PALEOCLIMATE CONSTRAINTS ON TERRESTRIAL HYDROCLIMATE,
SILICATE WEATHERING, AND THE CARBON CYCLE

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DOCTOR OF PHILOSOPHY

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Includes supplemental files:

1. Chapter 1 Lake Model Example Code (*Ibarra_Chapter1_ExampleCode.zip*)
2. Chapter 2 Lake Model Example Code (*Ibarra_Chapter2_ExampleCode.R*)
3. Chapter 2 Compilation Tables (*Ibarra_Chapter2_Tables.xlsx*)
4. Chapter 3 Concentration-Discharge Example Code (*Ibarra_Chapter3_ExampleCode.zip*)
5. Chapter 3 Results Tables (*Ibarra_Chapter3_Tables.xlsx*)
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ABSTRACT

Maintenance of a habitable planet requires connections and balance among Earth's biogeochemical cycles. Further, the strength of the feedbacks and couplings determines the stability of conditions in the surface climate system necessary for the evolution of life. Records of Earth's past climate, paleoclimate records, provide constraints beyond the reach of the instrumental record on the directionality, strength and co-evolution of key Earth system cycles. This includes the geologic carbon cycle, the water cycle and the planet's energy balance.

Crucially, the geography, topography and lithology of Earth's continents have two important features that are the focus of this dissertation. First, the continents provide boundary conditions that determine global circulation and hydroclimate patterns that couple Earth's water and carbon cycles (**Chapters 1 and 2**). Second, the land surface provides a stabilizing negative feedback in the form of silicate weathering fluxes (**Chapters 3 and 4, and Appendix E**), balancing the long-term carbon cycle through alkalinity and solute delivery to the oceans, and subsequent carbonate burial. In this dissertation I use data, observations and modeling to place mechanistic constraints on how interactions between Earth's surface and long-term biogeochemical cycles maintain balance and habitable conditions in our climate system conducive for the evolution of life.

Fundamental to understanding our climate system is predicting the anticipated sign of terrestrial hydroclimate change during periods of climatic change. To this end I have investigated the regional response of hydroclimate change using paleoclimate records from mid-latitude lake systems. First, in **Chapter 1**, I have developed an inverse

model to quantify how a mid-latitude lake system in Asia, the Songliao Basin, responded to a transient warming event during the Cretaceous. This model was also applied to a Holocene ostracod record from Lake Miragoane, Haiti. Second, in **Chapter 2**, I compile spatial distributions and size estimates of pluvial lake systems in western North America during the Pliocene-Pleistocene. By imposing mass and energy balance constraints (*sensu* Budyko) I forward modeled lake area distributions to demonstrate that now-arid western North America was wetter during both past colder and warmer periods during the Pliocene-Pleistocene, a result not predicted for future warming scenarios. Geologic observations primarily suggest wetter conditions globally during warmer-than-present periods. Importantly, this observation is a requirement for the operation of the stabilizing negative feedback between silicate weathering and climate.

Understanding the factors that control silicate weathering rates is fundamental to constraining the evolution of Earth's carbon cycle over geologic timescales. One challenge for reconstructing past weathering rates is determining the reactivity of Earth's surface. In **Chapter 3** I have quantified the reactivity of modern basalt and granite catchments using a process-based solute production model and concentration-discharge weathering relationships. This approach provides mechanisms that link runoff (i.e., terrestrial hydroclimate changes that were the focus of Chapters 1 and 2) with the distribution of global sub-aerial silicate lithologies. In **Chapter 4** I utilize an emerging metal isotope system, lithium isotopes, to investigate the terrestrial weathering response to a large perturbation in the carbon cycle during the Cretaceous. We determine that the background-state of the Cretaceous weathering system was more congruent and, hence, more sensitive to perturbations in the carbon cycle than during the Neogene. Finally, in

Appendix E I have quantified how step-wise geologic evolution of land plants strengthened the silicate weathering feedback over the Phanerozoic. I have developed a new reactive transport framework for evaluating the relative plant-controlled roles of hydrologic versus thermodynamic mechanisms that influence the coupling between the water cycle and silicate weathering fluxes on a continental scale.

The results described in this dissertation constrain links between two connected portions of the exogenic Earth system. I have provided constraints for how the land surface records past changes in regional atmospheric circulation patterns, as well as regional water and energy balances. Further, using reactive transport modeling, I have placed new constraints on the role of plants and lithology in determining the coupling between terrestrial hydroclimate and weathering. Collectively these results suggest that the surface Earth system, our planet's fluid envelope, has been progressively tuned by the advent of continents and the evolution of life.

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PALEOCLIMATE CONSTRAINTS ON TERRESTRIAL HYDROCLIMATE, SILICATE WEATHERING, AND THE CARBON CYCLE

INTRODUCTION

Maintaining habitable conditions in the exogenic Earth system over geologic time requires balance and feedbacks among Earth's biogeochemical cycles (e.g., Urey, 1952; Walker et al., 1981; Berner and Caldeira, 1997; Sleep and Zahnle, 2001; Payne and Kump, 2007; Caves et al., 2016; Bachan et al., 2017). Further, the establishment of subaerial continents, a bimodal hypsometry and an oxidized crust (e.g., Holland, 2002; Hayes and Waldbauer, 2006; Lee et al., 2018), as well as the evolution of life (e.g., Volk, 1987; Knoll, 2003; Sleep and Bird, 2008; Lenton et al., 2014; Boyce and Lee, 2017), has likely stabilized the climate system over geologic time. In this dissertation I have investigated how the geography, topography and lithology of Earth's continents provide boundary conditions and couplings that have progressively tuned and stabilized the Earth surface. The introduction to this dissertation includes: 1) a brief historical perspective on the use of geologic observations to infer past climatic conditions and links to the biosphere; and 2) a discussion of how modern scientific methods, such as advances in isotope geochemistry, have enhanced our ability to quantitatively trace surface Earth system processes over geologic time.

In this dissertation I have sought to investigate the Earth system in the spirit of previous scientific advances by using first-order observations of modern and past terrestrial systems to reconstruct key relationships that influence the co-evolution of

Earth's biosphere, hydrosphere and lithosphere. Specifically, I have focused on using the water balance recorded by terminal lake systems to reconstruct past changes in hydroclimate (**Chapters 1 and 2**), and used modeling approaches to investigate the influence of land plants and lithology on silicate weathering fluxes (**Chapter 3 and Appendix E**). Additionally, I have also investigated the response of terrestrial weathering systems to a large carbon cycle perturbations ~94 millions years ago in the Cretaceous using new isotope measurements (**Chapter 4**).

Examination of the landforms and sediments that cover Earth's continents today suggests considerable environmental change over geologic time. While the terrestrial paleoclimate record is fragmentary and incomplete, it provides direct evidence for changes in climate and environmental conditions. Earth scientists have long made observations suggesting dynamic changes in Earth's past climate, and recognized the influence of continental paleogeography and paleotopography in shaping terrestrial environmental conditions. Many of these inferences were established long before the advent of modern mass spectrometers, satellite imagery and coring technologies.

An example pertinent to Chapter 2 of this dissertation (Ibarra et al., 2018) is the geologic exploration of western North America in the 18th and 19th centuries. Early explorers of the American west documented lacustrine shorelines in the terminal basins of the Great Basin (see review by Orme, 2008). Study of these shorelines was subsequently first formally documented in detail by pioneering American geologists, J.W. Powell, G.K. Gilbert and I.C. Russell (e.g., Gilbert, 1875; 1884; 1890; Russell, 1884; 1885; 1889), who in doing so contributed to many classic Earth science concepts such as uniformitarianism, isostasy and diastrophism, and documentation of glacial-

interglacial cycles (Hunt, 1980; Orme, 2008). These and other Quaternary lakes, and the subsequent documentation of older Cenozoic lake systems in the American west and elsewhere, remain an active avenue of research to this day (e.g., Antevs, 1925; 1948; Hubbs and Miller, 1948; Broecker and Kaufman, 1965; Mifflin and Wheat, 1979; Benson and Paillet, 1989; Carroll and Bohacs, 1999; Hudson and Quade, 2013; Munroe and Laabs, 2013; Pound et al., 2014; Reheis et al., 2014; Ibarra et al., 2014).

Study of Earth's past climate was transformed by the development of isotope measurements and theory following World War II (Urey, 1974; Bigeleisen and Mayer, 1947). The use of isotope systems, as demonstrated in Chapters 1 and 4 of this dissertation, are now commonplace for reconstructing past climate states. Beginning with the measurement of oxygen, hydrogen and carbon isotopes pioneering geochemists, including Harold Urey and Harmon Craig, made the first measurements on mineral and water samples to make paleoenvironmental reconstructions using both marine and terrestrial materials (e.g., Urey, 1947; 1948; Urey et al., 1951; Craig, 1953; Epstein and Mayeda, 1953; Dansgaard, 1954; 1964; Craig and Gordon, 1965). Simultaneously radiometric age determination, primarily using radiocarbon dating, was developed and applied to terrestrial and marine carbonates (e.g., Arnold and Libby, 1951; Libby, 1952; 1954; Antevs, 1955; Broecker and Orr, 1958), allowing for absolute age determinations to test concepts such as Milankovitch theory (Milankovitch, 1920; see review by Berger, 1988). In combination with the expansion of ocean drilling efforts in the subsequent decades these isotope measurements lead to the establishment of seminal marine isotope records covering the Pliocene-Pleistocene (e.g., Hays et al., 1976; Shackleton and Opdyke, 1977; Lisiecki and Raymo, 2005), Mesozoic and Cenozoic (e.g., Zachos et al.,

2001; 2008; Payne et al., 2004; Friedrich et al., 2012), and the entire Phanerozoic (e.g., Veizer et al., 1999; Saltzman and Thomas, 2012). However, a key challenge of paleoclimatology has been to produce spatially resolved and temporally constrained changes in past climate from the more fragmentary terrestrial geologic record. Despite the potential for directly reconstructing atmospheric circulation changes and climate using terrestrial sediments (e.g., Mifflin and Wheat, 1979; Chamberlain et al., 1999; Reheis, 1999; Mulch et al., 2006; Ibarra et al., 2014; Maher et al., 2014; Oster et al., 2015), fundamental knowledge advances from the terrestrial realm have been much more limited thus far.

Reconstructing terrestrial climates in the past may also help refine the predicted impacts of anthropogenic climate change on the terrestrial hydrosphere. This is an important avenue of inquiry because the sensitivity and uncertainty of the terrestrial water cycle to hydrologic cycle intensification under warmer conditions (e.g., Huntington, 2006; Huntington et al., 2018), and the potential impacts of this intensification to human and natural systems, is still actively debated (Hoekstra and Mekonnen, 2012; Scheff and Frierson, 2014; Sherwood and Fu, 2014). For example, a long-standing paradigm proposed that “dry regions get drier and wet regions get wetter” in response to future warming (for further discussion see Greve et al., 2014). However recent historical studies have demonstrated mixed global and regional contrasting responses (e.g., Seager et al., 2007; Dai, 2011; Greve et al., 2014). Similarly, paleoclimate reconstructions have demonstrated a varied regional response to climatic changes over many different timescales caused by changes in moisture delivery mechanisms and recycling over continents (e.g., Munroe and Laabs, 2013; Chamberlain et al., 2014; Ibarra et al., 2014;

Oster et al., 2015; Caves et al., 2015; 2017). Most significantly, the mid-latitude desert regions, such as the western United States, have been observed to be wetter during both hotter (mid-Pliocene) and colder (Pleistocene glacial periods) periods of Earth's recent history (Reheis, 1999; Winnick et al., 2013; Pound et al., 2014; Oster et al., 2015; Burls and Federov, 2017; Ibarra et al., 2018).

