livermore National Laboratory thermo database) and Geochemists Workbench (GWB) 2022 Community Edition. For these plots and for simplicity, we chose the mineral clinochlore for chlorite and Mg-saponite for smectite. Although we downloaded all major cation data for these sites (see Section 4.2.1), we focus here on the Mg²⁺, SiO₂, and pH measurements because i) not all shales include both smectite and illite; ii) almost all shales include chlorite, iii) chlorite is much more reactive than illite and kaolinite. We therefore hypothesize that chlorite weathering is the SiO₂-producing reaction in the shale watersheds (see also Gu et al. (2020) and Liao et al. (2022) chlorite weathering dynamics in shales).

When HI < 0.55, we observe that the average river chemistry falls along the smectitekaolinite boundary as expected if smectite is transforming to kaolinite with weathering progress (Figure **4-5B**). In some of these very dry watersheds, the SiO₂ concentrations approach amorphous silica saturation. When we look at all of the measurements of SiO₂, Mg²⁺, and pH for sites with HI < 0.55, we observe that many individual samples reach amorphous silica saturation, but do not exceed it (Figure **4-5C**), consistent with precipitation of amorphous silica in some of the dry soils. When we analyze the specific sites that appear to be controlled by amorphous silica, we observe that all watersheds are located throughout the state of Iowa and are all underlain by the Ogallala Formation. In contrast to the low-HI sites, when HI > 0.55, we observe that the average river chemistry falls along the kaolinite-gibbsite and smectite-kaolinite boundaries, or within the kaolinite stability zone (Figure **4-5B**). None of the flow-weighted average compositions or individual samples for sites with HI > 0.55 reach saturation with respect to amorphous silica (Figure **4-5B,D**). Since increases in MAP largely result in increases in q, it is not surprising that we observe similar trends in [SiO₂] with respect to MAP as shown previously for q (Figure 4-4B,C). Changes in the concentration of weathering products (e.g., SiO₂) in streams are largely a balance between the net rate of release to concentrated porefluid solutions and the rate of dilution by less-concentrated waters. Maher and Chamberlain (2014) proposed a solute production model based on an earlier reaction-dilution model for watersheds (Berner, 1978; Kump et al., 2000) that related changes in concentrations to q (i.e., C-q).

$$C = \frac{C_0}{1 + \frac{Dw}{q}} + C_{max} \frac{\frac{Dw}{q}}{1 + \frac{Dw}{q}}$$
(4-9)

$$C = \frac{C_{max}Dw}{Dw+q} \tag{4-10}$$

Here, *C* is the concentration of a solute in the stream (i.e., [SiO₂]; mg/l), *C*₀ is the initial concentration of the solute for the water entering the system (i.e., rainwater; mg/l), *C*_{max} us the empirical maximum concentration of the solute (which may be an equilibrium concentration in some cases or a steady state in others; mg/l), and *Dw* is the Damköhler coefficient (m yr⁻¹). *Dw* is a function of the Damköhler number (*Da*; *Da* = *Dw*/*q*), which is the characteristic timescale of the reaction divided by the characteristic timescale of advection. As stated in Ibarra et al. (2016), for most catchments, *C*₀ can be assumed to be zero; therefore eq. 4-9 simplifies to eq. 4-10. Based on this model, when *q* is very small, *C* is constant and approaches *C*_{max} because the rate of solute production is much faster than the rate of advection. Following Godsey et al. (2009), we call this C-q modality "chemostatic". When *q* is very large, *C* decreases as q increases because the rate of advection is much larger than the rate of solute production. We call this C-q modality "dilution behavior". For our system, we assume *C*₀ = 0 because rainwater is very dilute with respect to SiO₂, and we fit eq. 4-10 to our data shown in Figure **4-4C** using a nonlinear regression in R. Based on our mineral activity diagrams (Figure **4-5**), we omit the sites that are controlled by amorphous silica saturation because their *C*_{max} is fundamentally different than the other sites.

We found that the solute production model successfully describes the trends we observe between [SiO₂] and q, where $C_{max} = 13.0 \pm 0.5$ mg/l and $Dw = 0.47 \pm 0.08$ m yr⁻¹ (p < 0.01). Based on Figure 4-5, the C_{max} value for SiO₂ is attributed to the SiO₂ concentrations for the equilibrium between Mg-smectite and kaolinite. Sites with HI < 0.55 are predominantly located within the chemostatic part of the *C*-*q* curve, whereas sites with HI > 0.55 are predominantly located within the part of the *C*-*q* curve characterizing dilution behavior (Figure 4-4C). A similar trend between average concentration and discharge across wet and dry watersheds has been observed elsewhere (Godsey et al., 2019).

4.3.4 SiO₂ Fluxes

SiO₂ Fluxes (F_{SiO_2}) vary across the different watersheds from 0.007 to 11.0 t km⁻² yr⁻¹ (Figure 4-6). The average F_{SiO_2} across watersheds when HI < 0.55 is 1.1 ± 1.8 t km⁻² yr⁻¹ (min = 0.007 t km⁻² yr⁻¹, max = 11.0 t km⁻² yr⁻¹). This, however, includes the three outlier sites discussed earlier. When these sites are removed, F_{SiO_2} (for HI < 0.55) = 0.9 ± 1.1 t km⁻² yr⁻¹. When HI > 0.55, F_{SiO_2} = 2.7 ± 1.1 t km⁻² yr⁻¹ (min = 1.2 t km⁻² yr⁻¹, max = 5.6 t km⁻² yr⁻¹). Overall, sites with HI < 0.55 have significantly lower fluxes than sites with HI > 0.55 (two-sided t-test; $p \ll 0.01$).

Similar to the concentration data, we observe that SiO₂ fluxes (F_{SiO_2}) increase with MAT when HI > 0.55, but do not show a temperature dependence when HI < 0.55 (Figure 4-6A). If weathering at high HI was ETL, we would expect an increase in F_{SiO_2} with an increase in erosion or sediment yield. We do not observe a noticeable correlation between F_{SiO_2} and sediment yield for sites with HI > 0.55 (Figure 4-6D).

Therefore, our original interpretation that sites with HI > 0.55 are likely ETL, KL, or TR, in combination with the observed temperature dependence and lack of strong erosion rate

dependence for these high-HI sites, leads to the inference that these high-HI sites are KL or TR. When sites are KL or TR, we would expect F_{SiO_2} to increase with temperature where the strength of the dependence is a function of what proportion of the watershed is KL. There could be a weak erosion dependence (i.e., $\alpha < 1$; eq. 4-6) for TR, which we explore in Section 4.3.6.

For sites with HI < 0.55, we observe an increase in F_{SiO_2} with increases in both MAP and q (Figure 4-6B,C). This is consistent with our interpretation that these sites are RL. We do not observe systematic variation in F_{SiO_2} with MAP or q for sites with HI > 0.55 (Figure 4-6B,C). When we fit eq. 4-7 to all sites (regardless of HI), we find that the parameters for the best fitting model are $\alpha = 0$, $\beta = 2.0 \pm 0.2$, and $Ea = 56 \pm 18$ (R² = 0.62; p < 0.01; Table 4-1; Table C-1). The β value for this regression shows that when wet and dry sites are not separated, F_{SiO_2} increases exponentially with MAP.

4.3.5 Climate Controls on Weathering: Dry Watersheds

As stated previously, for sites with HI < 0.55, we observe an increase in F_{SiO_2} with increases in both MAP and q (Figure 4-6B,C). When we fit eq. 4-7 to the sites with HI < 0.55, we find that the parameters for the best fitting model are $\alpha = 1.1 \pm 0.2$, $\beta = 4.9 \pm 0.5$, and $Ea = -83 \pm$ 31 (R² = 0.66; p < 0.01; Table 4-1; Table C-2). Fitting an exponential equation to F_{SiO_2} vs. q for these sites, we find that $F_{SiO_2} = (29.6 \pm 8.5)q^{1.2\pm0.1}$ (R² = 0.76, p < 0.01). For RL weathering, F_{SiO_2} increases linearly with q (and exponentially with MAP), and this is not surprising given the definition of RL. The Ea for these sites, however, is surprising given that the negative sign indicates that F_{SiO_2} decreases as MAT increases. Here, we explore this negative temperature dependence further. For RL weathering of shale, we observe the possibility that concentrations are

chemostatic because they are controlled by smectite-kaolinite equilibration. In that case, $F_{SiO_2} = qC_{eq}$, where C_{eq} is the equilibrium concentration, or at least the steady state concentration, of SiO₂ in solution for that mineral assemblage. As discussed in section 4.3.3, the river chemistry for sites with HI < 0.55 primarily plot on the line consistent with equilibrium between smectite and kaolinite (Figure **4-5B,C**). For this equilibrium, we used Mg-Saponite

 $(Mg_{3.165}Al_{0.33}Si_{3.67}O_{10}(OH)_2)$ as the smectite mineral and the reaction was written based on the assumption that all Al is retained in kaolinite as smectite transforms.

For the reaction as written, the equilibrium constant, K_{eq} , equals:

$$K_{eq} = \frac{\left[Mg^{2+}\right]^{3.165} [SiO_2]^{3.34}}{[H^+]^{6.33}}$$
(4-12)

Using the Van't Hoff equation, K_{eq} depends on temperature and can be written as:

$$K_{eq} = K_{eq}^{0} e^{\left(-\frac{\Delta H_r}{R} \left[\frac{1}{T} - \frac{1}{T_0}\right]\right)}$$
(4-13)

Here, K_{eq}^0 is the equilibrium constant at reference temperature T_0 and ΔH_r is the enthalpy of the reaction at T₀ (kJ mol⁻¹). If smectite \rightarrow kaolinite as in eq. 11, then ΔH_r = -194 kJ mol⁻¹, which means that as temperature increases, K_{eq} decreases and the reaction results in higher smectite:kaolinite ratios at equilibrium. Thus, as temperature increases in a closed system, we expect decreases in SiO₂ and Mg²⁺ concentrations and pH. Within the resolution of the field data, we observe evidence for SiO₂ and pH decreasing with MAT for sites with HI < 0.55 (Figure 4-**7A,C**), which is consistent with this equilibrium. Plotting the activity product (Q; eq. 4-12) vs. MAT, we find that the data fall along the smectite-kaolinite equilibrium when HI < 0.55 (eq. 4-13; Figure 4-8A). Scatter in the data around K_{eq} (Figure 4-8A), could reflect the general difficulty of measuring accurate thermodynamic data for clays, given their chemical and structural heterogeneity and lack of crystallinity. For example, differences in chemical composition of the smectite such as Fe substitution (Goddéris et al., 2010) can affect the K_{eq} significantly. To control for chemical composition across the 80 watersheds is not possible because clay compositions are highly variable and dependent on parent material. On the other hand, it has been shown that clay mineralogy (e.g., development of smectite and kaolinite) is driven more by climate than by parent lithology (Folkoff and Meenemeyer, 1985), especially when considered over larger spatial scales; therefore, we consider this unaccounted-for variable as likely leading to random error in our calculations.

Our observation of a negative Ea (Table 4-1) is consistent with the negative sign of ΔH_r for smectite-kaolinite equilibrium. Our Ea, however, has a smaller magnitude (i.e., less negative and less sensitive to changes in MAT) than ΔH_r for this reaction. An additional explanation for the scatter in Figure 4-8A and the lower apparent temperature sensitivity in our field data is variability in soil pCO₂. For example, Winnick and Maher (2018) emphasize that concentration of solutes derived from for mineral weathering reactions depend on CO₂ concentrations and the open versus closed nature of a weathering system. Following their treatment (for an opensystem), eq. 4-11 can be re-written with respect to CO₂ (assuming the same composition of clay as above).