These hydrologic cycle changes at local, regional and continent scales are the focus of **Chapters 1 and 2**, and **Appendix E** of this dissertation (Ibarra and Chamberlain, 2015; Ibarra et al., 2018; Ibarra et al., *Accepted*). Further, changes in the terrestrial water balance also influence the distribution of the regional to continental scale weathering response (e.g., Gibbs and Kump, 1994; von Blanckenburg et al., 2015), the focus of **Chapters 3 and 4**, and **Appendix E** of this dissertation (Ibarra et al., 2016; Ibarra et al., 2017; Ibarra et al., *Accepted*). This weathering response to hydroclimate changes directly links the Earth's water and carbon cycles through the silicate weathering negative feedback (Urey, 1952; Walker et al., 1981; Berner and Caldeira, 1997; Kump and Arthur, 1997; Kump et al., 2000; Maher and Chamberlain, 2014).

This dissertation uses the terrestrial geologic record and process-based modeling to understand how feedbacks and forcings have operated over long timescales (~10,000 to 100,000 years). Paleoclimate records and modeling approaches that I have used have allowed me to provide constraints beyond the reach of the instrumental record and test hypotheses for how the Earth system operates where the signal to noise is large and the sign of change is unequivocal. The following is a brief summary of the chapter contributions that make up this dissertation.

1. In **Chapter 1** (Ibarra and Chamberlain, 2015, *American Journal of Science*) I have developed a new inverse modeling framework to quantify how a mid-latitude lake system in Asia, the Songliao Basin, responded to a transient warming event during the Cretaceous, Oceanic Anoxic Event 3. This work builds on a previous dataset published by Chamberlain et al. (2013). This model was also applied for illustrative purposes to a previously published Holocene record from Lake Miragoane, Haiti.
2. In **Chapter 2** (Ibarra et al., 2018, *Geology*) I compile spatial distributions and size estimates of pluvial lake systems in western North America during the Pliocene-Pleistocene. I forward modeled lake area distributions to demonstrate that now-arid western North America was wetter during past colder and warmer periods during the Pliocene-Pleistocene, a result not predicted for future warming scenarios. Geologic observations primarily suggest wetter conditions globally during warmer-than-present periods; and importantly, this observation is a requirement for the operation of the stabilizing negative feedback between silicate weathering and climate. This analysis was inspired by feedback received on my previous work on Pleistocene Lake Surprise (California) carried out during my undergraduate and masters in Geological & Environmental Sciences (Ibarra et al., 2014, *Geological Society of America Bulletin*).
3. In **Chapter 3** (Ibarra et al., 2016, *Geochimica et Cosmochimica Acta*; Ibarra et al., 2017, *Acta Geochimica*) I have quantified the reactivity of modern basalt and granite catchments using a process-based solute production model and concentration-discharge weathering relationships. I expand on the process-based

solute production model from Maher and Chamberlain (2014) by applying their model to concentration-discharge relationships (see also additional prior and subsequent work: Maher et al., 2009; Maher, 2010; 2011; Maher and Druhan, 2014; von Blanckenburg et al., 2015; Wymore et al., 2017; Winnick and Maher, 2018). The approach and framework we use provides process-based mechanisms that link runoff and hydroclimate changes with the distribution of global sub-aerial silicate lithologies.

4. In **Chapter 4** I utilize a metal isotope system, lithium isotopes, to investigate the terrestrial weathering response to a large perturbation in the carbon cycle during the Cretaceous. I determine that the background-state of the Cretaceous weathering system was more congruent and, hence, more sensitive to perturbations in the carbon cycle than during the Neogene.
5. In **Appendix E** (Ibarra et al., *Accepted, American Journal of Science*) I have quantified how step-wise geologic evolution of land plants strengthened the silicate weathering feedback over the Phanerozoic. I have developed a new reactive transport framework for evaluating the relative plant-controlled roles of hydrologic versus thermodynamic mechanisms that influence the coupling between the water cycle and silicate weathering fluxes on a continental scale.

In sum, the contributions described herein constrain links between two crucial and connected portions of the exogenic Earth system, the water and carbon cycles.

Collectively, they suggest that the exogenic Earth system has been progressively tuned by the advent of continents and the evolution of life.

Contribution Statements and Scientific Result Dissemination

The manuscripts presented here reflect the collaborative nature of Earth science research and were not solely undertaken by myself. In the following section I describe the contributions to each chapter made by the co-authors for each chapter. Further, I state the publication status of each peer-reviewed manuscript and the peer-reviewers, if self-identified during the peer-review process. For each chapter I also describe which scientific conferences the material was presented at prior to and/or subsequent to publication. Following my first-author work I also list all co-authored manuscripts published during my time as PhD student in Earth System Science (encompassing September 2013 to June 2018).

Chapter 1

This chapter was published at the *American Journal of Science* (Ibarra and Chamberlain, 2015). Formal peer-reviews were received from Byron Steinman (University of Minnesota, Duluth) and Jay Quade (University of Arizona). Editor Danny M. Rye (Yale University) handled the peer-review of the manuscript.

C. Page Chamberlain conceived the study and selected the ostracod datasets from previously published literature. Together we co-designed the modeling and mathematical framework, and co-wrote the paper. I implemented the modeling in R, incorporated the Monte Carlo uncertainty propagation and produced all figures. A version of the model presented in this chapter was originally included into NSF Grant EAR-1423967

“Collaborative Research: High-resolution Cretaceous terrestrial climate records of temperature, weathering and hydrologic response to hyperthermals in the Songliao

Basin, China” (PI: C. Page Chamberlain; co-PIs: Stephan A. Graham, Bradley B. Sageman, Alan R. Carroll, Bradley S. Singer).

Prior to publication this chapter was presented at the 2014 Geological Society of America Annual Meeting. Following publication this model was updated for the Songliao Basin using new age constraints and presented at the 2015 Geological Society of America Annual Meeting.

Chapter 2

This chapter was published in *Geology* (Ibarra et al., 2018). Peer-reviews were received from Alan Carroll (University of Wisconsin, Madison) and three anonymous reviewers. Science Editor Mark C. Quigley (University of Melbourne) handled the peer-review of the manuscript. NSF Grant EAR-1450357 to C. Page Chamberlain funded this chapter.

I designed the study in collaboration with the co-authors, carried out the proxy dataset compilation, conducted the quantitative analysis and wrote the manuscript. Jessica L. Oster helped design the study, contributed to the proxy dataset compilation, and assisted in manuscript preparation and editing. Matthew J. Winnick helped design the study, helped conduct the quantitative analysis, and assisted in manuscript preparation and editing. Jeremy K. Caves Rugenstein helped design the study, helped conduct the quantitative analysis, and assisted in manuscript preparation and editing. Michael P. Byrne helped conduct the quantitative analysis and assisted in manuscript editing. C. Page Chamberlain guided the design the study and assisted in manuscript editing.

This chapter was presented at the 2015 American Geophysical Union Annual Meeting, and as an invited talk at both the 2016 Geological Society of America Annual Meeting and the 2016 American Geophysical Union Fall Meeting.

Chapter 3

This chapter was published in two parts, following suggestion by the original reviewers of the first apt to remove the analysis of the global rivers dataset from the monolithologic datasets. The primary contribution of this chapter was published in *Geochimica et Cosmochimica Acta* (Ibarra et al., 2016). The formal peer-reviewers were Lee Kump (Pennsylvania State University), Julien Bouchez (Institut de Physique du Globe de Paris) and an anonymous reviewer. The manuscript was handled by Associate Editor Anthony Dosseto (University of Wollongong). The remaining analysis was published and expanded upon in an extended abstract for the 11th Symposium of the Geochemistry of the Earth's Surface in *Acta Geochimica* (Ibarra et al., 2017). This chapter was primarily funded by NSF CAREER Grant EAR-1254156 to Kate Maher, and was also supported during a visit to UCLA to visit co-author Seulgi Moon by the California Alliance Research Exchange program NSF HRD-1306595 to C. Page Chamberlain.

I co-designed the study, compiled the monolithologic catchment datasets, carried out the bulk of the quantitative analysis, produced all figures, and wrote the manuscript. Jeremy K. Caves helped design the study, carry out the analysis and wrote portions of the manuscript. Seulgi Moon provided the global rivers dataset, which were originally compiled in Moon et al. (2014), helped with the quantitative analysis, and edited the

manuscript. Dana L. Thomas helped carry out the quantitative analysis and thermodynamic calculations, co-designed several of the figures, and edited the manuscript. Jens Hartmann provided additional monolithologic catchment datasets and edited the manuscript. C. Page Chamberlain helped design the study, edited the manuscript and provided editorial guidance. Kate Maher co-designed the study, provided quantitative analysis tools, wrote portions of the manuscript, and provided editorial guidance.

Components of this chapter were presented at the 2014 American Geophysical Union Fall Meeting, a Critical Zone Observatory Workshop at University of New Hampshire in 2015, the 11th Symposium of the Geochemistry of the Earth's Surface (GES-11) in Guiyang, China in 2017, and as an invited talk at the 2017 American Geophysical Union Fall Meeting.

Chapter 4

This chapter is being prepared for submission. I co-designed the study, wrote the manuscript, carried out the lithium isotope and trace metal concentration measurements, XRD measurements and co-developed the modeling framework. Matthew M. Jones selected the samples from the Aristocrat Angus core, carried out the weight percent carbonate, organic content analyses, measured the carbonate oxygen and carbon isotopes, re-calibrated the depth and age model for the core, and helped design the study. Geerke Floor helped carry out the lithium isotope and trace metal concentration measurements. Jeremy K. Caves Rugenstein helped developed the modeling framework. Bradley B. Sageman provided access to the samples from the Aristocrat Angus core and guided the

study design. Stephan A. Graham co-funded the project, and guided the study design. Friedhelm von Blanckenburg provided funding and facilities for the lithium isotope measurements, and helped conceive and design the study. C. Page Chamberlain helped conceive and design the study, co-funded the project and helped with dataset interpretation. This paper was part of a series of collaborative projects between Northwestern University and Stanford University that also involved the publication of an Oceanic Anoxic Event 3 record from the Songliao Basin, China (Jones et al., 2018).

NSF Grants EAR-1450357 to C. Page Chamberlain and Stephan A. Graham and EAR-1424474 to Bradley B. Sageman funded this chapter. Support for travel to Germany was partially covered by the Stanford EDGE-STEM Fellowship. This work will be presented at the 2018 Goldschmidt Conference.

Appendix E

This appendix manuscript has been accepted to *American Journal of Science* and is currently being revised. Formal peer-reviews have been received by Nathan Sheldon (University of Michigan) and Yves Goddris (Gosciences Environnement Toulouse). Editor Danny M. Rye (Yale University) handled the peer-review of the manuscript. The idea for this work was originally conceived collectively among the coauthors as part of class, *Evolution of Earth Systems*, at Stanford University. Jeremy K. Caves Rugestein, Aviv Bachan, and myself contributed equally to the final completion of this manuscript. I co-wrote the manuscript, co-developed the quantitative analysis, helped carry out the thermodynamic calculations, and designed and produced all figures. Jeremy K. Caves Rugestein co-wrote the manuscript, co-developed the quantitative analysis and helped

design figures. Aviv Bachan co-developed the quantitative analysis, helped design figures and edited the manuscript. Andres Baresch compiled the paired catchment datasets and edited the manuscript. Kimberly V. Lau helped develop the quantitative analysis, helped design figures and edited the manuscript. Dana L. Thomas carried out the thermodynamic calculations, helped design figures, and edited the manuscript. Jung-Eun Lee provided climate model output and edited the manuscript. C. Kevin Boyce helped develop the modeling framework, helped design figures and co-wrote the manuscript. C. Page Chamberlain compiled the original version of the manuscript, helped design figures and helped design the quantitative analysis.

I presented this chapter at the 2017 American Geophysical Union Fall Meeting. It was also presented by co-author Jeremy K. Caves Rugenstein at Goldschmidt 2017 in Paris, France, and by co-author C. Page Chamberlain at the University of Washington Earth and Space Sciences Seminar in 2018 and the 2017 Senckenberg Geobiodiversity meeting in Frankfurt, Germany.

First-Author Conference Contributions

DE Ibarra, S Moon, M Winnick, A Wymore, JK Caves, CP Chamberlain, WH

McDowell, K Maher, 2017, Partitioning Concentration-Discharge Patterns of Weathering Products from Monolithologic Catchments to Global Rivers. Invited Oral Presentation B54D-08, 2017 AGU Fall Meeting.