Smectite + 2.495 H_2O + 6.33 $CO_2(g)$ = 0.165 Kaolinite + 3.165 Mg^{2+} + 3.34 SiO_2 + 6.33 HCO_3^- (4-14)

The equilibrium constant (K_{eq}) can then be written as:

$$K_{eq} = \frac{\left[Mg^{2+}\right]^{3.165} [SiO_2]^{3.34} [HCO_3^-]^{6.33}}{(pCO_2)^{6.33}}$$
(4-15)

If we assume that concentration is equivalent to activity (i.e., activity coefficient = 1) and that reaction 4-14 is the only reaction changing the solute chemistry, then we eq. 4-15 shows that $[Mg^{2+}]$ and $[HCO_3^{-}]$ vary with $[SiO_2]$ according to stoichiometric ratios defined by mineral composition (Winnick and Maher, 2018). For example,

$$[Mg^{2+}] = \frac{3.165}{3.34} [SiO_2]$$
$$[HCO_3^-] = \frac{6.33}{3.34} [SiO_2]$$

(4-16a,b)

Eliminating $[Mg^{2+}]$ and $[HCO_3^{-}]$ from eq. 4-15 results in a prediction for $[SiO_2]$ as a function of pCO2 for the case where smectite-kaolinite equilibration is the only reaction at a given pCO2:

$$K_{eq} = \frac{\left(\frac{3.165}{3.34}[\text{SiO}_2]\right)^{3.165}[\text{SiO}_2]^{3.34} \left(\frac{6.33}{3.34}[\text{SiO}_2]\right)^{6.33}}{(pCO_2)^{6.33}}$$
(4-17)

Simplifying and solving for [SiO₂] leads to:

$$[SiO_2]_{eq} = \left(\frac{\kappa_{eq}}{48.26}\right)^{\frac{1}{12.835}} (pCO_2)^{\frac{6.33}{12.835}}$$
(4-18)

Incorporating eq. 4-13 into eq. 4-18 results in

$$[SiO_2]_{eq} = \left(\frac{K_{eq}^0}{48.26} e^{\left(-\frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right)}\right)^{\frac{1}{12.835}} (pCO_2)^{\frac{6.33}{12.835}}$$
(4-19)

 F_{SiO_2} in RL watersheds can then be written as:

$$F_{SiO_2} = q[SiO_2]_{eq} = q\left(\frac{K_{eq}^0}{48.26} e^{\left(-\frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right)}\right)^{\frac{1}{12.835}} (pCO_2)^{\frac{6.33}{12.835}}$$
(4-20)

Eq. 4-20 shows that F_{SiO_2} is dependent on q, MAT, and pCO₂. We do not have

measurements of pCO2 to include in our model; however, we can test for systematic differences

125

in pCO₂ across our sites using GWB. For example, Δ Hr for the reaction shown in eq. 14 is -248 kJ mol⁻¹. We can also calculate K_{eq}^0 in GWB by setting the temperature of the reaction to 8.2 °C (i.e., T_0), which then equals $10^{-21.3}$. If we assume the flow weighted average SiO₂ concentration equals $[SiO_2]_{eq}$, then we can solve eq. 4-19 for pCO₂ in each watershed for that value of K_{eq} and T_0 . For the parameters and assumptions utilized in this calculation, we observe that the calculated pCO₂ values increase linearly with increasing HI ($R^2 = 0.38$; p < 0.01; Figure 4-9). This dependence on HI is consistent with the common observation that soil moisture and temperature affect CO₂ production in soils (e.g., Raich and Schlesinger, 1992; Lloyd and Taylor, 1994). It has been observed, for example, that when soil moisture is low, CO_2 production is low (Wood et al., 2013). We infer that this is thus a defensible explanation for the trends that we see in the dry watersheds. Specifically, when PET >> MAP, soils are too dry for soil microbiota to produce significant CO_2 through respiration; therefore, p CO_2 is low. When HI increases, soil moisture increases, leading to higher pCO_2 in the system. The variability in pCO_2 across each watershed could explain the apparently weaker temperature sensitivity in our watershed data compared to the theoretical value. In this regard, the low temperature sensitivity for smectite-kaolinite is similar to the low T sensitivity reported by Maher and Chamberlain (2014) for several important silicate weathering reactions.

The pCO₂ values we derived here are relatively low for soil gases. This could be a result of several of our assumptions being incorrect. 1) we assumed here that the system is open, and CO_2 is constant; however, CO_2 can also be consumed along a flowpath leading to closed-system behavior. In this situation, we might expect CO_2 concentrations to be low because it is not being continuously resupplied by the atmosphere during the reaction progress. 2) We assumed that the equilibrium between smectite and kaolinite was the only reaction controlling the stream chemistry (eq. 4-16); however, we know that chlorite, illite, and feldspar also release cations, SiO_2 , and change pH. In this situation, the magnitude of our pCO₂ values could be incorrect because of an incorrect stoichiometric relationship that we assumed between pCO_2 and SiO_2 (eq. 4-18). This error would impact the magnitude of the pCO_2 calculated in Figure **4-9** but not the trend we observed.

4.3.6 Climate Controls on Weathering: Wet Watersheds

In order to explore how climate impacts weathering dynamics in wet watersheds, we fit eq. 4-7 to sites with HI > 0.55. For these sites, we found that three models provided equally valid results (Table 4-1; Table C-3):

As shown in the three models above, we find that weathering for sites with HI > 0.55 is always dependent on temperature but is only dependent on one of the two parameters, precipitation or erosion. Conceptually, we might expect transition regime watersheds to show both a temperature and erosion dependence because part of the watershed is KL, and part is ETL. If watersheds were only KL, then we expect that $\alpha = 0$ and if they were only ETL, then $\alpha = 1$. We observe $0 < \alpha < 1$, which is consistent with TR.

Regardless of which of the best-fitting models is deemed appropriate, the Ea values for each of the models are relatively consistent (i.e., 55-61 kJ mol⁻¹). The average of all the best-fitting models results in Ea = 55 ± 5 kJ mol⁻¹. This value is smaller than the Ea determined for Na in shale soils, 99 ± 15 kJ mol⁻¹ (Dere et al., 2013) or 112 ± 34 kJ mol⁻¹ (same data re-analyzed by
Brantley et al., in review). Although this Ea value was evaluated for Na and not SiO_2 , a higher Ea in soils compared to Ea in watersheds is nonetheless consistent with our interpretation that the watersheds in our dataset with HI > 0.55 are predominantly TR.

We infer that, when evaluated as a whole, sites with HI > 0.55 appear to be TR; however, we can also hypothesize that a subset of these sites are KL and some might be ETL. Watersheds with steep slopes might be KL because they have fast erosion rates compared to silicate dissolution rates, leading to incompletely developed weathering profiles (i.e., silicate minerals present at land surface). To test this idea, we analyzed the subset of watersheds with steep slopes, by defining a mean catchment slope >10° (n = 16). For these potentially KL sites, we find that the best fitting model has the parameters $\alpha = 0$, $\beta = 1$, and Ea = 92 ± 10 kJ mol⁻¹ (R² = 0.86; *p* < 0.01; Table **4-1**; Table **C-4**).

If watersheds with steep slopes are KL, then watersheds with gentle slopes might be ETL. In these watersheds, erosion is low compared to silicate dissolution rates, leading to completely developed weathering profiles (i.e., silicate minerals absent at land surface). To test this idea, we focus our analysis on the watersheds with gentle slopes, which we define as a mean catchment slope $<5^{\circ}$ (n = 31). The best fitting model for these sites have the parameters $\alpha = 0.35 \pm 0.08$, $\beta = 0$, and Ea = 45 ± 16 kJ mol⁻¹ (R² = 0.48; p < 0.01; Table **4-1**; Table **C-5**). Based on these parameters, we see that erosion and temperature control F_{SiO_2} in these watersheds. We propose two interpretations for this result. The first is that these sites are TR because they have an erosion dependence as expected for ETL but also a temperature dependence as expected for KL. In other words, it is possible that, because shales are relatively easy to erode, our dataset does not contain any strictly ETL watersheds. An alternative explanation is that these sites are in fact ETL. As seen in eq. 4-2, sediment yield (S_y), our proxy for erosion rate, is dependent on temperature. The temperature dependence that we observe for these sites could therefore reflect the increase in erosion rate with increasing temperatures. Noting, however, the dependence of erosion rate globally on temperature is not consistent (Schaller and Ehlers, 2022), we infer that shales are different from other lithologies, or that the climate systems represented in the USA are unique in showing a relatively small erosion rate dependence upon T. Regardless, we can calculate the fractional change in silicate weathering flux with each degree increase in temperature, f_{sw} , by increasing *T* in eq. 4-2 and evaluating how S_y changes.

$$f_{SW} = \frac{Ea}{RT^2} \tag{4-21}$$

Eq. 4-21 describes the relationship between f_{sw} and Ea (Berner, 1994; Hayworth and Foley, 2020). Here, we set T in eqs. 4-2 and 4-21 to 288 K, Earth's modern average surface temperature and find that $f_{sw} = 6.7\%/K$ and Ea = 46 kJ mol⁻¹. This Ea is consistent with the Ea observed in the wet watersheds with gentle slopes; therefore, these sites could be ETL. More analysis and data would be required to definitively classify these sites as ETL vs. TR.

4.3.7 Evaluation of Weathering Regimes in the United States

As seen in sections 4.3.4 through 4.3.6, F_{SiO_2} in different groups of watersheds have different sensitivity to temperature (i.e., Ea). When we look across all the sites (regardless of HI and slope), we find that Ea = 56 ± 18 kJ mol⁻¹ (Table **4-1**). We find that this Ea is consistent with other Ea values for silica fluxes in watersheds reported in the literature (typically 49-60 kJ mol⁻¹; Table **4-1**). Most of the sites previously studied are granitic and mixed sedimentary watersheds and this Ea has been attributed to feldspar dissolution. We, however, attribute this Ea in shales to TR weathering because they incorporate several different rate limiting steps across these landscapes. When we remove the very dry RL sites, we find that the Ea is 56 ± 8 kJ mol⁻¹ (Table **4-1**), which is still consistent with the Ea for all watersheds; however, the MAP dependence decreases from $\beta = 2$ to $\beta = 0.65$. White et al. (1999) found that the Ea for weathering release rate of SiO₂ was 51 kJ mol⁻¹. Their dataset contains some dry watersheds, and when only watersheds with MAP > 1000 mm yr⁻¹ were analyzed (from the same dataset), Oliva et al. (2003) found that the Ea was essentially the same (49 kJ mol⁻¹). We also observe that when dry sites (HI < 0.55) are included in analysis or not, Ea does not significantly change (see Table **4-1**). Like our shale dataset, dry watersheds (i.e., HI < 0.55) did not impact the temperature dependence of weathering.

When we separate sites in our shale dataset further, the Ea values we calculate can be interpreted through physical and chemical processes in the watersheds. For sites with HI < 0.55, we found that Ea = -83 ± 31 kJ mol⁻¹ (Table **4-1**). As discussed in section 4.3.5, this Ea value is consistent, although slightly smaller in magnitude, with the equilibrium between smectite and kaolinite. As temperatures increase, smectite is favored over kaolinite, leading to retention of base cations and SiO₂ in soils and a lower weathering flux. This sensitivity is lower than predicted in GWB, which is likely a result of diverse chemical compositions of secondary clays and the influence of pCO₂ in the weathering reactions. Nonetheless, we find that in watersheds with RL silicate weathering, the sensitivity to changes in q is much larger than the sensitivity to changes in MAT; therefore, the RL endmember for silicate weathering in watersheds can by simply expressed as $F_{SiO_2} = qC_{max}$ (see eq. 4-9 and 4-10).

For sites with HI > 0.55 and slopes > 10°, we found that $Ea = 92 \pm 10 \text{ kJ mol}^{-1}$ (Table 4-1). We interpreted these sites as showing KL silicate weathering; therefore, this Ea should represent the Ea of dissolution for the major SiO₂-producing mineral. As discussed earlier, chlorite is likely the primary silicate mineral dissolving in shale watersheds (Gu et al., 2020; Liao et al., 2022). Our Ea of 92 ± 10 kJ mol⁻¹ is consistent with the Ea for chlorite dissolution, 88 kJ mol⁻¹ (Palandri and Kharaka, 2004). We did find that one study in the literature reported a larger Ea (i.e., 160 kJ mol⁻¹; Wolff-Boenisch et al., 2009). This study focused on the high Himalayas in a mixed lithology setting. The average watershed relief was 940 ± 200 m, higher than the relief that we observed for our sites with slopes > 10° (654 ± 183 m). Based on our findings, this high Ea observed by Wolff-Boenisch et al. (2009) could be explained by strictly KL watersheds (rather than TR) as a result of fast eroding watersheds. Because their study features a mixed lithology, however, interpreting the Ea with respect to the primary dissolving mineral is difficult. Nonetheless, their results highlight that watersheds with steep slopes are more likely to be KL.

Lastly, for sites with HI > 0.55 and slopes < 5°, we found that $Ea = 45 \pm 16 \text{ kJ mol}^{-1}$ (Table 4-1). This value could reflect TR silicate weathering, or it could reflect the temperature dependence of erosion as shown by our analysis of the BQART model for sediment yields. Given our definition for S_y, we would expect a 6.7% increase in erosion with degree increase in temperature, which results in Ea = 46 kJ mol⁻¹, consistent with the Ea derived from our wet sites with gentle slopes.

If we accept that shale watersheds with HI < 0.55 are RL, watersheds with HI > 0.55 and slopes >10° are KL, watersheds with HI > 0.55 and slopes <5° are ETL, and all other watersheds are TR, then we can calculate the relative importance of each of these weathering regimes for shales across the continental United States. For this calculation we utilize HUC12 watersheds because they are small (typically ~100 km²) and have been mapped across the entire United States (Berelson et al., 2004). There are >100,000 HUC12 watersheds within the Watershed Boundary Dataset (WBD). Using the same method for identifying shale watersheds (see section 4.2.1), we found that 10,706 HUC12 watersheds are underlain by shale. We calculated HI and mean catchment slope for these watersheds following methods in sections 4.2.2 and 4.2.3. Of the shale HUC12 watersheds, we found that 48% (n = 5,142) were RL, 37% (n = 3,914) were ETL, 9% (n = 940) were TR, and 7% (n = 710) were KL (Figure **4-10**). Weighting the land area fractions by the average F_{SiO_2} observed for each of these weathering regimes, we find that silicate

weathering in US shales is 17% RL, 56% ETL, 16% TR, and 11% KL. Although RL watersheds cover the largest land area in the United States, their weathering fluxes are very low; therefore, they contribute significantly less to the silicate weathering fluxes on the continental scale than ETL and KL watersheds.

4.4 Conclusions

Understanding controls on silicate weathering rates is important in order to predict CO_2 weathering dynamics across space and time. We found that in the United States, shales can broadly be categorized as "dry" and "wet", depending on whether the ratio of MAP to PET is less than or greater than 0.55, respectively. In dry watersheds, weathering is limited by runoff. The stream chemistry in these watersheds is consistent with weathering products reaching equilibrium with respect to secondary formation of smectite and kaolinite. The temperature dependence of this equilibrium is consistent with this equilibrium but made more difficult to interpret due to potentially low and variable pCO_2 in very dry soils. These watersheds are best described as dependent upon runoff, temperature, pCO_2 , and the mineralogy of the system. For our specific

shale watersheds,
$$F_{SiO_2} = q \left(\frac{K_{eq}^0}{48.26} e^{\left(-\frac{-83}{R} \left[\frac{1}{T} - \frac{1}{281} \right] \right)} \right)^{\frac{1}{12.835}} (pCO_2)^{\frac{6.33}{12.835}}.$$

In contrast, silicate weathering in some wet watersheds may best be described as KL, some as ETL, and some as a combination of KL and ETL landscapes considered TR. When evaluating the temperature sensitivity for silicate weathering of these watersheds considered together as a group, we found an apparent activation energy of 55 ± 5 kJ mol⁻¹. This value is consistent with apparent activation energies for silica release rates reported in the literature for granitoid watersheds (49-60 kJ mol⁻¹; Table **4-1**). When all these watersheds are considered together as a group, however, the activation energy is difficult to interpret. Splitting these sites

into watersheds with steep (> 10°) and gentle (< 5°) slopes, we found that the Ea can be more easily interpreted. For sites with steep slopes, Ea = 92 ± 10 kJ mol⁻¹, which is consistent with the Ea for chlorite dissolution, 88 kJ mol⁻¹ (Palandri and Kharaka, 2004). We, therefore, consider silicate weathering in watersheds with steep slopes as KL. For sites with gentle slopes, Ea = 45 ± 16 kJ mol⁻¹, which is consistent with the temperature sensitivity for sediment yield (46 kJ mol⁻¹). We, therefore, consider silicate weathering in watersheds with gentle slopes as ETL. For watersheds where silicate weathering is KL, they are best described as dependent upon temperature and precipitation, and $F_{SiO_2} = 1.5 \times 10^{-3} \left(\frac{P}{831}\right) e^{\left(-\frac{92}{R}\left[\frac{1}{T} - \frac{1}{281}\right]\right)}$. For watersheds where silicate weathering is ETL, they are best described as dependent upon reosion and temperature, and $F_{SiO_2} = 2.5 \left(\frac{E}{60.3}\right)^{0.35} e^{\left(-\frac{45}{R}\left[\frac{1}{T} - \frac{1}{281}\right]\right)}$.

In the USA, 33% of HUC12 watersheds are underlain partially by shale, and 10% have >75% of their drainage area underlain by shale. Utilizing the criteria that RL silicate weathering develops in watersheds where HI < 0.55, we found that silicate weathering rates in 48% of shale watersheds are RL in the United States. Only 7% of shale watersheds have HI > 0.55 and slopes $>10^\circ$. Lastly, 37% of shale watersheds have HI > 0.55 and slopes $<5^\circ$. Most wet watersheds are ETL and only a very small fraction of watersheds are KL. Moreover, we also show that a large fraction of land surface (i.e., the fraction where silicate weathering is RL) contributes very little to weathering fluxes.

In conclusion, shales cover a large fraction of land surface globally and have temperature sensitivities similar to granitic watersheds. Unlike granites, however, shales are easily erodible, which may make them less likely to be ETL. It is important to consider shales when evaluating global weathering dynamics.

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4.5 Tables

Study	Ea (kJ mol ⁻¹)	Lithology	n	Correction	Notes
This Study	56 ± 18	Shale	139	$\begin{array}{l} \alpha=0,\beta=\\ 2.0\pm0.2 \end{array}$	All Sites (3 outliers removed)
This Study	-83 ± 31	Shale	79	$\begin{array}{l} \alpha = 1.1 \pm \\ 0.2, \ \beta = 4.9 \\ \pm 0.5 \end{array}$	HI < 0.55 & 3 outliers removed
This Study	56 ± 8	Shale	60	$\alpha = 0, \beta = 0.65 \pm 0.16$	HI > 0.55
This Study	92 ± 10	Shale	16	$\alpha = 0, \beta = 1$	$HI > 0.55 \& slope > 10^{\circ}$
This Study	45 ± 16	Shale	31	$\begin{array}{l} \alpha = 0.35 \pm \\ 0.08 \ \beta = 0 \end{array}$	HI > 0.55 & slope < 5°
White and Blum (1995)	59	Granite	68	$\alpha = 0, \beta = 1$	
White et al. (1999)	51	Granite	86	$\alpha = 0, \beta = 1$	Extended dataset of White and Blum (1995)
Dalai et al. (2002)	51	Granite/Mixed Sedimentary	15	$\alpha = 0, \beta = 0$	
Oliva et al. (2003)	49	Granite	36	$\alpha = 0, \beta = 0$	Same data as White and Blum (1995), but runoff $> 1000 \text{ mm yr}^{-1}$
West et al. (2005)	60 ± 20	Granite	12	$\alpha = 0, \beta = 1$	Data Reanalyzed for SiO ₂ fluxes
Wolff- Boenisch et al. (2009)	160	Granite/Mixed Sedimentary	10	$\alpha = 0, \ \beta = 0$	High Relief Himalayan catchments (R = 940 ± 200 m)
Yadav and Chakrapani (2011)	52	Granite/Mixed Sedimentary	11	$\alpha = 0, \beta = 0$	

Table 4-1: Temperature sensitivity for silica fluxes in watersheds from this study and from published literature.

**: *p* < 0.01 *: *p* < 0.05

4.6 Figures



Figure 4-1: Map showing the coverage of shale lithology and the sampling locations (n = 142) for shale watersheds. Gray and black points indicate sites where water chemistry and discharge have been reported and were used for analysis for HI < 0.5 and HI > 0.55 respectively (see section 4.3.1).



Figure 4-2: Holdridge classification triangle showing the climate classifications for the shale watersheds. Note that the potential evapotranspiration ratio is the inverse of HI (i.e., PET/MAP).



Figure 4-3: (A) Histogram (bars) and kernel density (solid black line) showing the distribution of HI values across the United States with shale as the outcropping lithology. (B) Plot showing HI vs. the between-group variance ($\sigma_{between}^2$) using the Otsu method for threshold determination for the same dataset in panel A. (C) Plot showing HI vs. SiO₂ Flux, i.e., F_{SiO_2} , for all shale watersheds (n = 142). In all three plots (A-C), the vertical dashed line represents the threshold HI value determined using its respective method.



Figure 4-4: Flow weighted SiO₂ concentrations as a function of MAT (A), MAP (B), Runoff (C), and Sediment Yield (D).



Figure 4-5: Activity diagrams of the chlorite-smectite-kaolinite-gibbsite system for Mg-SiO₂. (A) General stability zones for each of the minerals at T₀ (i.e., 8.2°C). (B) Flow-weighted average river composition for of the 139 watersheds. The 3 missing watersheds had an insufficient number of Mg and pH measurements to calculate the average river chemistry. Error bars in (B) denote the interannual variability for the average composition. Plot (C) shows every sample (n = 11,291) for the 82 watersheds with HI < 0.55, and plot (D) shows every sample (n = 9,991) for the 60 watersheds with HI > 0.55. In both (C) and (D) data are only shown where concentrations of SiO₂, Mg²⁺, and pH were measured in the same water sample.



Figure 4-6: SiO₂ Fluxes (F_{SiO_2}) as a function of MAT (A), MAP (B), Runoff (C), and Sediment Yield (D).



Figure 4-7: Plots showing how $[SiO_2]$ (A), $[Mg^{2+}]$ (B), and pH (C) vary with MAT for sites with HI < 0.55. Sites in equilibrium with amorphous SiO₂ were removed because their equilibrium is not consistent with eqs. 4-10 and 4-11.



Figure 4-8: Activity product (Q) for the kaolinite-smectite equilibrium as a function of MAT (A) and MAP (B). In both plots dashed line represents the equilibrium constant (K_{eq}) for the transformation of kaolinite to smectite, which was calculated using the thermo.tdat database in GWB 2022 Community Edition.



Figure 4-9: Plot showing the calculated pCO_2 concentrations using eq. 4-18 vs. HI for shale watersheds. Sites shown are watersheds with HI < 0.55. Sites in equilibrium with amorphous SiO₂ were removed because their equilibrium is not consistent with eqs. 4-12 and 4-14.



Figure **4-10**: Mapped distributions of weathering regimes calculated for shale-underlain HUC12 watersheds in the United States based on climate and topography.

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Appendix A

Supplemental Information for Chapter 2

Appendix A, published as the supplemental material for Shaughnessy, A. R., Gu, X., Wen, T., and Brantley, S. L. (2021). Machine learning deciphers CO₂ sequestration and subsurface flowpaths from stream chemistry. *Hydrology and Earth System Sciences*, *25*(6), 3397-3409, is included here in reformatted form.

A.1 NMF Model

To employ NMF on limited datasets of stream chemistry, a bootstrapped data set was generated using a multivariate normal distribution of log-transformed stream water chemistries, similar to the procedure outlined in Lautz et al. (2014). The bootstrapped dataset matches the measured means of the log-transformed stream water chemistries and maintains covariation between analytes. A comparison between the measured and bootstrapped data sets can be seen in Figure **A-2** in Appendix A.6. All of the input features were normalized to values between 0 and 1 to not bias the model training to any one input feature. Next, the model was trained to the bootstrapped dataset using NMF algorithms in the python library scikit-learn (Pedregosa et al., 2011). Lastly, the trained model was applied to measured stream water samples to delineate mixing proportions.

The model results are sensitive to the random initiation of the *H* matrix (i.e., endmember chemistries) used in the training. To produce a more robust decomposition, the starting *H* matrix was randomly initiated 20,000 times. For each stochastic iteration, we used NMF to calculate optimal *W* and *H* matrices (Eq 2-1) and then filtered out any models with proportions that did not add to 1 ± 0.05 . Additionally, the fit of the model was evaluated from SSE:

$$SSE = \sum_{m} \left(\left(\frac{[X_m]}{[SO_4^{2-}]} \right)_n - \sum_{p} \alpha_p \left(\frac{[X_m]}{[SO_4^{2-}]} \right)_p \right)^2$$
(A-1)

Here, SSE is the sum of square errors, α_p is the sulfate mixing proportion of endmember p derived from the model, X is the element "m" (i.e., Ca, Mg, Na, K, and Cl), and brackets denote concentration. The subscript "n" refers to measured concentrations at timepoint "n" in the stream. Using eq. A-1, we filtered out additional models that yielded poor fitting solutions following the procedure outlined in Torres et al. (2016). Here we define a reference SSE that is equal to the 5th percentile SSE for all the models for that sample and filtered out any models where the SSE was larger than the reference SSE. In other words, we kept only the 5th percentile of best fitting models for each sample. The remaining models were averaged and reported as the final result. Additionally, we calculate the standard deviation for the remaining samples to represent uncertainty in our modeling results and we propagate these errors throughout our calculations. This average number of valid models per sample after all filters were applied was 44 for Shale Hills, 104 for East River, and 55 for Hubbard Brook.