DE Ibarra, JK Caves Rugenstein, A Bachan, A Baresch, KV Lau, D Thomas, J-E Lee,

CK Boyce, CP Chamberlain, 2017, The Evolution of Land Plants and the Silicate Weathering Feedback. Abstract PP41B-1300, 2017 AGU Fall Meeting.

- DE Ibarra, S Moon, JK Caves, CP Chamberlain, K Maher, 2017, Concentration-discharge patterns of weathering products from global rivers. Abstract P-S02-21, 11th Symposium of the Geochemistry of the Earth's Surface (GES-11).
- DE Ibarra, JL Oster, MJ Winnick, JK Caves, AJ Ritch, CP Chamberlain, K Maher, 2016, Drivers of pluvial lake distributions in western North America. Invited Oral presentation PP51F-01, 2016 AGU Fall Meeting.
- DE Ibarra, JL Oster, MJ Winnick, AJ Ritch, CP Chamberlain, K Maher, 2016, Climatological drivers of Plio-Pleistocene pluvial lake distributions in western North America. Invited Oral presentation 30-9, 2016 GSA Annual Meeting.
- DE Ibarra, JL Oster, MJ Winnick, AJ Ritch, CP Chamberlain, K Maher, 2015, Climatological Conditions Driving Lake Levels During Past Cold and Warm Periods in Western North America. Abstract PP13B-2275, 2015 AGU Fall Meeting.
- DE Ibarra, MM Jones, SA Graham, BB Sageman, CP Chamberlain, 2015, Investigating the Coniacian-Santonian in the Songliao Basin and possible links to Oceanic Anoxic Event 3. Oral presentation 53-13, 2015 GSA Annual Meeting.
- DE Ibarra, JK Caves, S Moon, CP Chamberlain, K Maher, 2015, Constraining silicate weathering efficiency using concentration-discharge relationships of basaltic and granitic catchments. Critical Zone Observatory (CZO) Concentration-Discharge Workshop.
- DE Ibarra, JK Caves, DL Thomas, CP Chamberlain, K Maher, 2014, Quantifying the Chemical Weathering Efficiency of Basaltic Catchments, Abstract EP23B-3602, 2014 AGU Fall Meeting.

DE Ibarra and CP Chamberlain, 2014, Modeling terminal lake temperature and runoff using ostracod paleoclimate records. Oral presentation 80-3, 2014 GSA Annual Meeting.

Co-authored Peer-Review Manuscript Contributions

The following are the published peer-reviewed papers I contributed to during my time in the Earth System Science PhD program. This encompasses published work undertaken between September 2013 and June 2018.

AE Egger, DE Ibarra, R Weldon, RM Landgridge, B Marion, J Hall, In Press, The influence of pluvial lake cycles on earthquake recurrence in the northwestern Basin and Range, USA. In Starratt, S.W., Rosen M.R., (Editors), From Saline to Freshwater: The Diversity of Western Lakes in Space and Time, Geological Society of America Special Paper Series.

NW Hermann, JL Oster, DE Ibarra, 2018, Spatial Patterns and Driving Mechanisms of Mid-Holocene Moisture in Western North America, Journal of Quaternary Science, 33 (4), 421-434.

MM Jones, DE Ibarra, Y Gao, BB Sageman, D Selby, CP Chamberlain, SA Graham, 2018, Evaluating Late Cretaceous OAEs and the influence of marine incursions on organic carbon burial in an expansive East Asian paleo-lake, Earth and Planetary Science Letters, 484, 41-52.

AS Wymore, RL Brereton, DE Ibarra, K Maher, WH McDowell, 2017, Critical zone structure controls concentration-discharge relationships and solute generation in

- forested tropical montane watersheds, *Water Resources Research*, 53 (7), 6279-6295.
- JK Caves, BU Bayshashov, A Zhamangara, AJ Ritch, DE Ibarra, DJ Sjostrom, HT Mix, MJ Winnick, CP Chamberlain, 2017, Late Miocene uplift of the Tian Shan and Altai and reorganization of Central Asia climate, *GSA Today*, 17 (2).
- Y Tong, DE Ibarra, JK Caves, T Mukerji, SA Graham, 2017, Constraining basin thermal history and petroleum generation using paleoclimate data in the Piceance Basin, Colorado, *Basin Research*, 29 (4), 542-553.
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- HT Mix, DE Ibarra, SA Graham, A Mulch, CP Chamberlain, 2016, A Hot and High Eocene Sierra Nevada, *Geological Society of America Bulletin*, 128 (3-4), 531-542.
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Y Gao, CS Wang, ZF Liu, XJ Du, DE Ibarra, 2015, Diagenetic and paleoenvironmental controls on Late Cretaceous clay minerals in the Songliao Basin, northeast China, *Clays and Clay Minerals*, 63 (6), 469-484.

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CHAPTER 1

Quantifying closed-basin lake temperature and hydrology by inversion of oxygen isotope and trace element paleoclimate records

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Abstract

Lake systems are important paleoclimate archives that preserve ecosystem and hydrologic responses to critical periods in Earth history, such as carbon cycle perturbations and glacial-interglacial cycles. Geochemical measurements of biogenic carbonate (for example, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$, [Li], [U], [Sr], and [Mg]) are indicators of hydrologic variability in lake systems throughout the geologic record. In this study, we present a new closed-basin lake modeling approach, HyBIM (the Hydrologic Balance Inverse Model) that employs a system of total differential equations and uses the measured $\delta^{18}\text{O}$, Sr/Ca, and Mg/Ca of biogenic carbonate to determine changes in temperature, runoff, and lake evaporation. Using equally-spaced time steps, these equations are simultaneously solved to constrain the hydrologic parameters of the lake as recorded in biogenic carbonate. We use a Monte Carlo approach to account for uncertainty in the input parameters, such as $\delta^{18}\text{O}$ temperature relationships, partition coefficient uncertainty, and watershed solute chemistry.

For illustrative purposes, we apply the model to two ostracod valve datasets covering different timescales: (1) the Cretaceous Songliao Basin, northeast China, and (2) Holocene Lake Miragoane, Haiti. Modern water measurements of water isotopes and cation concentrations from each location are required as model inputs. We compare our modeling results with author interpretations and geologic observations. The modeling approach presented in this study can be applied to other closed-basin lake records, can be modified for other calcifying species (for example, gastropods or mollusks) or with calibration to inorganic lacustrine carbonate. In addition, this approach holds promise for extension with additional proxy measurements (that is, δD , U/Ca or Li/Ca) and changing

source area on tectonic timescales using proxies that reflect changing source lithology (that is, Sr and Pb isotopes). Future incorporation of age model uncertainty in the Monte Carlo approach will also provide utility by quantifying temporal uncertainty on the hydrologic response recorded by lake sediments.

Keywords: lakes, paleohydrology, inverse model, trace elements, oxygen isotopes

1.1 Introduction

Lake systems provide valuable paleoclimate archives as natural integrators of terrestrial processes. Lake deposits from hydrologically closed basins or terminal lakes record important changes in climate, human activity, hydrology, ecology, and tectonics (Antevs, 1948; Eugster and Jones, 1979; Currey, 1990; Binford and others, 1997; Carroll and Bohacs, 1999; Reheis, 1999; Demko and others, 2005; Horton and Chamberlain, 2006; Davis and others, 2009; Reheis and others, 2014; Hillman and others, 2014; Smith and others, 2014). Additionally, lake sediments provide the most widely available and continuous records of terrestrial climate available to reconstruct past climate (for example, Oviatt and McCoy, 1992; Colman and others, 1995; Williams and others, 1997; Bohacs and others, 2003; Melles and others, 2012). Accurate estimates of past precipitation, runoff, and/or temperature are important for studying the evolution of landscapes and the diversification and migration of species, as well as to test climate model predictions of past climate (for example, Rozanski and others, 1997; Partridge and others, 1997; Steinman and others, 2012; Ibarra and others, 2014).

Studies of ancient lake systems have long sought to infer climate conditions leading to the existence and persistence of lakes in terrestrial settings. Inferring the climatic setting and the open versus closed hydrology of a lake system using facies identification has been extensively investigated (for example, Nilsson, 1931; Eugster and Kelts, 1983; Kelts, 1988; Talbot, 1990; Carroll and Bohacs, 1999). Within the Carroll and Bohacs (1999) framework, closed-basin lakes are of two types: balanced-fill and underfilled. Underfilled lake systems are identified by evaporative facies (Jones and others, 1977; Eugster and Jones, 1979; Horita, 1990) and are typical of many Quaternary

playa-lake systems found in semi-arid regions of the mid-latitudes, such as the western United States (Mifflin and Wheat, 1979; Reheis and others, 2014). In contrast, balanced-filled lake systems are typical of freshwater to saline conditions with mixed carbonate and siliciclastic sediments (for example, Carrol, 1998; Kempf and others, 2009; Doebbert and others, 2014).

For closed-basin Quaternary lake systems, in which tectonic rearrangement is negligible, climatic conditions have been quantified using measures of lake surface area and tributary size (Snyder and Langbein, 1962; Mifflin and Wheat, 1979; Bowler, 1981; Benson and Paillet, 1989; Bengtsson and Malm, 1997; Reheis, 1999; Sack, 2009; Broecker, 2010; Munroe and Laabs, 2013; Hudson and Quade, 2013; Ibarra and others, 2014; Huth and others, 2015; Hudson and others, 2015). Additionally, recent work modeling stable isotopes in closed-basin balance-filled lakes takes advantage of longer (relative to overfilled/open lakes) residence times to infer climatic conditions by relating the $\delta^{18}\text{O}$ or δD to the hydrologic balance (Horita, 1990; Hostetler and Benson, 1994; Benson and White, 1994; Gibson and others, 2002; Gibson and Edwards, 2002; Benson and Paillet, 2002; Russell and Johnson, 2006; Jones and others, 2007; Jones and Imbers, 2010; Doebbert and others, 2010; Steinman and others, 2010a, 2010b, 2012, 2013; Steinman and Abbott, 2013; Jasechko and others, 2013; Stansell and others, 2013; Ibarra and others, 2014; Jasechko and others, 2014; Gibson and others, 2015). Fundamental to applying an isotopic modeling approach are assumptions concerning the watershed precipitation-runoff relationships (Jones and others, 2007; Ibarra and others, 2014), mixing or stratification of the lake (Imberger and Ivey, 1991), basin-scale and regional vapor recycling (Gat and Matsui, 1991; Gat and others, 1994; Burnett and others, 2003;

Winnick and others, 2014), and groundwater influences (Krabbenhof and others, 1990a, 1990b; Shapley and others, 2005; Guay and others, 2004; Steinman and others, 2013). While these models offer powerful methods to reconstruct the hydrology of lake systems they are limited by the numerous input parameters required that are difficult to constrain in ancient lake systems. Another approach, outlined here, is to use additional measurements, such as trace elements, that can be meaningfully related to climatic conditions and will reduce the assumptions necessary for accurate, quantitative climatic reconstructions. Using trace element and oxygen isotope measurements it is then possible to tightly constrain the system using far fewer input parameters.

In this paper, we develop a new modeling framework exploiting variations in $\delta^{18}\text{O}$ and trace elements (Mg and Sr) measured in lacustrine carbonates and utilizing a series of total differential equations. We apply this model to previously published ostracod paleoclimate records for closed basins. Lacustrine ostracod records are used here for illustrative purposes because of their broad paleoclimate applications in historical (for example, Engstrom and Nelson, 1991; Holmes and others, 2007a; Zhang and others, 2009), Quaternary (for example, Edney and others, 1990; Hodell and others, 1991; Curtis and Hodell, 1993; Lamb and others, 1999; Cohen and others, 2000; Holmes and others, 2007b; Gouramanis and others, 2010), and deep-time (for example, Forester, 1991; Chamberlain and others, 2013) settings. Extensive work has also been carried out on the ecology, taphonomy, and taxonomy of ostracod species (for example, Horne and others, 2002; Frogley and others, 2002; Bennett and others, 2011; Blome and others, 2014), and modern ostracod datasets have been extensively studied and provide the necessary empirical calibrations of trace element distribution coefficients and vital effects (for

example, Engstrom and Nelson, 1991; Xia and others, 1997a, 1997b; Wansard and others, 1998; De Deckker and others, 1999; Dettman and others, 2002; Holmes and Chivas, 2002; Dwyer and others, 2002; Ito and Forester, 2009; Gouramanis and others, 2010; Marco-Barba and others, 2012; Börner and others, 2013) necessary to constrain our model. The modeling framework presented in this paper applies, given the existence of relevant and accurate calibrations, to any biogenic carbonate records from a closed-basin lake setting.