A.2 Calculations

A.2.1 Solute Fluxes

The time-averaged flux of each species, *Flux*, was calculated using values for concentration and discharge following an equation adapted from Moatar et al. (2013):

$$Flux = \beta \frac{\sum_{n} [X]_{n} Q_{n}}{\sum_{n} Q_{n}} \bar{q} A^{-1}$$
(A-2)

Here, *Flux* has the units of mmol m⁻² yr⁻¹, [X]_n is the concentration of a weathering product in the stream (e.g., $X = SO_4^{2-}$, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^-) at timepoint *n*, Q_n is the discharge measured at timepoint *n*, \bar{q} is the mean discharge over the period of record (i.e., sum of daily discharge measurements/number of daily discharge measurements), *A* is the basin area (Shale Hills = $8.0x10^4$ m²; East River = $8.5x10^7$ m²; Hubbard Brook = $4.0x10^5$ m² (W3), $1.5x10^5$ m² (W6), $7.7x10^5$ m² (W7), $6.1x10^5$ m² (W8), $7.0x10^5$ m² (W9)), and β is a coefficient for unit conversions to mmol m⁻² yr⁻¹ (i.e., 3.15×10^{10} l s m⁻³ yr⁻¹) or to meq m⁻² yr⁻¹ (i.e., 3.15×10^{10} l s m⁻³ yr⁻¹ multiplied by species charge (meq/mmol)).

We calculate the uncertainty for our flux calculations by propagating errors in $[X]_n$ from equation A-2. For sulfate concentrations, we assume 5% error on the measured concentrations. Uncertainties in mixing proportions (i.e., α) from the NMF model are utilized as uncertainties in the pyrite-derived and acid rain-derived sulfate concentrations. Lastly, error in the total cation concentration is determined from the uncertainties in the NMF modeled total cation concentrations. For Hubbard Brook, there are 5 sub-catchments that we use in analysis. Reported fluxes in Table 1 are the average of the sub-catchments.

A.2.2 Using Stream Chemistry to Calculate CO₂ Drawdown or Release

Here we calculate the inferred CO₂ release or sequestration resulting from weathering as recorded in the sum of all base cation concentrations (meq/l) in each stream sample, $[\Sigma^+]_{total}$:

$$[\Sigma^+]_{total} = 2[Ca^{2+}]_{total} + 2[Mg^{2+}]_{total} + [Na^+]_{total} + [K^+]_{total}$$
(A-3)

Here, we use the modeled base cation concentrations from NMF in eq. A-3, and we use the uncertainty in the modeled concentrations for the error in $[\Sigma^+]_{total}$. To calculate the inferred CO₂ release or sequestration resulting from weathering, we use the results of NMF, as described below, to identify the extents of 4 weathering reactions recorded in each stream sample: 1) CO₂driven weathering (CO₂-weathering) of silicates, 2) H₂SO₄-driven weathering (H₂SO₄weathering) of silicates, 3) CO₂-weathering of carbonates, and 4) H₂SO₄-weathering of carbonates. We note these four quantities respectively as 1) $[\Sigma^+]_{carbonate-cO_2}$; 2) $[\Sigma^+]_{silicate-H_2SO_4}$; 3) $[\Sigma^+]_{silicate-CO_2}$; 4) $[\Sigma^+]_{carbonate-H_2SO_4}$. These are the four unknowns we seek to calculate for SH and ER, as described below.

Based on the high proton and low metal concentrations of the measured rain chemistry, the rain contributes negligibly to the base cation concentrations of the study streams; therefore, we apportioned all the base cations to weathering reactions. First, we note that the meq/l of cations derived from carbonate minerals, $[\Sigma^+]_{carbonate}$, equal $[\Sigma^+]_{carbonate-CO_2}$ + $[\Sigma^+]_{carbonate-H_2SO_4}$. Likewise, the meq/l of cations derived from silicate minerals, $[\Sigma^+]_{silicates}$ equal $[\Sigma^+]_{silicate-H_2SO_4}$ + $[\Sigma^+]_{silicate-CO_2}$. The summation of silicate-cations ($[\Sigma^+]_{silicate}$) is the difference between the summation of total cations ($[\Sigma^+]_{total}$) and that of carbonate-derived cations $([\Sigma^+]_{carbonate})$:

$$[\Sigma^+]_{silicate} = [\Sigma^+]_{total} - [\Sigma^+]_{carbonate}$$
(A-4)

We use a few field observations to complete the calculations for SH and ER, as explained in the main text. First, carbonate minerals only dissolve in water flowing along the deep path because carbonates have been depleted from shallow depths. Second, although some chlorite dissolves into water flowing along the deep path, the release of Mg at depth is insignificant compared to Mg released from carbonate. We ignore shallow dissolution of carbonates and deep dissolution of silicates in both SH and ER.

With these observations, we can write:

$$[\Sigma^+]_{carbonate} = 2\alpha_{deep}[SO_4^{2-}]_{total} \left(\left(\frac{[Ca^{2+}]}{[SO_4^{2-}]} \right)_{deep} + \left(\frac{[Mg^{2+}]}{[SO_4^{2-}]} \right)_{deep} \right)$$
(A-5)

Here, α_{deep} is the proportion determined through NMF of sulfate in a given water sample that was derived from reactions along the deep flowpath, $[SO_4^{2-}]_{total}$ is the total concentration of sulfate in the stream water sample under consideration, $([Ca^{2+}]/[SO_4^{2-}])_{deep}$ and $([Mg^{2+}]/[SO_4^{2-}])_{deep}$ are the model-derived ratios of $[Ca^{2+}]$ and $[Mg^{2+}]$ to $[SO_4^{2-}]$, respectively, that characterize the deep flowpath endmember for that sample.

Remembering that Mg release from chlorite dissolution at depth is insignificant compared to Mg from carbonates, all of the generated sulfate in the deep weathering endmember is balanced by cations from dissolved carbonate minerals:

$$[\Sigma^+]_{carbonate-H_2SO_4} = 4\alpha_{deep}[SO_4^{2-}]_{total}$$
(A-6)

(We multiply the concentration of deep sulfate by 4 because 4 eq of cations are released per mol of sulfate, noting that $[\Sigma^+]$ is in eq/L and $[SO_4^{2-}]$ is in mol/L). Any carbonate-derived base cations that are in excess of what could have been produced by pyrite-derived sulfuric acid are attributed to CO₂-weathering of carbonates:

$$[\Sigma^+]_{carbonate-CO_2} = [\Sigma^+]_{carbonate} - [\Sigma^+]_{carbonate-H_2SO_4}$$
(A-7)

Remembering that no carbonates dissolve into water flowing along the shallow path, then similar arguments for the shallow flowpath yield:

$$[\Sigma^+]_{silicate-H_2SO_4} = 2\alpha_{shallow}[SO_4^{2-}]_{total}$$
(A-8)

$$[\Sigma^+]_{silicate-CO_2} = [\Sigma^+]_{silicate} - [\Sigma^+]_{silicate-H_2SO_4}$$
(A-9)

From these equations, values for the four unknowns can be calculated for SH and ER. A similar approach was taken for HB except that no carbonate minerals were present, and only two unknowns were determined ($[\Sigma^+]_{silicate-H_2SO_4}, [\Sigma^+]_{silicate-CO_2}$).

With respect to the atmosphere considered over the long-term (10^5-10^6 yr), H₂SO₄weathering of silicates and CO₂-weathering of carbonates are CO₂ neutral, while CO₂-weathering of silicates sequesters CO₂ and H₂SO₄-weathering of carbonates releases CO₂ (Figure **2-1**). As seen in Figure 1, per mole of CaSiO₃ or CaCO₃ weathered, CO₂-weathering of silicates sequesters 1 mol of CO₂ and H₂SO₄-weathering of carbonates releases 0.5 moles of CO₂. In terms of [Σ^+]_{total}, CO₂-weathering of silicates sequesters 0.5 moles of CO₂ per base cation equivalent released into solution and H₂SO₄-weathering of carbonates releases 0.25 moles of CO₂ per base cation equivalent released into solution (Figure **2-1**; Reactions 2, 3, 6, and 7). For a given water sample, the cation concentrations record the extent of dissolution of carbonate and silicates, as long as the contribution of these base cations from acid rain is minimal. (For simplicity, we do not correct

$$\Delta CO_2 = 0.5 [\Sigma^+]_{silicate-CO_2} - 0.25 [\Sigma^+]_{carbonate-H_2SO_4}$$
(A-10)

Using ΔCO_2 , we calculate the flux of CO₂ using the discharge measurements for each sample (see Figure A-4 in Appendix A.6).

Next, we will derive κ_{stream} , the modern CO₂ sequestration coefficient. In general, both κ_{stream} and κ_{rock} (see Appendix A.2.3) are used as ways to note the extent that weathering in a watershed is sequestering or releasing CO₂. κ_{stream} is the amount of CO₂ emitted or sequestered calculated from $[\Sigma^+]_{total}$ as described above, normalized by $[\Sigma^+]_{total}$ (meq/l):

$$\kappa_{stream} = -\frac{\Delta CO_2}{[\Sigma^+]_{total}} \tag{A-11}$$

The negative sign is used so that a negative κ_{stream} represents sequestration (uptake of CO₂), and a positive κ_{stream} represents release. From eq. A-11 it is apparent that the CO₂ emitted or sequestered equals the product, $\kappa_{stream} [\Sigma^+]_{total}$, with the appropriate sign. Total dissolved base cations in a stream draining a watershed with no carbonate nor pyrite are attributed here entirely as CO₂-weathering: this watershed demonstrates the highest capacity to sequester CO₂ and κ_{stream} equals -0.5. Substituting from eq. A-10 into eq. A-11 yields:

$$\kappa_{stream} = -\frac{0.5 \left[\Sigma^{+}\right]_{silicate-CO_{2}} - 0.25 \left[\Sigma^{+}\right]_{carbonate-H_{2}SO_{4}}}{\left[\Sigma^{+}\right]_{total}}$$
(A-12)

We can further expand eq. A-12 by substituting eq. A-6 for $[\Sigma^+]_{carbonate-H2SO4}$, eq. A-9 for $[\Sigma^+]_{silicate-CO2}$, eq. A-4 for $[\Sigma^+]_{silicate}$ and eq. A-8 for $[\Sigma^+]_{silicate-H2SO4}$

$$\kappa_{stream} = -\frac{0.5\left([\Sigma^+]_{total} - [\Sigma^+]_{carbonate} - 2\alpha_{shallow}[SO_4^{2-}]_{total}\right) - \alpha_{deep}[SO_4^{2-}]_{total}}{[\Sigma^+]_{total}}$$
(A-13)

This can be rearranged and simplified as:

$$\kappa_{stream} = -\frac{1}{2} + \frac{1}{2} \frac{[\Sigma^+]_{carbonate}}{[\Sigma^+]_{total}} + \frac{[SO_4^{2-}]_{total}}{[\Sigma^+]_{total}}$$
(A-14)

We then define the second term (ratio of carbonate-derived base cations to total base cations in the stream sample) as γ_{stream} and the third term (ratio of the sulfate equivalents (from sulfuric acid) to the equivalents of base cations in the stream) as ζ_{stream} . Note that to obtain the sulfate equivalents, we multiply $[SO_4^{2-}]_{\text{total}}$ by 2, resulting in the third term equal to $0.5\zeta_{\text{stream}}$. Given these definitions, eq. A-14 yields eq. 2-2 from the main text:

$$\kappa_{stream} = \frac{1}{2}(-1 + \gamma_{stream} + \zeta_{stream})$$

A.2.3 Using Rock Chemistry to Calculate CO₂ Drawdown or Release

Here we compare the bulk elemental composition of parent rock to topsoil and calculate the difference to determine if the system acted on net as a source or a sink of CO_2 over the weathering duration. Of course, this calculation involves inspection only of rock versus soil chemistry and cannot therefore be used to separate CO₂- versus H₂SO₄-weathering when the latter is derived from acid rain. The three most important factors are i) the ratio of base cations in carbonates relative to silicates in the rock, ii) the ratio of acid-generating units of pyrite relative to total base cations in carbonate+silicate minerals, and iii) the ratio of base cations still retained in regolith at the land surface relative to total base cations. This latter ratio is related to the chemical depletion factor (written below as $-\tau$), i.e., the relative ratio of loss of a component in a rock to chemical weathering versus total loss by physical + chemical weathering (Riebe et al. 2003). For (i), we define the carbonate/silicate factor, γ_{rock} , which is the proportion of base cation equivalents in the rock derived from carbonate minerals divided by the total base cations:

$$\gamma_{rock} = \frac{2C_{Ca,carb} + 2C_{Mg,carb}}{2C_{Ca,Total} + 2C_{Mg,Total} + C_{Na,Total} + C_{K,Total}}$$
(A-15)

Here $C_{X,k}$ is the mole fraction (mol/kg) of base cation (X = Ca, Mg, Na, or K) in carbonates (k = carb) or in carbonate + silicate minerals (k = Total). By definition, γ_{rock} ranges from 0 (where all base cations derive from silicates) to 1 (where all base cations derive from carbonates). Likewise, 1- γ_{rock} is the proportion of base cations derived from silicate minerals.

When pyrite oxidizes it produces sulfuric acid that can dissolve carbonate and silicate minerals. This impacts CO₂ dynamics over 10^5 - 10^6 yr timescales by releasing CO₂ (H₂SO₄-weathering of carbonates). But it also diminishes the silicate content of the rock, thereby diminishing the rock's capacity to sequester CO₂. Here, we define a new variable, ζ_{rock} , which is the acid generation capacity expressed relative to the base cations in the rock (all on an equivalents basis):

$$\zeta_{rock} = \frac{4C_{py}}{2C_{ca,Total} + 2C_{Mg,Total} + C_{Na,Total} + C_{K,Total}}$$
(A-16)

Here, the subscript *py* refers to pyrite (mol/kg rock). We multiply the concentration of pyrite (i.e., C_{py}) by 4 (eq/mol) because 4 equivalents of sulfate are produced per mole of pyrite as shown in reaction A-17.

$$FeS_2 + \frac{15}{4}O_2 + 2H_2O \rightarrow \frac{1}{2}Fe_2O_3 + 4H^+ + 2SO_4^{2-}$$
 (A-17)

Lastly, in many catchments, the bulk chemistry of parent rock is not indicative of the CO_2 sequestration during weathering because silicate minerals are kinetically slow to dissolve and they do not completely dissolve before the rock physically erodes. On the other hand, we assume here that all carbonate minerals chemically weather away before exposure at land surface, an assumption most useful for wet climates and relatively low-carbonate content rocks. The relative depletion of an element in a weathered rock with respect to the parent rock is easily calculated from the mass transfer coefficient, τ .

$$\tau_{i,j} = \frac{c_{j,weathered}c_{i,parent}}{c_{j,parent}c_{i,weathered}} - 1$$
(A-18)

Here, C is the concentration of a base cation (j) or an immobile element (i) in the parent or weathered rock. When τ at the top of the weathering profile is 0, the composition of the weathering material is the same with respect to base cations and immobile element i as the parent and none of these elements have been lost to solution (they will be eroded instead of chemically weathered). When $\tau = -1$, all of the element has been lost to solution and none is left to erode away. Using the variables γ_{rock} , ζ_{rock} , and τ , we now define κ_{rock} , the long-term CO₂ sequestration coefficient of the rock:

$$\kappa_{rock} = \frac{1}{2} \tau_{silicate\ cations} (1 - \gamma_{rock}) - \frac{1}{2} \zeta_{rock} \tag{A-19}$$

Here, $(1 - \gamma_{rock})$ is the proportion of base cation equivalents associated with silicate minerals. We multiply this by 0.5 because 1 mol of CO₂ is sequestered during weathering of 2 eq of base cations when considered over 10⁵ to 10⁶ yr timescales (see Figure **2-1** reactions 1 and 2). If pyrite oxidation is coupled to carbonate dissolution, 2 mols of CO₂ are released per mole of pyrite in the rock (see Figure **2-1** reaction 7), yielding the term $-\frac{1}{2}\zeta_{rock}$ based on eq A-16. Likewise, pyrite oxidation could be coupled to silicate dissolution. In this case, 1 mol of pyrite consumes 2 mols of silicate minerals. Because 1 mol of Ca-silicate mineral sequesters 1 mol of CO₂ over 10⁵ to 10⁶ yr timescales (see Figure **A-1** reactions 1 and 2), CO₂ sequestration is reduced by 2 mols of CO₂ per mole pyrite in the rock. Again, based on eq A-16, this is equivalent to $-\frac{1}{2}\zeta_{rock}$. Lastly, $\tau_{silicate cations}$ is the mass transfer coefficient for base cations in silicates at the land surface. It ranges from 0 (no base cations in silicate minerals have been removed by dissolution) to -1 (all the base cations in silicate minerals have been removed by dissolution).

Finally, noting that t_{silicate cations} is generally not reported, we must instead calculate it from t, the mass transfer coefficient for total base cations in the bulk rock:

$$\tau = \tau_{silicate\ cations} (1 - \gamma_{rock}) + \tau_{carbonate\ cations} \gamma_{rock} \tag{A-20}$$

Again, we emphasize wet climates and low-carbonate terrain and implicitly assume that all carbonates are fully dissolved at the land surface (i.e., $\tau_{carbonate cations} = -1$) to solve for $\tau_{silicate}$ cations:

$$\tau_{silicate\ cations} = \frac{\tau + \gamma_{rock}}{(1 - \gamma_{rock})} \tag{A-21}$$

Now we substitute eq. A-21 in eq. A-19 and simplify to the final equation 2-3 from the main text:

$$\kappa_{rock} = \frac{1}{2} (\tau + \gamma_{rock} + \zeta_{rock})$$

When $\kappa_{rock} < 0$, the rock has sequestered CO₂ from the atmosphere over the residence time of the soil and when $\kappa_{rock} > 0$ the rock released CO₂.

Mathematically, this equation is only valid as long at $\tau < -\gamma_{rock}$. The minimum value of κ_{rock} is -0.5, which is a pure silicate rock dissolved only by CO₂. The maximum value of κ_{rock} is 0.25, which is a pure carbonate rock weathered only by sulfuric acid. It is mathematically impossible for $\kappa_{rock} < -0.5$; however, it is mathematically possible to have $\kappa_{rock} > 0.25$. In these situations, there is more sulfuric acid in the system than can be buffered by both carbonate and silicate weathering.

A.2.4 Lag-time Calculation

Using rain chemistry data from the National Atmospheric Deposition Program (NADP; http://nadp.slh.wisc.edu/) site PA42, we calculated the annual flux of sulfate into Shale Hills from wet deposition. We used the flux data to calculate a trend in wet deposition over time and then used the regression to calculate when 39.5 mmol m⁻² yr⁻¹ was deposited (i.e., 31 years prior to today). Next we added dry deposition as an input (estimated as 30% wet deposition; Lynch and Corbett; 1989), fit a new regression to wet+dry deposition over time, and recalculated the lag time (i.e., 19 years; Figure **2-4C**). Although not explicitly calculated here, Hubbard Brook also shows a lag in deposition to export on similar timescales, which is consistent with the excess sulfate export observed in other studies (Likens et al., 2002).

A.2.5 Mineral-derived Solute Concentrations

The contributions of ankerite and calcite to the Ca^{2+} budget were calculated using the composition of the appropriate endmember (deep flowpath for SH and ER). Based on the stoichiometry of ankerite at Shale Hills and assuming all Mg²⁺ in deep flowpath water derives from ankerite, the concentration of Ca²⁺ from ankerite in any given stream sample, $[Ca^{2+}]_{ankerite}$, is calculated using the following equation.

$$[Ca^{2+}]_{ankerite} = 1.6 \left(\frac{Mg^{2+}}{SO_4^{2-}}\right)_{deep} \alpha_{deep} [SO_4^{2-}]_{Total}$$
(A-22)

Here, 1.6 is the stoichiometric number relating Mg^{2+} to Ca^{2+} in Ankerite (see Table S3). $[Ca^{2+}]_{calcite}$ is calculated as the difference between the total Ca^{2+} and the ankerite-derived Ca^{2+} .

Similarly, the contributions of chlorite and illite to the Mg²⁺ budget were calculated using the composition of the appropriate endmember (shallow flowpath for SH). Based on the stoichiometry of illite at Shale Hills and assuming all K⁺ in shallow flowpath water derives from illite, the concentration of Mg²⁺ from illite in any given sample, $[Mg^{2+}]_{illite}$, is calculated using the following equation:

$$[Mg^{2+}]_{illite} = 0.28 \left(\frac{K^+}{SO_4^{2-}}\right)_{shallow} \alpha_{shallow} [SO_4^{2-}]_{Total}$$
(A-23)

Here, 0.28 is the stoichiometric number relating K^+ to Mg^{2+} in illite (see Table A-3 in Appendix A.5). The concentration of chlorite-derived Mg^{2+} is calculated as the difference between the total Mg^{2+} , the ankerite-derived Mg^{2+} and the illite-derived Mg^{2+} . Fluxes of solutes derived from each mineral are summarized in Table A-5 (Appendix A.5) for Shale Hills.
A.3 Seasonality of Pyrite-sulfate Fluxes

At Shale Hills, the proportion of pyrite-derived sulfate leaving the catchment accounts for 23% of the annual sulfate flux (Table **2-1**) but ranges from 99% of total sulfate in the dry season (summer, fall) to as low as 3% in the wet season (winter, spring, Figure **2-5A**). This is easily explained because the stream is sustained by deep groundwater that flows up into the stream from the deep pyrite reaction front during the dry summer and fall but not in the winter and less acid rain enters the catchment in the dry season (Li et al., 2017).

A.4 Rain-correction

For simplicity, we do not correct $[\Sigma^+]_{total}$ (eq. A-3) for rain chemistry; however, it is likely that some of the cations in the stream are derived from rain, rather than weathering. Because Cl in the stream is only derived from precipitation, we can apply a basic correction by subtracting cations from $[\Sigma^+]_{total}$ that balance the Cl in the stream water. Because all of our calculations rely on $[\Sigma^+]_{total}$, and individual cations, it does not matter which cations are subtracted to balance the Cl. The correction results in very little change in the calculated fluxes and does not change the interpretations of the study (see Table **A-6** in Appendix A.5).

A.5 Supplemental Tables

	-	-
	Endmember1	Endmember2
$[Ca^{2+}]/[SO_4^{2-}]^a$	8±0.7	0±0.2
$[Mg^{2+}]/[SO_4^{2-}]$	3±0.3	0.5 ± 0.1
[Na ⁺]/[SO ₄ ²⁻]	2±0.1	4±0.2
[K ⁺]/[SO ₄ ²⁻]	2±0.3	1±0.1
[Cl ⁻]/[SO ₄ ²⁻]	0±0.1	5±0.6

Table A-1: Endmember compositions for synthetic dataset

a) All analytes are reported in molar concentration ratios.

	Shale Hills		East River		Hubbard Brook		
Component	1	2	1	2	1	2	3
$[Ca^{2+}]/[SO_4^{2-}]^a$	0.0 ± 0.0	10.0±3.6	1.6±0.6	3.2±0.6	0.2±0.1	1.0±0.2	0.2±0.1
$[Mg^{2+}]/[SO_4^{2-}]$	1.6±0.7	2.9±1.0	0.4 ± 0.1	0.7 ± 0.1	0.2 ± 0.1	$0.4{\pm}0.1$	0.3±0.1
[Na ⁺]/[SO ₄ ²⁻]	0.5 ± 0.2	0.6 ± 0.2	0.1 ± 0.0	0.2 ± 0.0	2.1±0.5	0.4 ± 0.2	0.4 ± 0.2
[K ⁺]/[SO ₄ ²⁻]	0.6±0.3	0.7 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.5 ± 0.1
[Cl ⁻]/[SO ₄ ²⁻]	1.6±0.7	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.4 ± 0.1	0.2 ± 0.1	0.4 ± 0.1
Interpretation	Shallow	Deep	Shallow	Deep	Shallow Till	Moderately Shallow Till	Deep

Table A-2: Chemical composition and interpretations of end members from NMF model (see also Figure A-3 in Appendix A.6)

a) All analytes are reported in molar concentration ratios.