1.2 Model Development

We present the Hydrologic Balance Inversion Model (HyBIM), an inverse model using a system of total differential equations that are inverted to solve for the extensive variables in lake chemistry. The structure of the model is similar to models that quantify changes in the global carbon cycle and/or other biogeochemical cycles as recorded in marine sediments (for example, Goddris and Franois, 1996; Derry and France-Lanord, 1996; Franois and Goddris, 1998; Li and others, 2009; Li and Elderfield, 2013). We solve for the relative changes in temperature and lake volume, and thus rely only on the first derivative of the input dataset and not the absolute value of the isotopic and trace element measurements. Because of this formulation order of magnitude fluctuations in lake volume cannot be modeled by this approach. Fundamentally, this model quantifies the observations made by previous studies that qualitatively employed end-member mixing (from a fresh source to an evaporative lake) in closed-basin lacustrine deposits based on the covariance of Sr/Ca, Mg/Ca, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (for example, Mller and others, 1972; Eugster and Kelts, 1983; Talbot, 1990; Li and Ku, 1997; Garnett and others, 2004;

Davis and others, 2009; Horton and Oze, 2012; McGee and others, 2012; Chamberlain and others, 2013; Horton and others, 2015). We do not incorporate variations in $\delta^{13}\text{C}$ in this initial iteration of HyBIM; however, evaporative processes and lake residence times should also control the systematics of the $\delta^{13}\text{C}$ of carbonates from terminal lake systems (see discussion in Horton and others, 2015).

First, we establish the modeling framework using a system of total differential equations. Second, we describe the Monte Carlo routine used to account for parameter and input data uncertainty (for example, Fantle, 2010; Royer and others, 2014). Third, we discuss the input dataset (the time series of measurements) and necessary input parameters. Finally, we describe the quantification of the partial derivatives necessary to constrain the model and necessary input parameters. This model is available as an example R code for modification at:

<http://earth.geology.yale.edu/~ajs/SupplementaryData/2015/Ibarra/>. For illustrative purposes, we apply HyBIM to two ostracod valve datasets covering different timescales: (1) the Cretaceous Songliao Basin, northeast China, and (2) Holocene Lake Miragoane, Haiti. All model parameters are summarized in table 1 and a schematic of the model structure is presented in figure A1.

Model Framework

Here, we present a modeling framework that produces a time series of temperature changes, effects of evaporation, and relative volume estimates for runoff for carbonate-bearing (here ostracods) paleolake records. Chivas and others (1986) previously suggested a quantitative framework by which a unique solution for

paleotemperature and paleosalinity could be calculated using paired Mg/Ca and $\delta^{18}\text{O}$ measurements. Following this observation, we write three total differential equations for lake water that describe the effects of temperature, evaporation, and runoff/precipitation on the oxygen isotopic and trace element concentration of ostracods in a hydrologically closed lake. The three total differential equations (for lake water $\delta^{18}\text{O}$, [Mg], and [Sr]) are:

$$d(\delta^{18}\text{O}) = \left(\frac{\partial(\delta^{18}\text{O})}{\partial T} \right) dT + \left(\frac{\partial(\delta^{18}\text{O})}{\partial F_{\text{evap}}} \right) dF_{\text{evap}} + \left(\frac{\partial(\delta^{18}\text{O})}{\partial F_{\text{input}}} \right) dF_{\text{input}} \quad (1)$$

$$d[\text{Sr}] = \left(\frac{\partial[\text{Sr}]}{\partial T} \right) dT + \left(\frac{\partial[\text{Sr}]}{\partial F_{\text{evap}}} \right) dF_{\text{evap}} + \left(\frac{\partial[\text{Sr}]}{\partial F_{\text{input}}} \right) dF_{\text{input}} \quad (2)$$

$$d[\text{Mg}] = \left(\frac{\partial[\text{Mg}]}{\partial T} \right) dT + \left(\frac{\partial[\text{Mg}]}{\partial F_{\text{evap}}} \right) dF_{\text{evap}} + \left(\frac{\partial[\text{Mg}]}{\partial F_{\text{input}}} \right) dF_{\text{input}} \quad (3)$$

where $\delta^{18}\text{O}$ is the oxygen isotopic composition of the lake water determined from biogenic carbonate measurements corrected for species-specific vital effects, [Mg] and [Sr] are the lake water concentrations of Mg^{2+} and Sr^{2+} determined from the Sr/Ca and Mg/Ca ratios measured in the biogenic carbonate, T is mean annual surface air temperature (K) for the lake basin, F_{evap} is the fraction of the lake evaporation, and F_{input} is the fractional lake volume increase due to changes in runoff and precipitation (see table 1).

We treat equations 1–3 as a system of total differential equations that can be solved for each time step of the first derivative of the [Mg], [Sr], and $\delta^{18}\text{O}$ time series [that is, $x = A^{-1}b$, where matrix A is composed of the partial derivatives, the b vector is the first derivative of the input dataset (left side of eqs 1 to 3) and x is the solution vector of (dT, dF_{evap} , and dF_{input})]. We do so by determining the partial derivatives for a specific

lake system, calibrated using modern watershed/lake chemistry data and knowledge of the specific ostracod species. Interpolation to an evenly spaced time series is required, which we accomplish using an Epanechnikov kernel smoother applied to the input data. We assume that within each time step, lake evaporation and/or lake volume change does not change more than 20 percent, and we approximate all derivatives according to this assumption (that is at 10%). The model output is a time series of the solution vector (dT , dF_{evap} , and dF_{input}). dF_{evap} and dF_{input} are combined to give the fractional net volume increase for each time-step (see fig. A1). We use a Monte Carlo approach to account for uncertainty in the input parameters and in the input dataset, which we derive from kernel smoothing.

Monte Carlo Routine for Uncertainty Quantification

Given the assumptions that underlie the input parameters and data set for this model it is critical to quantitatively assess the errors associated with the calculated runoff input, temperature changes, and evaporative effects. Thus, we use a Monte Carlo routine to account for two types of uncertainty. The first is uncertainty in the input dataset. Since most paleoclimate records display uneven variance and non-uniform sampling density, it is necessary to account for this by producing datasets for each iteration based on the statistics (time series of the mean and residuals) derived from kernel smoothing of the dataset (see below). To do so, for each Monte Carlo iteration we implement a bootstrapping method whereby we account for input dataset uncertainty by re-sampling residuals. The second type of uncertainty accounted for by our model is the uncertainty in the input parameters. The input parameters are best determined by modern watershed and

lake chemistry (when available) and knowledge of the species precipitating the biogenic carbonate (described below). Within each Monte Carlo iteration, we derive a time series of partial derivatives based on the input parameters. Input parameter uncertainty distributions are assumed to be normal distributions, requiring that uncertainty is quantified by as many modern measurements of watershed chemistry as possible. The partial derivatives are substituted into the **A** matrix at each time step.

Input Dataset Requirements and Interpolations

There are two requirements for the input dataset that need to be met for this model. First, the modeled Mg/Ca, Sr/Ca, and $\delta^{18}\text{O}$ time series must be of sufficient resolution to resolve climatic events of interest and the time step must be greater than the residence time of these elements in a lake. Thus, in order to use the dataset in the system of equations (left side of eqs 1–3), the time series must be interpolated to even time steps, requiring a sufficiently resolved age model for the Mg/Ca, Sr/Ca, and $\delta^{18}\text{O}$ measurements. Smoothing of each time series (Mg/Ca, Sr/Ca, and $\delta^{18}\text{O}$) is performed using an Epanechnikov kernel and interpolated to an even time step following a data driven least squares cross-validation to select the appropriate kernel bandwidth (Hayfield and Racine, 2008). The Epanechnikov kernel (Epanechnikov, 1969) is used because it has finite boundaries (instead of Gaussian kernel) and is smooth (compared to a triangle or uniform kernel) (see Fan, 1992; Danese and others, 2014). Kernel smoothing of the time series is implemented using the ‘np’ package in R (Hayfield and Racine, 2008). The additional advantage of using a kernel smoother is that uncertainty of the interpolated

dataset can be quantified along the time series (mean and residuals) and input into the Monte Carlo routine.

While high-resolution interpolation of the smoothed dataset is desirable to resolve climatic events of interest, linear interpolation of the input dataset to an even time step (Δt) must be such that $\Delta t \gg \tau_{\text{res}}$, where τ_{res} is the residence time (inferred from lake geometry and average input or evaporative fluxes, for example Gibson and others, 2002; Jasechko and others, 2014). For lakes with no modern analogue (see Cretaceous Songliao Basin example), first-order estimates for τ_{res} can be approximated using scaling relationships between outcrop size and basin geometry (Hendriks and others, 2012), which in combination with facies identification can be used to determine estimates of the relationship between potential accommodation and basin average precipitation/evaporation (Carroll and Bohacs, 1999). Thus, due to the formulation and assumptions of the mixing and mass conservation relationships derived below, resolving hydrologic or climatic events over intervals equal to or shorter than τ_{res} is not possible within this modeling framework. This implies that, given the ‘water equivalency rule’ for a region of interest (Hendriks and others, 2012), paleoclimate records from small lake systems, which integrate smaller watersheds and have shorter residence times, provide the highest fidelity temporal records of hydrologic cycle changes. Furthermore, determination of the lake hypsometry and/or outcrop extent (for example, Reheis 1999; Sack, 2009; Steinman and others, 2013; Smith and others, 2014; Doebbert and others, 2014) ensures that the modeling assumptions outlined above are met.

The second requirement for the model is that all of the input data need to be placed in terms of lake composition. Although we use measured values of Mg/Ca, Sr/Ca,

and $\delta^{18}\text{O}$ of ostracods, these values need to be corrected so that they represent the values of these elements and isotopes in the lake water. To make this correction one must correct for “vital effects” and temperature. Correcting for vital effects is relatively straightforward as the measured vital effect is simply subtracted from the measured ostracod values. Vital effects associated with the calcification of biogenic carbonate are observed because shell carbonate is not precipitated in isotopic equilibrium with water (Holmes and Chives, 2002). Vital effects observed in ostracod $\delta^{18}\text{O}$ are positive (0.3 – 2.5 ‰) and have been observed to be constant within individual genera (Xia and others, 1997a, 1997b; von Grafenstein and others, 1999; Chivas and others, 2002; Didie and Bauch, 2002). Since vital effects are not temperature-dependent, data from a variety of different modern species fall on slopes close to the inorganic calcite equilibrium slope (–0.250 ‰/K) of Kim and O'Neill (1997) (see compilation by Marco-Barab and others, 2012). Our model ideally should be used with a time series produced by a single ostracod species or genera. Although, if multiple species are measured (for example, Lister and others, 1991) this could be accounted for using vital effect offsets.

In contrast, correcting for temperature effects is less straightforward and could, if done incorrectly, lead to “circular reasoning” since we are attempting to constrain temperature changes in the model. We assume temperature could vary from 10 to 35 °C (uniform distribution). For each Monte Carlo iteration we select a starting temperature and assume that $\delta^{18}\text{O}$ of the lake water is in equilibrium with the measured $\delta^{18}\text{O}$ of ostracods using the temperature-dependent fractionation relationship of Kim and O'Neill (1997) corrected for vital effects. We avoid “circular reasoning” since our system of linear equations calculates the relative changes in temperature, dT (in the x vector), using

the first derivative of the $\delta^{18}\text{O}$ of the lake water (in the b vector), not the absolute temperature.