Table A-3: Mineral reactions with CO₂ and H₂SO₄

Reaction	Equation					
1	$Calcite + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^{-}$					
2	Dolomite + $2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$					
3	Ankerite + $2CO_2 + 2H_2O \rightarrow Ca^{2+} + 0.62Mg^{2+} + 4HCO_3^-$					
4	$2\text{Calcite} + \text{H}_2\text{SO}_4 \rightarrow 2\text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SO}_4^{2-}$					
5	Dolomite + $H_2SO_4 \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- + SO_4^{2-}$					
6	Ankerite + $H_2SO_4 \rightarrow Ca^{2+} + 0.62Mg^{2+} + 2HCO_3^- + SO_4^{2-}$					
7 ^a	Chlorite $+ 0.60_2 + 1.2C0_2 + 1.2H_20 \rightarrow 1.2$ Hematite $+$ Vermiculite $+$					
	$0.6 Mg^{2+} + 3.6 H_2 O$					
8^{a}	Illite $+ 0.91CO_2 + 4.15H_2O \rightarrow 1.08$ Kaolinite $+ 0.48$ Goethite $+ 0.07Mg^{2+} + 0.07Mg^{2+}$					
	$0.77K^{+} + 1.15H_{4}SiO_{4} + 0.91 HCO_{3}^{-}$					
Calcite: CaC	O ₃					
Dolomite: Ca	$Mg(CO_3)_2$					
Ankerite: Ca(Fe _{0.34} Mg _{0.62} Mn _{0.04})(CO ₃) ₂						
Chlorite: (Fe	$^{2+}_{0.40}Mg_{0.15}Al_{0.35})_6(Si0.7_6Al_{0.24})_4O_{10}(OH)_8$					

Chlorite: $(Fe^{2^{+}0.40}Mg_{0.15}Al_{0.35})_6(S10.76Al_{0.24})_4O_{10}(OH)_8$ Illite: $K_{0.69}(Si_{3.24}Al_{0.76})(Al_{1.69}Fe^{3^{+}}_{0.10}Fe^{2^{+}}_{0.16}Mg_{0.19})O_{10}(OH)_2$ Hematite: Fe_2O_3 Vermiculite: $(Mg_{0.3}Al_{2.1})(Si_{0.76}Al_{0.24})_4O_{10}(OH)_2$ Kaolinite: $Al_2Si_3O_{10}(OH)_2$ Goethite: FeOOH a) Mineral stoichiometries for chlorite and illite are reported in Sullivan et al. (2016)

	Shale Hills ^a		East River ^b		Hubbard Brook ^c	
(meq/kg)	Mean	sd	Mean	sd	Mean	sd ^h
Cation concentrations in parent	2309	439	4003	999	3321	664
Cation concentrations in topsoil	1368	552	1810	263	1528	306
Total sulfur in parent rock	100	19	686	312	119	24
Inorganic carbon in parent rock	250	42	1083	417	42	8
$\gamma_{ m rock}$	0.22	0.05	0.54	0.25	0.03	0.01
ζrock	0.04	0.01	0.17	0.09	0.04	0.01
$ au^{ m g}$	-0.43 ^d	0.19	-0.55 ^e	0.16	-0.45 ^f	0.13
$\tau_{silicate\ cations}$	-0.27	0.26	-0.01	0.64	-0.43	0.18
$\kappa_{ m rock}$	-0.08	0.11	0.08	0.17	-0.19	0.11

Table A-4: Relevant element concentrations and parameters to determine κ_{rock}

^aValues from Gu et al. (2020b)

^bValues from Wan et al. (2019)

^cValues from Johnson et al. (1968) and Bailey et al. (2004)

 ${}^{d}\tau$ calculated as averages from samples taken at the land surface for bulk composition data for 3 boreholes ${}^{e}\tau$ calculated from the average of the top 8 cm of 5 cores as reported in Wan et al. (2019)

 ${}^{\rm f}\tau$ calculated from unweathered schist and reported soil data in Johnson et al. (1968)

^gimmobile element used in τ calculations is Ti

^hNo error on measurements were reported (Johnson et al., 1968); we therefore assumed 20% error.

Analyte	Fraction	Flux (mmol m ⁻² yr ⁻¹)
	Total	50.3 ± 0.3
SO ₄ ²⁻	Rain-derived	$38.9 \pm 1.0 \; (77\%)^{a}$
	Pyrite	11.2 ± 0.9 (23%)
	Total	99.5 ± 15.2
Ca^{2+}	Calcite	56.1 ± 8.4 (56%)
	Ankerite	43.3 ± 6.9 (44%)
	Total	51.8 ± 7.4
$M\alpha^{2+}$	Ankerite	28.2 ± 4.4 (54%)
wig	Chlorite	21.3 ± 5.7 (41%)
	Illite	2.4 ± 0.6 (5%)

Table A-5: Fluxes of SO_4^{2-} , Ca^{2+} , and Mg^{2+} by contributor at Shale Hills

^aNumber in parentheses is the percent of the total flux for that element

	Shale Hills		East River		Hubbard Brook			
	Base Cation Fl	uxes (meq m ⁻²	yr ⁻¹)					
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected		
Total base cation flux Base cation	336 ± 13	316 ± 13	1540 ± 30	1530 ± 30	84.6 ± 0.8	74.4 ± 0.8		
weathering of silicates Base cation flux from CO ₂ - weathering of	12.6 ± 21.1	5.0 ± 21.1	315 ± 58	300 ± 58	24.1±0.8	14.8 ± 0.8		
carbonates	216 ± 16	216 ± 16	587 ± 48	587 ± 48	-	-		
Base cation flux from H ₂ SO ₄ - weathering of silicates Base cation flux from	62.4 ± 1.0	66.0 ± 1.0	152 ± 4	152 ± 4	60.5 ± 0.2	59.5 ± 0.2		
H ₂ SO ₄ - weathering of								
carbonates	44.8 ± 1.9	44.8 ± 1.9	488 ± 9	488 ± 9	-	-		
	Fluxes (mmol m ⁻² yr ⁻¹)							
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected		
Total sulfate flux Sulfide-	50.3 ± 0.3		197.5 ± 1.0		30.3 ± 0.1			
flux Rain-derived	11.2 ± 0.9		122.1 ± 4.3		9.1 ± 0.1			
sulfate flux CO ₂	38.9 ± 1.0		75.9 ± 4.2		21.2 ± 0.6			
sequestration				-27.9 ±				
or release	4.9 ± 10.7	8.7 ± 10.7	-35.6 ± 30.4	30.4	-12.1 ± 0.4	-7.4 ± 0.4		
	CO ₂ Sequestrat	tion Coefficien	ts					
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected		
κ _{stream}	0.01 ± 0.03	0.03 ± 0.03	-0.02 ± 0.02	-0.02 ± 0.02	-0.14 ± 0.01	-0.10 ± 0.01		
$\kappa_{ m rock}$	$\textbf{-0.08} \pm 0.11$		0.08 ± 0.17		$\textbf{-0.19} \pm 0.02$			

Table A-6: Fluxes of SO_4^{2-} , Cations, and CO_2 and CO_2 Sequestration Coefficients Corrected for Rain Cl



Figure A-1: Time series showing $[SO_4^{2-}]$ in stream water for the three components calculated from NMF for the 5 analyzed sub-catchments for Hubbard Brook. The measured stream sulfate concentrations (i.e. total sulfate) are also shown. Components 1 through 3 have been inferred to indicate weathering along flowpaths that are shallow, moderately shallow, and deep, respectively (see text and Table A-2 in Appendix A.5).



Figure A-2: Matrix of plots showing measured concentration ratios in stream water at Shale Hills normalized to their maximum value (red) and the bootstrapped normalized concentration ratios (black). Off-diagonal plots show every combination of element ratio pairs to illustrate covariation in the dataset. Plots on the diagonal are element ratio distributions to illustrate that the bootstrapped dataset matches the distribution of the measured stream samples.



Figure A-3: Plot showing the variation in end member composition over time for shallow and deep weathering end members at Shale Hills.



Figure A-4: Plots showing the CO_2 fluxes at Shale Hills (A), East River (B), and Hubbard Brook (C) through weathering reactions inferred from the stream chemistry (see Appendix A.2.2).

A.7 Supplemental References

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Appendix B

Supplemental Information for Chapter 3

B.1 Oxidation Model Derivation

Here we provide the full derivation and rationale for the oxidation model presented in the main text (i.e., Eqs. 3-1 and 3-2). We provide an initial model explaining how C-q can be conceptualized as a balance between the rate of production of solute and the rate of dilution of solute. For this derivation, we use a previously presented model but make it explicit for pyrite oxidation (Berner, 1978):

$$\frac{\partial C_{sulf}}{\partial t} = R - C_{sulf} \frac{Q}{V}$$
(3-1)

As discussed in the main text, C_{sulf} is the concentration of pyrite-derived sulfate (denoted as p-sulfate), R is the rate of pyrite oxidation (mol sulfate m⁻³ yr⁻¹), Q is the volumetric flow rate of water through the system (m³ yr⁻¹), and V is the volume of water in the watershed at any given time (m³). The rate of oxidation, R, at the mineral surface can furthermore be expressed for any packet of water moving through the watershed as

$$R = -\frac{\partial C_{DO}}{\partial t} = k_1 C_{DO} \tag{B-1}$$

Here, k_1 is the rate constant (yr⁻¹) and C_{DO} is the dissolved oxygen (DO) in the groundwater interacting at the pyrite interface. Here we assume that the packet of fluid can continue interacting with pyrite in the bedrock until all the DO is consumed. Next, we rewrite *R* with respect to C_{sulf} , rather than C_{DO} . To transform from C_{DO} to C_{sulf} , we note that 15 moles of O₂ are consumed for every 8 moles of sulfate produced:

$$150_2 + 4\text{FeS}_2 + 8\text{H}_20 \leftrightarrow 2\text{Fe}_20_3 + 8\text{S}0_4^{2-} + 16\text{H}^+$$
 (B-2)

The concentration of DO in water entering the subsurface is assumed to be equilibrated either with O₂ in the atmosphere or, if other mineral or organic matter reductants are present in soil, with the soil-atmosphere at the soil-bedrock interface. For simplicity, we denote either concentration as C_{DO}^{atm} . As noted in the main text, if water (at 10 °C) is in equilibrium with the atmosphere, C_{DO}^{atm} equals 353 µM and if in equilibrium with the soil atmosphere at Shale Hills, this value equals 260 µM (Gu et al., 2020). For any packet of water that enters the subsurface with C_{DO}^{atm} and then reacts with pyrite, the stoichiometry of reaction S2 dictates that:

$$C_{DO} = C_{DO}^{atm} - \frac{15}{8}C_{sulf}$$
 (B-3)

We define the concentration of sulfate when $C_{DO} = 0$ as $C_{sulf}^{max,pred}$. Given this definition and the stoichiometry of reaction B-2,

$$C_{sulf}^{max,pred} = \frac{8}{15} C_{DO}^{atm}$$
(B-4)

Substituting eqs. B-3 and B-4 into eq B-1 yields

$$R = k_1 \frac{15}{8} \left(C_{sulf}^{max, pred} - C_{sulf} \right)$$
(B-5)

Inserting eq. B-5 into eq. 3-1, and solving for steady-state concentration of sulfate (i.e., $\frac{\partial C_{sulf}}{\partial t} = 0$) results in:

$$C_{sulf} = \frac{k_1' C_{sulf}^{max, pred}}{k_1' + k_f} = \frac{k_1' C_{sulf}^{max, pred} z}{k_1' z + q}$$
(B-6)

For simplicity, we have rewritten the rate constant to include the stoichiometric coefficient $(k'_1 = \frac{15}{8}k_1)$. In the derivation of eq S6, we assumed that V is constant as Q varies. Again, following a previous treatment (Berner, 1978), the frequency that the watershed is flushed, Q/V, is therefore k_f (yr⁻¹) and the inverse of k_f is the residence time for water in the watershed. Conceptualizing the watershed as a one-dimensional chemical reactor in these equations, we furthermore consider the flushing frequency in terms of runoff q (m yr⁻¹) along an average representative flowpath of length z: $q = zk_f$.

Both of the terms in the denominator of eq. B-6 are related to the Damköhler number, Da, for a watershed:

$$Da = \frac{k_1'}{k_f} = \frac{k_1'z}{q}$$
(B-7)

In effect, Da is the ratio of the characteristic time scale of advection divided by that of dissolution. When $Da \gg 1$, reaction is fast compared to transport $(k'_1 \gg k_f)$ and the system is transport-limited but when $Da \ll 1$ $(k'_1 \ll k_f)$, the system is kinetic-limited. For chemical engineers, Da is usually expressed as a function of the length of the chemical reactor z. For the simple approximation for a watershed presented here, z is the length of the weathering flowpath (Brantley and Lebedeva, 2021). Conceptually, for kinetic-limited oxidation (where $Da \ll 1$), water leaves the watershed before it reaches equilibrium for the mineral reaction but for transport limitation where $Da \gg 1$ water leaves the watershed after equilibration. We can then substitute eq. B-7 into B-6, which results in:

$$C_{sulf} = \frac{C_{sulf}^{max, pred} Da}{Da + 1} = \frac{C_{sulf}^{max, pred} Dw}{Dw + q}$$
$$Da = \frac{Dw}{q}$$
$$Dw = k_1' z$$

(B-8a,b,c)

This treatment is directly comparable to another model derivation (Maher and Chamberlain, 2014). Maher and Chamberlain (2014) define a new term Dw as the Damköhler coefficient (m yr⁻¹). Eq. B-8a is mathematically identical to their solute production model (Maher and Chamberlain, 2014) (assuming an initial concentration of zero), although they use C^{eq} (i.e., concentration of solute in equilibrium with the bedrock) instead of C^{max} in their model. In later

iterations of the model (Ibarra et al., 2016), they replace C^{eq} with C^{max} , which is the empirical maximum solute concentration. Their results for weathering reactions in many watersheds (Ibarra et al., 2016) show that C^{max} is often less than what would be expected at equilibrium. Based on this observation, we also replace $C^{max,pred}_{sulf}$ (a theoretical equilibrium value) with $C^{max,obs}_{sulf}$ (an empirical, observed value) in eq. B-8a, which results in the final equation used in the main text:

$$C_{sulf} = \frac{c_{sulf}^{max,obs} Dw}{Dw+q}$$
(3-2)

B.2 Logistic Regression for Coal

As a watershed gets larger, we would expect the probability that the watershed integrates coal-bed lithology to increase. We tested this hypothesis by utilizing a logistic regression model. Logistic regression models work by fitting explanatory variables (i.e., drainage area) to binary responses (i.e., a watershed contains coal or does not). Our logistic regression model takes the form of the following equation:

$$P = \frac{e^{(b_0 + b_1 X_1)}}{1 + e^{(b_0 + b_1 X_1)}}$$

$$\ln\left(\frac{P}{1-P}\right) = b_0 + b_1 X_1 \tag{B-9a,b}$$

Here, *P* is the probability that the watershed contains coal, b_0 is a scaler intercept parameter, b_1 is the slope coefficient, and X_1 is the log-transformed drainage area of a watershed. Eq. B-9b is the linearization of eq. B-9a, which we use to fit the model. The result of the logistic regression is a probability distribution relating drainage area to coal containing lithology. For this analysis, we utilized delineated watersheds from the National Hydrography Dataset (NHD) and calculated the drainage area and percent coal lithology for each of the watersheds within the SRB (n = 335). Watersheds were then assigned a value of 1 or 0 if it did or did not contain any coal, respectively. After fitting the logistic regression, we set *P* equal to 0.5 and solve for X_I to determine the scaling threshold for when a watershed is more likely than not to contain coal. We calculated the threshold to be > 1,355 km².

B.3 Supplemental Tables

Analyte	Endmember	Shaver's Creek	Juniata River	Susquehanna River
	1	12.5 ± 3.3	6.4 ± 1.6	4.2 ± 1.7
Ca ²⁺ /SO ₄ ²⁻	2	2.4 ± 0.5	1.7 ± 1.6	3.3 ± 1.4
	3	0.9 ± 0.7	1.7 ± 1.2	1.1 ± 0.4
	1	3.7 ± 1.0	1.3 ± 0.3	2.3 ± 0.9
Mg^{2+}/SO_4^{2-}	2	0.1 ± 0.1	0.3 ± 0.3	0.5 ± 0.4
	3	1.3 ± 0.3	0.3 ± 0.2	0.4 ± 0.3
	1	0.1 ± 0.0	1.1 ± 0.8	1.7 ± 1.1
Na^{+}/SO_{4}^{2-}	2	7.4 ± 1.8	8.0 ± 1.5	6.7 ± 3.1
	3	0.0 ± 0.0	1.4 ± 1.0	0.3 ± 0.3
	1	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.2
K^+/SO_4^{2-}	2	0.5 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
_	3	0.3 ± 0.1	0.5 ± 0.1	0.1 ± 0.1
	1	0.0 ± 0.0	1.4 ± 1.0	1.2 ± 1.1
Cl ⁻ / SO ₄ ²⁻	2	8.3 ± 2.1	9.7 ± 1.8	7.7 ± 3.6
	3	0.5 ± 0.1	0.9 ± 1.0	0.6 ± 0.4
	1	0.0 ± 0.0	0.1 ± 0.2	0.0 ± 0.0
NO3 ⁻ / SO4 ²⁻	2	0.0 ± 0.0	0.2 ± 0.2	0.0 ± 0.0
	3	1.1 ± 0.3	1.4 ± 0.4	0.8 ± 0.3

Table **B-1**: NMF-derived endmember chemistries for sites located along the mainstem of Shaver's Creek, Juniata River, and Susquehanna River.

Site ID	Location	Type	[SO4 ²⁻]	$\delta^{34}S$	
Site ID	Location	туре	(mg/L)	mean	error
SS3	Shaver's Creek	Surface Water	3.9	4.91	0.01
SS4	Shaver's Creek	Surface Water	4.0	5.02	0.07
SS6	Shaver's Creek	Surface Water	5.8	4.93	0.01
SS7	Shaver's Creek	Surface Water	9.1	4.63	0.03
SS8	Shaver's Creek	Surface Water	11.3	4.46	0.01
SS67	Shaver's Creek	Surface Water	11.3	4.78	0.00
SS9	Shaver's Creek	Surface Water	12.1	4.57	0.02
SS10	Shaver's Creek	Surface Water	12.1	4.59	0.03
SS11	Shaver's Creek	Surface Water	22.4	9.06	0.07
SS12	Shaver's Creek	Surface Water	21.4	9.57	0.06
SS19	Shaver's Creek	Surface Water	22.1	9.91	0.04
SS20	Shaver's Creek	Surface Water	19.8	9.18	0.07
SS21	Shaver's Creek	Surface Water	21.2	8.98	0.01
SS25a	Shaver's Creek	Surface Water	25.4	12.55	0.00
SCAL	Shaver's Creek	Surface Water	6.5	4.23	0.11
CFW4	Cole Farm	Groundwater	24.4	3.90	0.03
HV3	Garner Run	Groundwater	5.3	5.63	0.04
GR	Garner Run	Surface Water	5.3	5.16	0.05
SH	Shale Hills	Surface Water	9.0	-0.76	0.06
CZMW10	Shale Hills	Groundwater	12.3	-2.86	0.09
CFW1	Cole Farm	Groundwater	34.5	9.24	0.07

Table **B-2**: Concentrations of sulfate and sulfur isotope values for samples collected in this study.

Site ID	Latitude	Longitude	Drainage Area (km²)	Percent Coal	Data Source	USGS Site Name	USEPA Site Name
SH	40.66	-77.91	0.08	0	SSHCZO		
SCAL	40.67	-77.90	15.8	0	SSHCZO		
SCCF	40.63	-77.94	40.3	0	SSHCZO		
SCO	40.61	-78.01	121	0	SSHCZO		
						USGS-	21PA_WQX-
J2	40.22	-78.27	1,958	3.3	WQP	0156200	WQN0223
71	40.40	77.10	0.606	2.2	WOD	USGS-	21PA_WQX-
JI	40.48	-77.13	8,686	3.3	WQP	01567000	WQN0214
						01502771	
						USGS-	21PA WOX-
S 9	42.04	-75.80	5,780	0	WOP	01503000	WON0306
			,			USGS-	21PA_WQX-
S 8	41.77	-76.44	20,194	0.5	WQP	01531500	WQN0305
						USGS-	21PA_WQX-
S 7	41.46	-75.85	24,450	1	WQP	01534090	WQN0323
96	41.25	75.00	25.706	2.0	WOD	USGS-	21PA_WQX-
86	41.25	-75.88	25,796	2.9	WQP	01536500	WQN0302
\$5	10.96	-76.62	29.060	1	WOP	01540500	21PA_wQA- WON0301
35	40.90	-70.02	29,000	+	WQI	USGS-	WQN0501
						01553990.	
						USGS-	21PA_WQX-
S4	40.83	-76.83	47,397	16.1	WQP	01554000	WQN0203
						USGS-	21PA_WQX-
S 3	40.25	-76.89	62,419	13.5	WQP	01570500	WQN0202
~ •						USGS-	21PA_WQX-
S 2	40.05	-76.53	67,314	12.7	WQP	01576000 USCS	WQN0201
S 1	39.66	-76.17	70,189	12	WOP	01578310	

Table **B-3**: Sampling locations and data sources for sites in the Susquehanna River Basin. Multiple USGS and USEPA sites are co-located for each of the sites with data from the WQP.

fur depletion (i.e., τ_{sulfur}) for
Formation
Clinton Group
Bloomsburg and Mifflintown
Formations
Bloomsburg and Mifflintown

Table B-4:Sampling locations, lithology, and calculated sulfsamples collected in outcrops in Shaver's Creek. rock

Latitude Longitude τ_{sulfur}

ID

Roadcut	40.63	-77.94	-1	Clinton Group
				Bloomsburg and Mifflintown
CF-SC1	40.64	-77.94	-1	Formations
				Bloomsburg and Mifflintown
CF-SC2	40.64	-77.94	-1	Formations
	10 61	77 0 1		Bloomsburg and Mifflintown
CFW7	40.64	-77.94	-1	Formations
SS7	40.64	-77.93	0	Clinton Group
0000	10 (1	70.01	0	Bloomsburg and Mifflintown
SS20	40.61	-/8.01	0	Formations
SS21	40.58	-78.05	0	Wills Creek Formation
	40.61	79.01	0	Bloomsburg and Mifflintown
SCO-Bedrock	40.61	-/8.01	0	Formations Bloomsburg and Mifflintown
SCO Core	40.61	-78.01	0	Formations
SS0 5	40.63	77.04	1	Clinton Group
0.9.0	40.05	-77.94	-1	Bloomsburg and Mifflintown
Outcrop 2	40.63	-77.94	-1	Formations
Outcrop 3	40.66	-77 90	-0.55	Clinton Group
R26 chin	40.69	-77.90	-0.2	Clinton Group
MBS #1	40.65	-77 92	-1	Clinton Group
MBS #2	40.65	-77 92	-1	Clinton Group
MBS #2	40.66	-77 91	-0.8	Clinton Group
MBS #4	40.66	-77 91	-1	Clinton Group
MBS #5	40.66	-77.91	_1	Clinton Group
MBS #6	40.65	77.02	-1	Clinton Group
MDS #0	40.03	-77.92	05	Clinton Group
NIDS #7	40.03	-77.92	-0.5	Clinton Group
R20 #1	40.69	-77.90	-0.85	Clinton Group
R26 #2	40.69	-77.90	-0.9	Clinton Group
LR #1	40.67	-77.94	-1	Clinton Group
LR #2	40.67	-77.94	-1	Clinton Group
LD #2	10 67	77.02	1	Bloomsburg and Mifflintown
LR #3	40.67	-77.93	-1	Formations
SCR #1	40.65	-77.92	-1	Clinton Group
SCR #2	40.65	-77.92	-0.75	Clinton Group
SCR #3	40.64	-77.93	-1	Clinton Group
				Bloomsburg and Mifflintown
SCR #4	40.64	-77.93	-1	Formations



Figure **B-1**: Map showing the 29 locations where in-place bedrock was sampled from outcrops in Shaver's Creek where presence or absence of pyrite, partially oxidized pyrite, and fully oxidized pyrite was measured on drilled or hammered samples using electron microscopy and S analysis. Colors represent extent of oxidation at land surface, where white is fully oxidized (n = 16), pink is partially oxidized (n = 7), and red is unoxidized (n = 6). Location and lithologic information for each sampling site can be found in Table **B-4** in Appendix B.3.



Figure **B-2**: (A) Map showing the location of the outlets of the catchments used in the logistic-regression analysis as well as the distribution of coal in the SRB. (B) Plots showing percent of the drainage area covered by coal (upper) and the probability that a watershed contains coal (lower) as a function of drainage area in the SRB.



Figure **B-3**: Boxplots comparing $C_{sulf}^{max,obs}$ (A) and the power law exponent (i.e., b-value) (B) for watersheds with and without coal-lithologies.



Figure **B-4**: Boxplot comparing $C_{sulf}^{max,obs}$ between watersheds that do (gray) and do not (white) contain coal across various watershed sizes in the Western US.

Appendix C

Supplemental Information for Chapter 4

C.1 Sensitivity Analysis

As discussed in Section 4.3.2 in the main text, the HI threshold we choose to define the cutoff for RL weathering varies between methods used to determine the threshold (e.g., values range from HI = 0.5 to HI = 0.62). Here we test how changing our threshold changes Ea (see section 3.6.1). For this analysis, we fit eq. 4-7 to F_{SIO_2} for different groups of "wet" watersheds defined by a variety of thresholds. For simplicity, we will only fit the linear-MAP correction model to each group (i.e., model 8 in Table **C-6**; $\alpha = 0$ and $\beta = 1$). We test HI values ranging from 0.45 to 0.75 (in 0.5-unit increments; Table **C-6**) as threshold values. We find that Ea is relatively insensitive to the selected threshold value and remains relatively constant across all tested HI values (Table **C-6**). Ea for these tests range from 47 ± 7 kJ mol⁻¹ to 61 ± 8 kJ mol⁻¹. All Ea values are within error of each other and, therefore, are not significantly different.

Because RL weathering is, by definition, limited by runoff in a watershed, it might be more intuitive to set a threshold based on runoff rather than HI. Practically, however, runoff is not measured everywhere, thus, selecting a threshold based on runoff would eliminate upscaling to ungagged watersheds. It is true that there are global datasets available for runoff; however, these datasets either 1) define runoff as MAP-PET or 2) are spatially coarse. The issue with (1) is that, as discussed earlier PET is often greater than MAP; therefore, these datasets typically define runoff in these areas as zero. In reality, these watersheds still experience runoff although low and typically seasonal. The issue with (2) is that coarse models typically are unresolved at the hillslope and watershed scales. Nonetheless, we can still test how selecting a threshold based on runoff would change Ea for our sites. Visually, we see that a break in slope for F_{SiO_2} vs q (Figure **4-6C**) occurs at $\sim q = 0.1$ to 0.3 m yr⁻¹. We test q values ranging from 0.1 to 0.3 m yr⁻¹ (in 0.5 m yr⁻¹ increments; Table **C-6**) as threshold values and found, again, that Ea remains relatively constant. Ea for these thresholds range from 48 ± 10 kJ mol⁻¹ to 62 ± 9 kJ mol⁻¹ (Table **C-6**). These values are all insignificantly different than each other and are consistent with the Ea values determined for the HI thresholds.