Distribution coefficients (K_D -values) relating trace element to calcium ratios are commonly determined for biogenic carbonates through modern and/or culturing studies. The distribution (or partition) coefficient is defined as:

$$K_D[M] = \frac{M / \text{Ca}_{\text{water}}}{M / \text{Ca}_{\text{shell}}} \quad (4)$$

where M is the trace metal, such as Sr, Mg, or U, and M/Ca are molar ratios. K_D -values for Mg and Sr are both less than one, meaning that both trace metals are actively excluded during calcification. Additionally, Chivas and others (1986) demonstrated that K_D -values are similar among members of the same or closely related genera.

In many species, K_D has been shown to be temperature-dependent. In most ostracod species, there is little or no temperature effect on Sr/Ca (Chivas and others, 1986; Holmes and Chivas, 2002, Marco-Barab and others, 2012), but the Mg/Ca K_D in ostracods is temperature-dependent (Engstrom and Nelson, 1991; DeDecker and others, 1999; Holmes and Chivas, 2002). For the example datasets used in this paper, we use species-specific K_D -values (or from related genera when not available), and uncertainties are obtained from regression statistics of the original datasets (table 2). To place the input data [Mg] and [Sr] in terms of lake composition (b vector) we calculate the Mg/Ca K_D (and Sr/Ca K_D if necessary) using the temperature and lake water [Ca] selected for each Monte Carlo iteration.

Determining Partial Derivatives

In the following sections each of the partial derivatives are derived or determined using either mass conservation (for example, $\frac{\partial[\text{Mg}]}{\partial F_{\text{evap}}}$) and mixing (for example, $\frac{\partial[\text{Mg}]}{\partial F_{\text{vol}}}$), or empirical relationships from environmental and/or laboratory measurements (for example, $\frac{\partial(\delta^{18}\text{O})}{\partial T}$).

Temperature Partial Derivatives

To solve for the oxygen isotope partial derivative $\frac{\partial(\delta^{18}\text{O})}{\partial T}$ requires knowing how $\delta^{18}\text{O}$ of meteoric water (precipitation and runoff) varies as a function of temperature. We recognize that there are numerous factors affecting the $\delta^{18}\text{O}$ of precipitation beyond that of temperature, which include seasonality, vapor recycling, moisture source et cetera. However, the commonly held assumption that underpins terrestrial paleoclimate studies is the well-known positive correlation between $\delta^{18}\text{O}$ values of precipitation and temperature for temperate and high latitude areas (Dansgaard, 1964). For the mid-latitude site (Songliao Basin) we use the observed relationship between temperature and precipitation Rozanski and others (1993) of 0.58 ‰/K, as has been used in numerous studies to calculate the temperature for paleoclimate archives in mid- to high-latitude sites, such as paleosols (for example, Koch and others, 2003), paleolakes (for example, Anderson and others, 2001), and ice cores (see Jouzel and others, 1997 and references therein). For the low latitude site (Lake Miragoane, Haiti) it is unlikely that the correlations of Rozanski and others (1993) apply as these are for mid- to high-latitudes. Although it is not ideal to use the approach we outline in this paper to low latitudes

because temperature is not as well correlated to the $\delta^{18}\text{O}$ of precipitation, we use this site only as an example of how this approach can be used in lakes because this record offers the type of data that are necessary for these calculations. Recognizing these limitations we use a slope of 0.26‰/K for the tropical sites (see fig. A2). For both cases we incorporate the error associated with the empirical temperature versus $\delta^{18}\text{O}$ correlation in the Monte Carlo.

In our model, thus, one of the assumptions inherent in our calculations is that temperature is the primary driver of $\delta^{18}\text{O}$ value of water input to the lake. Note that since the slope between temperature and $\delta^{18}\text{O}$ of precipitation can and does vary geographically, more accurate approaches can be tailored for individual sites by measurements of site-specific correlations between temperature and $\delta^{18}\text{O}$ of precipitation.

In addition, to the partial $\frac{\partial(\delta^{18}\text{O})}{\partial T}$ discussed above it is necessary to place the ostracod values as the $\delta^{18}\text{O}$ of lake water for these calculations (b vector of eqs 1 to 3). To do this we need to account for both vital effects and the temperature-dependent isotopic fractionation (see above).

In addition, there are minor temperature effects on the Sr/Ca (typically none) and Mg/Ca (see above discussion). Since the inputs (b vector of eqs 1 to 3) are placed in terms of lake composition, after accounting for the Mg/Ca or Sr/Ca of the lake water and selected temperature for the Monte Carlo iteration the temperature partial derivatives (

$\frac{\partial[\text{Mg}]}{\partial T}$ and $\frac{\partial[\text{Sr}]}{\partial T}$) are equal to zero.

Evaporation Partial Derivatives

To account for the evaporative concentration of trace elements, we assume mass conservation of Sr and Mg. Thus, this model is not applicable to brine or saline environments (see Jones and others, 1977; Eugster and Jones, 1979) nor is it applicable to systems that form large deposits of chemical sediments with high Mg and/or Sr concentrations. For biogenic carbonates, we apply the applicable distribution coefficient (K_D) and take the first derivative. In doing so, we assume that the Sr/Ca and Mg/Ca measured in the biogenic carbonates are faithfully recording changes in the Sr and Mg concentrations of the lake water. Assuming mass conservation, the change in solute M concentration (from the initial concentration to an increased concentration at time 2) during fractional lake evaporation (F_{evap} , fraction remaining, from 0 to 1, where 1 is fully evaporated) is given by the equation (fig. 1):

$$[M]_2 = \frac{[M]_{\text{initial}}}{(1 - F_{\text{evap}})} \quad (5)$$

Solving for the partial derivative of equation 5 has the analytical solution:

$$\frac{\partial [M]}{\partial F_{\text{evap}}} = \frac{[M]_{\text{initial}}}{(1 - F_{\text{evap}})^2} \quad (6)$$

This relationship is non-linear; thus, to provide a linear slope for $\frac{\partial [M]}{\partial F_{\text{evap}}}$ we assume that

for any given time step, the lake does not evaporate more than 20 percent by volume. By inspection of equation 6, the average evaporation between 0 to 20 percent, given by

$F_{\text{evap}} = 0.1$, yields a slope of $\frac{[M]_{\text{initial}}}{(0.9)^2}$. Therefore, the initial trace element concentration

(that is, the Mg and Sr concentrations), which we assume to be approximated using the

observed distribution of trace element measurements, is important for setting $[M]_{\text{initial}}$ at each time step.

The evaporative enrichment of lake water $\delta^{18}\text{O}$ with progressive evaporation was originally parameterized by Craig and Gordon (1965). The limitation of applying the Craig and Gordon (1965) evaporation model to lacustrine paleoclimate records, as outlined in detail by Gonfiantini (1986), is the large number of input parameters and the difficulty in constraining the isotopic composition of the evaporated water vapor (see discussion in Jones and Imbers, 2010). Recent work has attempted to simplify evaporative assumptions (Benson and White, 1994; Jones and others, 2007; Jones and Imbers, 2010; Placzek and others, 2011), but numerous input parameters are still required, making the generic application of these lake water evaporation models to paleoclimate records challenging.

Central to the difficulties encountered by previous researchers is the influence of humidity on the evolution of the isotopic composition of an evaporating water body (Gonfiantini, 1986). This is due to changes in the kinetic enrichment factor due to changes in humidity (Gat, 1970; Merlivat, 1978; Merlivat and Jouzel, 1979). However, if within a given time step lake evaporation does not exceed ~25 percent total lake volume and humidity is <90 percent, the isotopic evolution of an evaporating water body can be approximated by a Rayleigh relationship (Gonfiantini, 1986). Thus, we derive the partial derivative for $\delta^{18}\text{O}$ and fractional lake evaporation as the first derivative of the Rayleigh equation (fig. 1):

$$\frac{\partial(\delta^{18}\text{O})}{\partial F_{\text{evap}}} = (\alpha - 1)(\delta^{18}\text{O}_1 + 1000)(1 - F_{\text{evap}})^{(\alpha-2)} \quad (7)$$

where α is the combined fractionation factor of the temperature-dependent equilibrium fractionation factor (Horita and Weslowski, 1994) and humidity-dependent kinetic fractionation factor (Gonfiantini, 1986), F_{evap} is the fraction of the lake evaporation (as above) and $\delta^{18}\text{O}_{\text{initial}}$ is the initial isotopic composition of the lake from the measured $\delta^{18}\text{O}$ of the biogenic carbonate corrected for vital effects (see below). While a simplification of evaporative processes, assuming a Rayleigh relationship and a combined fractionation factor in this manner has successfully been applied to both surface soil reservoir and lake system modeling (for example, Chamberlain and others, 2014; Caves and others, 2015). We assume that relative humidity for each Monte Carlo iteration can vary from 50 to 90 percent (uniform distribution), and temperature varies from 5 to 35 °C (uniform distribution) as determined for each iteration (as described above). By doing so we calculate the combined fractionation factor, α , using the equations of Horita and Weslowski (1994) and Gonfiantini (1986) (see fig. 1). The humidity and temperature ranges selected here are conservative and broadly apply to both illustrative lake systems used in the examples below. The relevant latitude and geographic setting of the lake system being modeled should inform the humidity and temperature ranges chosen as model input.

Lake Input Partial Derivatives

Determination of the lake input partial derivatives is similar for both trace elements and oxygen isotopes. We rely on binary mixing equations assuming that the isotopic and chemical composition of water entering the lake is sufficiently well characterized and relatively invariant (relative to the lake water). Water in terminal lakes is sufficiently evaporatively enriched relative to the input $\delta^{18}\text{O}$ that in most examples, the

input water $\delta^{18}\text{O}$ composition is typically statistically distinguishable from the lake water $\delta^{18}\text{O}$ composition (see for example compilation by Horton and Oze, 2012). This is similar for trace elements in terminal lake systems, such that the input concentration of Sr and Mg in terminal lakes is typically more dilute than the lake water.

Given these principles, we define the partial derivative relating increased lake volume, from the addition of source water (F_{input} , which varies from 1 to infinity, where 1 is the original lake volume) and variations in $\delta^{18}\text{O}$ as the first derivative of a binary mixing relationship (fig. 2):

$$\frac{\partial(\delta^{18}\text{O})}{\partial F_{\text{input}}} = \frac{(\delta^{18}\text{O})_{\text{source}} - (\delta^{18}\text{O})_{\text{initial}}}{(F_{\text{evap}})^2} \quad (8)$$

where $\delta^{18}\text{O}_{\text{source}}$ is the meteoric water composition and $\delta^{18}\text{O}_{\text{initial}}$ is determined as previously described. The meteoric water $\delta^{18}\text{O}$ composition should be determined by direct observation, by upstream fluvial carbonates (for example Ibarra and others, 2015) or by assuming an empirical relationship related to the amount of annual rainfall (amount effect), as observed in many tropical systems (Risi and others, 2008). Similarly for trace element concentrations:

$$\frac{\partial[M]}{\partial F_{\text{input}}} = \frac{[M]_{\text{source}} - [M]_{\text{initial}}}{(F_{\text{evap}})^2} \quad (9)$$

where M is the Sr or Mg concentration, $[M]_{\text{source}}$ refers to the runoff water concentrations, and $[M]_{\text{initial}}$ is determined as previously described from the measured Mg/Ca and Sr/Ca of the biogenic carbonate.

Input Parameter Requirements

There are several input parameter requirements that need to be satisfied for robust use of this model. First, measurements of solute chemistry ([Sr], [Mg], and [Ca] from lake water and/or runoff) and $\delta^{18}\text{O}$ of meteoric water are necessary to constrain the mixing equation end-members. This can best be done by measuring the elemental and isotopic composition of modern rivers and precipitation in the lake to be studied or the site of the ancient lake as is done here in the Songliao Basin (table 2). There are obvious complications to this approach since the drainage basin may have changed through time as well as the isotopic composition of precipitation – for example by a change in moisture source. In addition, the uncertainty (standard deviation) of the end-members is required. This can be quantified through repeat measurements of stream water/subsurface runoff chemistry.

Second, empirical relationships for temperature effects on the species-specific partition coefficient (for Mg/Ca) are required; such as those fit by Engstrom and Nelson (1991) and DeDeckker and others (1999). As discussed above, species-specific vital effects for $\delta^{18}\text{O}$ offsets are applied uniformly prior to derivation of the partial derivatives from the mixing and mass conservation equations. Input parameters are supplied to HyBIM as the mean and standard deviation, assuming a normal distribution. However, implementation of other probability distributions (such as uniform distributions) is possible. The probable temperature and relative humidity ranges (used for the $\delta^{18}\text{O}$ equilibrium fractionation equations and Mg/Ca K_D values), which are treated as uniform distributions, are specified by the user and should be informed by paleoenvironmental, latitudinal, climate modeling, and/or modern observations.

1.3 Example Applications

We apply HyBIM to two lacustrine paleoclimate records covering differing timescales, geochemical conditions, ostracod species, and dataset resolutions (figs. 3 and 4). We chose these two data sets because: (1) they had the elemental and isotopic measurements necessary for using this model and; (2) they represent two very different cases that demonstrate the utility and flexibility and limitations of the HyBIM for a variety of biogenic carbonate paleoclimate records. In each case, the original age model is used for all datasets and input parameters are constrained using modern catchment and lake chemistry and species-specific partition coefficient calibrations. Sampling resolution, the least squares cross-validated kernel bandwidths, length of the paleoclimate record, and input parameter sources are listed in table 2.

Lake Miragoane, Haiti (Hodell and others, 1991; Curtis and Hodell, 1993)

The paleoclimate records from Holocene Lake Miragoane in Haiti (Hodell and others, 1991; Curtis and Hodell, 1993; Higuera-Gundy and others, 1999) were one of the first to use detailed, high-resolution stable isotope and trace element measurements on lacustrine ostracods. This hydrologically closed lake provides a complete record of the Holocene at high resolution (see age resolutions for $\delta^{18}\text{O}$, Mg/Ca and Sr/Ca records in table 2). Two cores were recovered and sampled at fine (~ 10 cm) resolution for $\delta^{18}\text{O}$ and coarser (~ 150 cm) resolution for Mg/Ca and Sr/Ca (Curtis and Hodell, 1993). The discrepancy in sample resolution results in the cross-validated kernel bandwidth for $\delta^{18}\text{O}$ (bandwidth = 39 years) to be much shorter than the Mg/Ca and Sr/Ca records (422 and

440 years, respectively) (fig. 3A). Data from both cores were combined and kernel smoothed using the original age model.

The elemental and isotopic data for these studies were from ostracods identified as *Candona sp.*, by R. Forester (see discussion in Curtis and Hodell, 1993), which is an ostracod species closely related to *Candona rawsoni*. See table 2 for detailed model input parameters, including the partition coefficients for *Candona rawsoni* as determined by Engstrom and Nelson (1991).

The modeled temperature and lake volume changes for the Lake Miragoane record are largely in accordance with the expected response (see interpretation in Curtis and Hodell, 1993, their fig. 8). These authors suggested based on the isotopic and elemental data that lake levels were highest and climate was “mesic” (wetter and hotter) during the early Holocene, peaking between 7,000 and 4,000 years BP (Hodell and others, 1991; Curtis and Hodell, 1993). In the late Holocene they suggest that between ~4,000 and ~2,500 years BP there was a two-step increase in aridity towards lower lake level and increased salinity, based primarily on the oxygen isotopes (Hodell and others, 1991), followed by wetter conditions beginning at ~1,000 year BP based on additional evidence from the trace element measurements (Curtis and Hodell, 1993).

Our model agrees with this interpretation and shows that modeled temperature and lake volume covary. Lake volume and temperature increase to a peak at ~6300 years BP, decline to a minimum at ~2000 years BP, and increase again nearing present day. The deglacial warming (~10,000 – 7,000 years BP), and increasing aridity (from ~4,000 – 1,000 years BP) are captured by the predicted temperature fluctuations. Driven by the covariation in the input datasets, the modeled temperature is substantially different than

that expected from just using the $\frac{\partial(\delta^{18}\text{O})}{\partial T}$ empirical relationship of 0.26 ‰/°C (thin red line of fig. 3B; relationship derived in fig. A2). In addition, while the higher resolution $\delta^{18}\text{O}$ record determines the sub-1000-year variations in temperature, the long-term trends largely reflect the trace element records. The sampling resolution discrepancy of the trace elements (low resolution) and $\delta^{18}\text{O}$ records (high resolution) is not necessarily ideal, but our results demonstrate that, by kernel smoothing the records and interpolating to even time-steps, the problem of differing sampling resolution can be resolved.

Songliao Basin, China (Chamberlain and others, 2013)

The Songliao Basin is a Cretaceous terrestrial lake basin that contains up to 10,000 m of fluvial-lacustrine, volcanoclastic and alluvial sediments (Feng and others, 2010; Wang and others, 2013). During the first phase (SK-1) of the International Continental Scientific Drilling Project's (ICDP) efforts to recover strata covering the entire Cretaceous, a total of 2,486 m of core were recovered that span the late Turonian to the end Cretaceous (Wan and others, 2013; Deng and others, 2013; Wu and others, 2014). Recent paleoclimate reconstruction efforts have used a variety of proxies, including ostracods from lacustrine facies (Chamberlain and others, 2013) and paleosol carbonate nodules (Huang and others, 2013; Gao and others, 2015). We model the Sr/Ca, Mg/Ca and $\delta^{18}\text{O}$ ostracod record originally published by Chamberlain and others (2013) spanning 84 to 88 Ma (fig. 4A). Data is kernel smoothed on the original age model (Wan and others, 2013; Wang and others, 2013; Chamberlain and others, 2013), and this portion of the record was selected because of the high density sampling through this period, relatively stable source area (based on $^{87}\text{Sr}/^{86}\text{Sr}$), and the likely existence of

Ocean Anoxic Event 3 (OAE 3 at ~85.5 Ma; Wagreich, 2012). Because the ostracod genus *Cypridea* sampled by Chamberlain and others (2013) is extinct, we use partition coefficient and vital effect calibrations for the extant genus *Cyprideis*, a closely related genus also of the *Cyprididae* family (table 2). See table 2 for detailed model input parameters.

The relatively invariant (kernel smoothed) Mg/Ca and Sr/Ca records (fig. 4A) result in several interesting observations when HyBIM is applied to the Songliao Basin ostracod record. The Mg/Ca and Sr/Ca records demonstrate much greater spread around the mean kernel-smoothed values and, due to slightly lower sampling density, have a greater cross-validated kernel bandwidth than the $\delta^{18}\text{O}$ record (62 kyrs vs. 241 kyrs and 219 kyrs; fig. 4A). Because of the relatively invariant Mg/Ca and Sr/Ca record, the modeled temperature is similar to the result expected if a $\frac{\partial(\delta^{18}\text{O})}{\partial T}$ empirical relationship of 0.58 ‰/°C is applied to the kernel smoothed mean of the $\delta^{18}\text{O}$ record (red line in fig. 4B), unlike the Lake Miragoane record.

We applied the HyBIM to a portion of the Songliao record given in Chamberlain and others (2013) from 88 to 84 Ma because this time interval captures a portion of the Oceanic Anoxic Event 3 (OAE 3) during a time of global warming. Moreover, we have excellent oxygen and trace element data for this time range in the Songliao Basin. It is recognized that unlike earlier OAEs, OAE 3, may be a series of events distributed over longer time frames and is recorded predominantly in the western hemisphere (Wagreich, 2012). Thus, we are interested in how the temperature record in the Songlia Basin recorded this “event”. Our results show peaks of warming of ~6 °C between 86 and 85

Ma and again between 85 and 84 Ma. These two warm periods are consistent with multiple events defining OAE 3, but cannot be correlated with those in marine sections because: 1) the age constraints in the Songlia Basin lack the necessary time resolution; and 2) there are multiple carbon isotope excursions during OAE 3 that vary both temporally and spatially across the globe (Wagreich, 2012). Nevertheless, our results do show multiple warming events during this time interval of OAE 3. In addition, the HyBIM results agree with the interpretation of increasing lake size, based on outcrop extent, during this time interval (Feng and others, 2010), suggesting that over this interval lake volume increased by ~10 percent. However, we point out that due to the large spread in the measured Sr/Ca and Mg/Ca, the modeled volume changes are not particularly robust.

1.4 Limitations and Guidelines

The modeling framework presented in this paper represents a new approach to quantitatively constraining the hydrologic balance and temperature fluctuations as recorded by the trace elements and stable isotopes of biogenic lacustrine carbonate. Inherently the modeling of paleoclimate records requires simplifying assumptions. As such, we provide several guidelines for assessing the potential application of HyBIM to a lake system:

1. Lake systems with highly variable (inorganic) chemical sedimentation, typically driven by order of magnitude changes in lake level, cannot be modeled using HyBIM. A fundamental assumption of the evaporation partial derivatives is that we assume mass conservation of the trace elements within each time step. In

addition, we assume that within each time step lake volume does not change by more than 10 percent (see derivation of partial derivatives). Thus, HyBIM solutions should be limited to “balanced-filled” (Caroll and Bohacs, 1999) lake systems with biogenic carbonate from periods of similar lithologic deposition.

2. Many large lakes break up into smaller lakes during desiccation due to complex hypsometric basin geometries and watersheds (for example Quaternary Lake Lahontan; Reheis and others, 2014). While this is not readily assessed from sediment cores alone, we emphasize the need for determination of the lake hypsometry via shoreline and/or outcrop extent (for example, Reheis, 1999; Sack, 2009; Zimmerman and others, 2011; Steinman and others, 2013; Ibarra and others, 2014; Smith and others, 2014; Doeberbert and others, 2014). HyBIM should not be applied to these systems over intervals of breakup, as the river chemistry of the smaller lake basins within a large system may differ due to bedrock heterogeneity and catchment weathering processes.
3. Well-constrained partition coefficients are necessary to place the measured Mg/Ca and Sr/Ca (or other trace element measurements) in terms of lake water concentrations. Presently modern studies of terrestrial biogenic carbonates from ostracods (for example, Engstrom and Nelson, 1991; Xia and others, 1997a, 1997b; Wansard and others, 1998; De Deckker and others, 1999; Dettman and others, 2002; Holmes and Chivas, 2002; Dwyer and others, 2002; Ito and Forester, 2009; Gouramanis and others, 2010; Marco-Barba and others, 2012; Börner and others, 2013) represent some of the only calibrated partition coefficients available for use in the HyBIM modeling framework outlined here.

Future application of this modeling framework to inorganic carbonate or other types of biogenic carbonate from lake systems will require further measurement of trace elements and calibration of partition coefficients.

4. We assume that lake water temperature and the basin average air temperature are directly proportional. HyBIM solves for temperature changes (ΔT), not absolute values of temperature, but selects an absolute temperature for each Monte Carlo iteration used for placing the measured Mg/Ca and $\delta^{18}\text{O}$ into lake water composition (see previous discussion). For the lake systems with mean annual air temperature greater than 0 °C included in a recent global lake temperature compilation the slope between the mean annual water temperature and mean annual surface air temperature is indistinguishable from 1 (slope = 1.02 ± 0.03 (1σ), $r^2 = 0.94$, $n = 81$, mean annual air temperatures from 0 to 27 °C; see dataset from Appendix A of Hren and Sheldon, 2012), suggesting that this assumption of proportionality is valid.

1.5 Conclusions and Future Model Refinement

In this paper, we develop and apply a new modeling framework using variations in $\delta^{18}\text{O}$ and trace elements (Mg and Sr) measured in biogenic lacustrine carbonates for closed basin lacustrine paleoclimate records. By applying this modeling approach to two ostracod records, we demonstrate the utility of HyBIM to quantify paleoenvironmental changes across different timescales. Due to a lack of significant variation in the (kernel smoothed) Mg/Ca and Sr/Ca records from the Songliao Basin, the $\delta^{18}\text{O}$ record primarily controls the predicted temperature fluctuations and the volume changes are minimal.