Given the issues with utilizing q as a threshold for RL weathering, a natural alternative might be MAP. In the man text, we chose HI opposed to MAP because HI incorporated bot MAP and PET. Here, we test MAP thresholds. Again, visually, we see that a break in slope for F_{SiO_2} vs MAP (Figure **4-6B**) occurs at ~MAP = 600 to 1000 mm yr⁻¹. We test MAP values ranging from 600 to 1000 mm yr⁻¹ (in 500 mm yr⁻¹ increments; Table **C-6**) as threshold values. Ea for these thresholds range from 49 ± 8 kJ mol⁻¹ to 64 ± 8 kJ mol⁻¹ (Table **C-6**). Again, these values are all insignificantly different than each other and are consistent with the Ea values determined for the HI and q thresholds. Overall, we see that our analysis is insensitive to the selection value of the RL threshold as long as the threshold is relatively reasonable given plots in Figure **4-6**.

C.2 Shale Age

Some shales contain primary smectite in the bedrock and some do not; therefore, the trend we observe in the activity diagrams (Figure **4-5**) might be related to differences in the parent composition of the shale rather than differences in weathering regime. Hower et al. (1976) show that young shales (i.e., Mesozoic and Cenozoic) tend to have smectite while old shales (i.e., Paleozoic) tend to have illite. This variation in mineralogy can be attributed to increases in burial metamorphic grade with time. To test if smectite as a primary versus secondary mineral (age) is an important factor when considering weathering regimes, we classify each watershed as

Mesozoic, Cenozoic, or Paleozoic based on the era of the shale reported in the SGMC lithology database.

We found that for watersheds with HI < 0.55, 78/82 watersheds have Cenozoic (n = 34) or Mesozoic (n = 44) shales, and only 4 watersheds have Paleozoic shales. For watersheds with HI > 0.55, 57/60 watersheds have Paleozoic shales and only 2 watersheds have Mesozoic shales. Overall, In the United States, dry watersheds tend to have young shales and wet watersheds tend to have old shales. The 4 watersheds with Paleozoic shales and HI < 0.55 fall within the upper bound of RL weathering and fall along the general trendline for F_{SiO_2} vs q for RL weathering. The 2 watersheds have Mesozoic shales and HI > 0.55 follow the trendline for F_{SiO_2} vs MAT for KL/TR weathering. Although there are not many wet Cenozoic/Mesozoic shales in the United States due to the geography of the country, RL weathering is unlikely to be controlled by the underlying bedrock and is more likely to be controlled by long term climate. It is possible that young vs. old shale could change the equilibrium concentration of SiO₂; however, that value does not change the rate limiting step of the weathering reaction.

Table C-1: Full model results for all watersheds.

ln(K)	Ea	α	β	\mathbb{R}^2	р
0.09 ± 0.09	$57.53 \pm 18.47 **$	0.06 ± 0.11	$1.93 \pm 0.26^{**}$	0.62	5.75E-31
$0.22\pm0.1*$	$127.16 \pm 18.72^{**}$	$0.6\pm0.1^{**}$	0	0.47	7.46E-21
0.06 ± 0.08	$56 \pm 18.22^{**}$	0	$2.03 \pm 0.2^{**}$	0.62	6.79E-31
0.1 ± 0.09	0	0.01 ± 0.11	$2.35 \pm 0.23^{**}$	0.6	6.84E-29
-0.11 ± 0.1	$162.91 \pm 20.14^{**}$	0	0	0.32	2.87E-13
$0.33 \pm 0.12^{**}$	0	$0.8\pm0.11^{**}$	0	0.3	4.63E-12
0.09 ± 0.08	0	0	$2.37 \pm 0.17^{**}$	0.6	6.88E-29
$-6.75 \pm 0.08 **$	$110.36 \pm 16.49 ^{**}$	0	1	0.25	5.18E-10
$* \cdot n < 0.05$					

* : *p* < 0.05 **: *p* < 0.01

ln(K)	Ea	α	β	R ²	р
$2.12 \pm 0.27 **$	$-82.96 \pm 30.71 **$	$1.08 \pm 0.18^{**}$	$4.86 \pm 0.49^{**}$	0.66	5.74E-20
0.25 ± 0.3	$82.19 \pm 38.92*$	$0.92 \pm 0.27 ^{**}$	0	0.23	9.17E-06
$1.02 \pm 0.25^{**}$	-28.43 ± 35.42	0	$4.6 \pm 0.59^{**}$	0.5	2.23E-13
$1.86 \pm 0.27 ^{**}$	0	$0.94 \pm 0.18^{**}$	$4.14 \pm 0.43^{**}$	0.63	2.10E-18
$-0.61 \pm 0.18 **$	$121.58 \pm 39.62^{**}$	0	0	0.11	0.002971038
0.23 ± 0.31	0	$1.09 \pm 0.26^{**}$	0	0.18	9.11E-05
$0.97 \pm 0.24 ^{**}$	0	0	$4.34 \pm 0.49^{**}$	0.5	3.10E-13
$-6.98 \pm 0.16^{**}$	$88.97 \pm 36.05*$	0	1	0.07	0.015812646

Table C-2: Full model results for sites with HI < 0.55.

* : p < 0.05**: p < 0.01

194

ln(K)	Ea	α	β	R ²	р
$0.65 \pm 0.1^{**}$	$56.2 \pm 8.14 **$	$0.12\pm0.06*$	0.24 ± 0.26	0.5	2.57E-10
$0.74 \pm 0.04^{**}$	$55.02 \pm 8.03 ^{stst}$	$0.16 \pm 0.03^{**}$	0	0.49	4.05E-10
$0.51 \pm 0.08^{**}$	$55.71 \pm 8.37 **$	0	$0.65 \pm 0.16^{**}$	0.46	2.29E-09
$0.93 \pm 0.13^{**}$	0	0.1 ± 0.07	$\textbf{-0.04} \pm 0.34$	0.08	0.032735
$0.78 \pm 0.05^{**}$	$46.16\pm9^{**}$	0	0	0.31	3.50E-06
$0.92 \pm 0.05^{**}$	0	$0.1\pm0.04*$	0	0.08	0.032951
$0.8 \pm 0.09^{**}$	0	0	0.34 ± 0.21	0.04	0.104431
-6.36 ± 0.04**	$60.76 \pm 8.26^{**}$	0	1	0.48	7.31E-10

Table C-3: Full model results for sites with HI > 0.55.

* : p < 0.05 **: p < 0.01

slope > 10° .			
β	R ²	р	

ln(K)	Ea	α	β	R ²	р
0.09 ± 0.26	$89.36 \pm 20.97 ^{stst}$	0.17 ± 0.22	0.86 ± 0.52	0.75	1.61E-05
0.28 ± 0.25	$59.88 \pm 11.5^{**}$	$0.42\pm0.17*$	0	0.69	6.85E-05
0.15 ± 0.24	$97.37 \pm 17.82^{**}$	0	$1.13\pm0.38*$	0.73	2.25E-05
0.64 ± 0.34	0	$0.65\pm0.29*$	$\textbf{-1.05} \pm 0.41 \texttt{*}$	0.36	0.013598
$0.86 \pm 0.06^{**}$	$53.75 \pm 13.03^{**}$	0	0	0.55	0.001028
0.61 ± 0.4	0	0.22 ± 0.29	0	0.04	0.450478
$1.22 \pm 0.24 **$	0	0	$\textbf{-0.54} \pm 0.38$	0.12	0.181795
$-6.49 \pm 0.05 **$	$92.31 \pm 10.05^{**}$	0	1	0.86	2.63E-07
* : <i>p</i> < 0.05					
**: <i>p</i> < 0.01					

Table C-4: Full model results for sites with HI > 0.55 and

•			

 \mathbf{R}^2 ln(K) Ea β α р $0.83 \pm 0.17 **$ $41.18\pm16.8*$ $0.3\pm0.11^{**}$ 0.35 ± 0.48 0.49 1.31E-05 $0.93\pm0.1^{**}$ $44.57 \pm 15.97 ^{**}$ $0.35 \pm 0.08^{**}$ 0 0.48 1.73E-05 $0.46 \pm 0.12^{**}$ 32.83 ± 18.42 $1.2 \pm 0.42^{**}$ 5.99E-04 0.34 0 $0.88 \pm 0.18^{**}$ 0 $0.25\pm0.12^*$ 0.68 ± 0.51 0.37 2.72E-04 $0.69 \pm 0.1^{**}$ $44.49 \pm 20.06 *$ 0 0 0.15 0.034528 $1.11 \pm 0.08 **$ 0 $0.35 \pm 0.09^{**}$ 0 0.33 7.12E-04 $0.55 \pm 0.11^{**}$ 0 0 $1.36 \pm 0.42^{**}$ 0.26 0.003163 0 0.059385 $-6.22 \pm 0.09 **$ 34.77 ± 17.72 1 0.12

Table C-5: Full model results for sites with HI > 0.55 and slope $< 5^{\circ}$.

* : *p* < 0.05

**: *p* < 0.01

Test	Ea (kJ mol ⁻¹)	R ²	p
HI > 0.45	50 ± 8	0.35	< 0.0001
HI > 0.5	47 ± 7	0.38	< 0.0001
HI > 0.55	61 ± 8	0.48	< 0.0001
HI > 0.6	58 ± 9	0.44	< 0.0001
HI > 0.65	58 ± 9	0.44	< 0.0001
HI > 0.7	59 ± 9	0.44	< 0.0001
HI > 0.75	58 ± 9	0.45	< 0.0001
q > 0.1	48 ± 10	0.26	< 0.0001
q > 0.15	51 ± 8	0.38	< 0.0001
q > 0.2	61 ± 8	0.48	< 0.0001
q > 0.25	62 ± 9	0.49	< 0.0001
q > 0.3	61 ± 9	0.51	< 0.0001
MAP > 600	64 ± 13	0.22	< 0.0001
MAP > 650	57 ± 10	0.3	< 0.0001
MAP > 700	49 ± 8	0.34	< 0.0001
MAP > 750	56 ± 8	0.42	< 0.0001
MAP > 800	56 ± 8	0.43	< 0.0001
MAP > 850	58 ± 8	0.47	< 0.0001
MAP > 900	58 ± 8	0.46	< 0.0001
MAP > 950	62 ± 8	0.51	< 0.0001
MAP > 1000	64 ± 8	0.56	< 0.0001

Table C-6: Sensitivity analysis for different thresholds defining RL weathering.

C.4 Supplemental Figures



Figure C-1: Activity diagrams of the chlorite-smectite-kaolinite-gibbsite system for Mg-SiO₂. Blue arrow shows the expected evolution of solute composition for the dissolution of chlorite. Red arrow shows the expected evolution of solute composition when evapotranspiration removes water from the system after equilibration with chlorite. Schematic arrows are drawn based on batch calculations in Geochemists Workbench.

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Featured Publications

- Shaughnessy, A. R., Prener, C. G., & Hasenmueller, E. A. (2019). An R package for correcting continuous water quality monitoring data for drift. *Environmental monitoring and* assessment, 191(7), 445.
- Shaughnessy, A.R., Sloan, J.J., Corcoran, M.J., Hasenmueller, E.A. (2019). Sediments in Agricultural Reservoirs Act as Sinks and Sources for Nutrients Over Various Timescales. *Water Resources Research*, 55(7), 5985-6000.
- Shaughnessy, A.R., Wen, T., Niu, X., Brantley, S.L. (2019). Three Principles to Use in Streamlining Water Quality Research through Data Uniformity. *Environmental Science* and Technology, 53(23), 13549.
- Shaughnessy, A. R., Gu, X., Wen, T., & Brantley, S. L. (2021). Machine learning deciphers CO₂ sequestration and subsurface flowpaths from stream chemistry. *Hydrology and Earth System Sciences*, 25(6), 3397-3409.
- Shaughnessy, A.R., Forgeng, M.J., Wen, T., Gu, X., Hemmingway, J., Bratley, S.L. (2022). Linking Stream Chemistry to Subsurface Redox Architecture. *Submitted. (Water Resources Research)*

Invited Seminars

Karst Water Institute: Frontiers in Karst Colloquium Series (2021). Date of presentation: 21 April, 2021. https://karstwaters.org/conferences/frontiers-in-karst-colloquium-series/

Zhejiang University: Earth Data Webinar (2022). Invited Talk. Date of Presentation: 23 March 2022.