Additionally, the Lake Miragoane results demonstrate how the combination of high-resolution and low-resolution datasets are accounted for by HyBIM via kernel smoothing and interpolation to even time steps. Future application of HyBIM to a high-resolution historical record from a small, constrained terminal lake system will provide the best independent validation of this modeling methodology.

Two additions could provide further extensions to this modeling approach. First, over-determination of the A matrix by adding a fourth equation to the system of equations describing additional trace elements (such as U or Li; for example Holmes and others, 1995), δD (for example Tierney and others, 2008; Feakins and others, 2014; Kirby and others, 2014) or $\delta^{13}C$ (controlled by similar processes described in Li and Ku, 1997; Horton and Oze, 2012; Horton and others, 2015) would provide greater control on the partitioning of salinity changes due to evaporation and dilution by volumetric increases. Second, additional isotope systems, such as Sr or Pb isotopes, could be included as a fourth equation (the A matrix would be 4x4) and would extend the function of HyBIM to also de-convolve other possible variables, such multiple riverine inputs, rearrangement of the drainage basin, et cetera. For example, assuming different watershed source regions have different Sr or Pb isotope signatures (and also trace element concentrations and/or meteoric water $\delta^{18}O$ inputs), a fourth set of partial derivatives can be derived to define the relationship between two distinct end-members. This approach could be applied to the full Songliao Basin record (lower resolution) presented in Chamberlain and others (2013), or to basins with sufficient data and known tectonic changes, such as Cenozoic basins in the western United States (for example, Davis and others, 2009; Smith and others, 2014; Doebbert and others, 2014).

The application of this modeling framework is not limited solely to lake systems. For example, recently published speleothem records have measured $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca, in addition to other trace elements (such as U/Ca, Ba/Ca) and isotope systems (such as $^{234}\text{U}/^{238}\text{U}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) (for example, Oster and others, 2009; Steponaitis and others, 2015). By modifying the modeling framework presented here the relative influence of temperature and vadose zone residence times (influenced by prior carbonate precipitation) on the stable isotope and trace element measurements could be quantitatively deconvolved. However, modern cave monitoring studies to assess the variability and controls on the stable isotope and trace element variations in cave drip water (for example, Fairchild and others, 2000; Musgrove and Banner, 2004; Wong and others, 2011; Oster and others, 2012a), would be necessary for calibration. Similarly, trace element and stable isotope measurements on pedogenic soil minerals and the associated soil pore water in arid soil systems (for example Amundson and others, 1996; Oster and others, 2012b; Maher and others, 2014) may provide an additional avenue for quantitative paleoclimate reconstruction using a similar modeling framework.

Finally, the Monte Carlo approach presented in this paper only includes uncertainty in the input parameters and input dataset. However, age-models in sedimentary settings, and many terrestrial paleoclimate archives, including lakes, can be highly uncertain due to sedimentation rate changes, hiatuses and a lack of dateable material (for example, Huybers and Wunsch, 2004; Blaauw and Christen, 2011). Further extension of HyBIM to include incorporation of age model uncertainty would provide added utility by including temporal uncertainty quantification of the hydrologic response to climatic events and trends recorded by the lake carbonate geochemistry. Recent work

has included this type of Monte Carlo age model uncertainty into paleoclimate reconstructions for individual records and large paleoclimate compilations (for example, Shakun and others, 2012; Anchukaitis and Tierney, 2012; Tierney and others, 2013; Marcott and others, 2013; Steinman and others, 2014). Ultimately paleoclimate proxy modeling efforts, such as those illustrated in this paper, are only valuable if the uncertainty of the timing and magnitude of climatic changes is robustly quantified.

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1.8 Tables

Table 1. Definition of model parameters for HyBIM as used in the text

Parameter	Description
$dT, \partial T$	Change in basin air temperature (mean annual surface temperature)
$dF_{\text{evap}}, \partial F_{\text{evap}}$	Change in amount of lake water (volumetrically) evaporated, where $F_{\text{evap}} = 1$ is fully evaporated and $F_{\text{evap}} = 0$ is no evaporation
$dF_{\text{input}}, \partial F_{\text{input}}$	Change in volumetric increase in lake water, where $F_{\text{input}} = 1$ is no change
Δt	Time step of model
τ_{res}	Residence time of lake water
α	Combined fractionation factor for Rayleigh equation (kinetic and equilibrium)
$d(\delta^{18}\text{O}), \partial(\delta^{18}\text{O})$	Change in oxygen isotopic composition of lake water
$(\delta^{18}\text{O})_{\text{source}}$	Oxygen isotopic composition of incoming meteoric water
$(\delta^{18}\text{O})_{\text{initial}}$	Oxygen isotopic composition of lake water for a given time step, derived from the measured $\delta^{18}\text{O}$ in biogenic carbonate, corrected for vital effects
Sr/Ca	Strontium to calcium ratio measured in biogenic carbonate
Mg/Ca	Magnesium to calcium ratio measured in biogenic carbonate
$d[\text{Sr}], \partial[\text{Sr}]$	Change in strontium concentration of lake water
$d[\text{Mg}], \partial[\text{Mg}]$	Change in magnesium concentration of lake water
$d[\text{M}], \partial[\text{M}]$	Change in magnesium or strontium concentration of lake water
$[\text{M}]_{\text{source}}$	Magnesium or strontium concentration of incoming meteoric water (weighted stream water and rainwater)
$[\text{M}]_{\text{initial}}$	Magnesium or strontium concentration of lake water for a given time step, derived from the measured Sr/Ca and Mg/Ca in biogenic carbonate using the appropriate partition coefficient and calcium concentration.
$K_D[\text{M}]$	Partition coefficient for Sr/Ca or Mg/Ca

Table 2. Details of input dataset and input parameters for HyBIM application to Lake Miragoane and Songliao Basin

Record	Age Range	Original References	$\delta^{18}\text{O}$ Average Resoluti on	Mg/Ca Average Resoluti on	Sr/Ca Average Resoluti on	$\delta^{18}\text{O}$ Kernel Bandwid th	Mg/Ca Kernel Bandwidth	Sr/Ca Kernel Bandwidth
Lake Miragoane, Haiti	Holocene (10.56 - 0.05 ka BP)	Hodell and others (1991); Curtis and Hodell (1993)	16.9 years	176.5 years	173.5 years	38.9 years	422.6 years	440.1 years
Songliao Basin, China	Cretaceous (88.04-84.02 Ma)	Chamberlain and others (2013)	24.4 kyrs	27.9 kyrs	27.9 kyrs	61.7 kyrs	240.9 kyrs	219.0 kyrs
Record	Ostracod Genus	Partition Coefficient	Vital Effect		Input Solute Concentrations		Input $\delta^{18}\text{O}$	
Lake Miragoane, Haiti	<i>Candona</i> genus (identified by R. Forester, see details in Curtis and Hodell, 1993)	As determined for <i>Candona rawsoni</i> by Engstrom and Nelson (1991). Temperature effect for Mg/Ca only.	+ 2.5 $\pm$ 0.2 ‰ based on <i>Candona candida</i> . (Keatings, 1999)		Average of watershed [Sr] and [Mg], and lake [Ca] from Holmes and others (1995a,b)		-8 $\pm$ 2 ‰ (OIPC; Bowen and Revenaugh, 2003)	
Songliao Basin, China	Sampled extinct <i>Cypridea</i> genus, closely related to extant genus <i>Cyprideis</i>	As determined for <i>Cyprideis</i> by DeDecker and others (1999). Temperature effect for both Sr/Ca and Mg/Ca.	Assumed to be 1.3 $\pm$ 0.2 ‰ (Average of compilation in Holmes and Chivas, 2002)		Average of watershed [Sr] and [Mg], and lake [Ca] from Han and Huh (2009), Wang and others (2012), Liu and others, (2013), Moon and others (2009)		-18 $\pm$ 2 ‰ (estimated from Poulsen and others, 2007)	

1.9 Figures

Figure 1. Illustration of evaporation relationships used to parameterize the partial derivatives. Inset plots show regions of linear approximation assuming $F_{\text{evap}} < 0.2$ within each time step gray shading. Dashed lines are uncertainty. See text for equations describing relationships. (A) Rayleigh evaporation of $\delta^{18}\text{O}$, total (kinetic and equilibrium) fractionation, ϵ , is $13.5 + 4.7/-3.6\text{‰}$ ($5 - 35\text{ °C}$ and $50 - 90\%$ humidity). (B) Mass conservation of solute, M (that is, Mg or Sr), with an initial lake concentration of $10 \pm 2\text{ mmol}$.

Figure 2. Illustration of mixing relationships used to parameterize the partial derivatives for volume increase. Inset plots show regions of linear approximation assuming $F_{\text{input}} < 1.2$ within each time step. Dashed lines are uncertainty. See text for equations describing relationships. (A) $\delta^{18}\text{O}$ mixing (input water of $-15 \pm 2\text{‰}$, initial lake water of -3‰). (B) Mixing of initial concentration ($10 \pm 2 \text{ mmol}$) with a dilute input solute concentration of 3 mmol .

Figure 3. Illustrative Application of HyBIM to the Lake Miragoane Ostracod (*Candona sp.*) record. (A) Original $\delta^{18}\text{O}$, Mg/Ca and Sr/Ca records (gray dots) from Hodell and others (1991) and Curtis and Hodell (1993). Data are plotted on the original age model. For model input the data are kernel smoothed using an Epanechnikov kernel. The cross validated bandwidth (BW; see text for explanation) is listed for each record ($\delta^{18}\text{O}$, Mg/Ca and Sr/Ca). The solid black line is the mean and the dashed black lines (dashed blue lines) are the 1σ . (B) HyBIM results for the Lake Miragoane records using partition coefficient and vital effect data from Engstrom and Nelson (1991) and Keatings (ms, 1999) derived for *Candona sp.* The thin gray line (thin red line) is the empirical relationship for isotopes in precipitation ($0.26\text{‰}/^\circ\text{C}$) derived from empirical tropical GNIP stations (fig. A2; after Rozanski and others, 1993).

Figure 4. Illustrative Application of HyBIM to the Songliao Basin Ostracod (*Cypridea sp.*) Record. (A) Original $\delta^{18}\text{O}$, Mg/Ca and Sr/Ca records (gray dots) from Chamberlain and others (2013). Data are plotted on the original age model of Wan and others (2013). For model input the data are kernel smoothed using an Epanechnikov kernel from 84 to 88 Ma (densely sampled portion of the record). The cross validated bandwidth (BW; see text for explanation) is listed for each record ($\delta^{18}\text{O}$, Mg/Ca and Sr/Ca). The solid black line is the mean and the dashed black lines are the 1σ . (B) HyBIM results for the Songliao Basin record using partition coefficient data from DeDeckker and others (1999) derived for *Cyprideis sp.*, the extant, closely related genus of *Cypridea sp.* The solid line is the median and the dashed black lines (dashed blue lines) are the 95% confidence interval of the Monte Carlo estimation. The approximate position of OAE 3 is denoted by the red bar, which corresponds to a peak the predicted temperature. The light gray line (red line) is the empirical relationship of Rozanski and others (1993) for isotopes in precipitation (0.58 ‰/°C) derived from mid-latitude Global Network of Isotopes in Precipitation (GNIP) stations.

CHAPTER 2

Warm and cold wet states in the western United States during the Pliocene-Pleistocene

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Abstract

The size distribution of lakes records the competition between precipitation delivery and evaporation. Lakes were abundant in the terminally draining basins of the western United States (USA) during both the colder-than-preindustrial latest Pleistocene glacial period (ca. 14–29 ka) and the warmer-than-preindustrial mid-Pliocene (ca. 2.9–3.3 Ma). To understand the hydroclimatic conditions that permitted lakes, we couple lake mass balance equations with a water and energy balance framework (*sensu* Budyko). Further, we compare paleo-lake area distributions to forward-modeled lake areas using climate model simulations of the Last Glacial Maximum (LGM, 19–26 ka) and mid-Pliocene. We conclude that both warmer- and colder-than-modern periods of the Pliocene–Pleistocene resulted in wetter-than-modern conditions in the terminally draining basins of the western USA through similar mechanisms. Specifically, the presence of lakes during the LGM reflects increased precipitation in addition to decreased evaporative demand. In the southern Great Basin, LGM lakes require large increases in precipitation across the region. During the mid-Pliocene, increased evaporative demand necessitated increased precipitation to maintain lakes. Further, the increase in precipitation and dominantly southwestern distribution of mid-Pliocene lake deposits is consistent with proposed mean "El Niño–like" conditions altering regional hydroclimate during this period. These observations suggest that during interglacial periods, the western USA resides within a local aridity maximum, and both long-term increases and decreases in global temperatures have been associated with wetter conditions across much of the western USA in the past.

2.1 Introduction

The presence and size of lakes reflects the balance between moisture delivery and evaporative demand. Mid-latitude regions, such as the western United States (USA), exhibit evidence of large lake-level fluctuations during the Pliocene–Pleistocene in underfilled to balance-filled basins (Benson et al., 1990; Reheis et al., 2014; Pound et al., 2014). Barring large changes in rates of potential accommodation (i.e., tectonics), these fluctuations reflect changes in climate that control water and sediment supply to each basin’s termini (cf. Carroll and Bohacs, 1999). Lacustrine deposits and paleo-shorelines found throughout the terminally draining (closed) basins of the western USA (Mifflin and Wheat, 1979; Reheis et al., 2014; Pound et al., 2014) suggest a hydrologic balance dramatically different from that of the present during intervals of the Pliocene–Pleistocene (Matsubara and Howard, 2009; Ibarra et al., 2014; Oster et al., 2015; Barth et al., 2016; Putnam and Broecker, 2017).

We compile observations of lake presence and extent during the Last Glacial Maximum (LGM) and the mid-Pliocene. To understand what hydroclimatic factors controlled lake extents during these two periods, we use a framework that enforces mass and energy balance on precipitation-runoff relationships. We compare observations of the distributions of basin area–normalized lake areas to scaling of modern climatological distributions and climate model simulations.

2.2 Methodology

Compilation of Geologic Observations

We compile lake distributions for the LGM and mid-Pliocene in the western USA along with hydroclimate-sensitive proxies from previous studies (Dowsett et al., 1994; Molnar and Cane, 2007; Winnick et al., 2013; Oster et al., 2015) (Fig. 1). For the LGM, we use maps and tables of pluvial lake extent during the end of the last glacial cycle (ca. 14–29 ka; Fig. 1A; see Table DR1 in the GSA Data Repository). Because terminally draining basin areas have not significantly shifted since the LGM (e.g., Benson et al., 1990; Reheis et al., 2014), we directly compare surface area estimates. Basin areas were derived from modern watersheds using the HydroSHEDS mapping product (<http://www.hydrosheds.org>). We also account for shoreline geochronology that has demonstrated that lakes in the northern Great Basin (GB) reached maximum levels after the LGM, with LGM lake levels (stillstands) covering ~50%–75% of their maximum areas (Benson et al., 1990; Ibarra et al., 2014; Reheis et al., 2014).

Pound et al. (2014) compiled the spatial distribution and estimated size of lakes during the mid-Pliocene warm period (defined as ca. 2.9– 3.3 Ma for climate model simulations; Fig. 1B) within the chronostratigraphically defined Late Pliocene (Piacenzian; 2.58–3.6 Ma), which we pair with modern drainage areas only in cases where the lake was terminal and drainage divides have not been greatly influenced by major tectonic drainage reconfiguration processes (see the Data Repository, and Table DR3 therein). Their lake size compilation is largely based on mapping and fish genetics work in Southern California and southwestern Nevada, and other documented outcrops of Pliocene lacustrine sediments. Given that structural basin configurations are mostly

unchanged since the Pliocene, it is possible that lakes filled the terminally draining basins in the GB during the late Pliocene. As supporting evidence for lake presence, we also conduct a search for 2.9–3.3 Ma strata in the Macrostrat platform (<https://macrostrat.org/>). We identify lacustrine strata that overlapped this range with sufficient thickness (>10 m of sedimentation) to indicate a possible long-lived lake system (Fig. 1B). Tectonic and drainage capture processes may have influenced basin boundaries since the Pliocene, introducing potential uncertainties in quantitative comparisons; however, we note that the presence of lakes in terminally draining regions indicates a hydrologic balance wetter than modern.

Lake Areas and Hydroclimate Changes

We combine a water and energy balance model with climate variables to forward model lake areas. We extend a framework proposed by Broecker (2010) by combining the commonly used basin area–normalized mass balance (cf. the pluvial hydrologic index of Mifflin and Wheat [1979]) with a Budyko framework (cf. Broecker, 2010; Greve et al., 2015) to determine changes in precipitation-runoff scaling. For a terminally draining basin, the steady-state water balance (Mifflin and Wheat, 1979; Broecker, 2010; Ibarra et al., 2014) is:

$$Pk_{\text{run}}(A_B - A_L) + PA_L = E_L A_L, \quad (1)$$

where P is precipitation, k_{run} is a coefficient that determines the fraction of P converted to runoff, A is area (subscripts: B —terminal basin area, L —lake area), and E_L is lake evaporation. Rearranging, the proportional surface area of the lake relative to the basin area (Hudson and Quade, 2013) is:

$$\frac{A_L}{A_B} (\%) = \frac{Pk_{run}}{E_L - P + Pk_{run}} \times 100 . \quad (2)$$

We relate E_L to net radiation (RN) and temperature using the Priestley-Taylor equation (see the Data Repository). To directly quantify the precipitation-runoff relationship under different climatic conditions, we impose a Budyko curve (cf. Broecker, 2010; Greve et al., 2015). We determine k_{run} as:

$$1 - k_{run} = \frac{ET}{P} = 1 + \frac{E_p}{P} - \left(1 + \left(\frac{E_p}{P}\right)^\omega\right)^{1/\omega}, \quad (3)$$

where E_p is potential evapotranspiration, ET is evapotranspiration, and ω is a free parameter that integrates the hydroclimatic properties of a watershed (Roderick et al., 2014; Greve et al., 2015). This framework ensures that lake water balance calculations are constrained to realistic bounds, and imposes a nonlinear response of runoff to changes in precipitation. Previous modeling for terminally draining basins in the GB (Matsubara and Howard, 2009; Barth et al., 2016) shows that, for determining firstorder trends in terminally draining basins, more complex hydrologic simulations follow the precipitation-runoff relationship imposed by the Budyko framework.

We populate the parameters P and E_p , and assume ω values (see below), in Equation 3 to solve for k_{run} , and populate P , E_L and k_{run} in Equation 2 to solve for A_L/A_B . We use the energy, evapotranspiration, and precipitation fields from the North American Regional Reanalysis (NARR, <https://www.esrl.noaa.gov/psd/data/gridded/data.narr.html>) for the modern sensitivity analysis, the Paleoclimate Modelling Intercomparison Project 3 (PMIP3, <https://pmip3.lsce.ipsl.fr/>; Braconnot et al., 2012) ensemble for the LGM (ca. 21 ka), and the Pliocene Model Intercomparison Project (PlioMIP, https://geology.er.usgs.gov/egpsc/prism/prism_1_23/prism_pliomip.html; Haywood et al., 2013)

ensemble for the mid-Pliocene (defined as 2.9–3.3 Ma). This analysis is implemented over model land grid cells across the western USA (30°–45°N, 102°–121°W). For a subset of the analysis, we use a smaller region representing the southern GB (34°–39°N, 114°–119°W). Potential evapotranspiration (E_p) is approximated as the liquid water equivalent of the net downward radiation at the surface (R_N), which is balanced by the sensible (H) and latent (LE) heat fluxes:

$$E_p = \frac{R_N}{L} = \frac{R_{S,i} - R_{S,o} + R_{L,i} - R_{L,o}}{L} = \frac{LE + H}{L}, \quad (4)$$

where L is the latent heat of evaporation, and radiation (R) subscripts denote incoming (i) and outgoing (o), and long-wave (L) and short-wave (S), radiation (Roderick et al., 2014). These variables are taken as average annual sums from climate model simulations and NARR data for the domains in Figure 1.

We also forward model lake areas using climate model output. Using the climate model– derived E_p and P values, along with domainwide ω values derived from the climate model’s individual output (see the Data Repository), we calculate the runoff coefficient (k_{run}) and forward model normalized lake areas (A_L/A_B).

To analyze the sensitivity of the regional water balance, we use the distribution of the variables in Equations 2 and 4 from NARR (see the Data Repository). Using changes in temperature of -15 K to $+10$ K relative to modern, we scale potential evapotranspiration ($E_p = R_N / L$) by $1.6\%/K$ and lake evaporation (E_L) using the Priestley-Taylor equation (see the Data Repository). We scale precipitation from $0.2\times$ to $3.25\times$ of modern. For the sensitivity analysis, $\omega = 2.6$, following Greve et al. (2015) (see the Data Repository for further discussion). These ranges encapsulate proxy-derived precipitation and temperature estimates for the mid-Pliocene and LGM intervals (Dowsett et al., 1994;

Molnar and Cane, 2007; Matsubara and Howard, 2009). This normalization is consistent with other approaches that assess hydroclimate change relative to modern observations (e.g., Ibarra et al., 2014; Barth et al., 2016).

2.3 Proxy Comparisons

The spatial distributions of lakes and moisture proxies during the LGM and mid-Pliocene (Fig. 1) were similar despite different climate states. During the LGM, most terminally draining basins in the western USA contained lakes covering ~9.2% (4.6%–19.2%, median and interquartile range [IQR]) of their basin areas, with the largest basin area–normalized lake areas located in the northern GB (up to 49.0%). During the mid-Pliocene, early Piacenzian lake sediment areas compiled by Pound et al. (2014) are proportionally smaller, and primarily located in the modern-day southwest GB and Mojave Desert region (Fig. 1B). These lakes cover ~4.8% (1.2%–6.5%) of their basin areas, though we note large potential uncertainties in determining basin areas. Extant (playa) lakes in the dry western GB (Table DR2) cover 1.0% (0.3%–3.2%) of modern terminally draining basins.

Macrostrat suggests that Pliocene lakes existed elsewhere in the western USA, likely within modern terminally draining basins (see the Data Repository). Proxy evidence from vegetation, glaciers, speleothems, and soils for the LGM suggests mostly drier-than-modern conditions approaching the ice sheet to the north, with some dry conditions east and northeast of the GB (Oster et al., 2015). Conversely, mid-Pliocene wet conditions appear to have extended farther east than in the LGM (Fig. 1), consistent with proposed “El Niño–like” climatological conditions involving a south-shifted Pacific

storm track and increased precipitation (Molnar and Cane 2007; Winnick et al. 2013). Interpretation of wetter or drier conditions from vegetation records is complicated by the effect of changing atmospheric $p\text{CO}_2$ (Prentice et al., 2011; Scheff et al., 2017). Pollen records that indicate drier conditions during the LGM (wetter in the Pliocene) may, in part, be responding to lower (higher) atmospheric $p\text{CO}_2$ (~180 versus 400 ppm). Regardless, the distribution of wetter and drier pollen records supports the inferred spatial changes in hydroclimate from terminally draining lakes in the LGM and mid-Pliocene.

2.3 Hydrologic Modeling

To better understand the role of temperature and precipitation in driving patterns of lake size distributions, we analyze how lake area cumulative distribution functions (CDFs) respond to changes in temperature (via EL , E_p , and k_{run}) and precipitation (Fig. 2A). We vary temperature and precipitation, and assume the modern median Budyko scaling parameter ($\omega = 2.6$; Greve et al., 2015). Precipitation changes result in an increasing or decreasing proportion of larger basin area–normalized lake areas with increasing or decreasing precipitation. Changes due to temperature are smaller in magnitude than those of precipitation, with decreasing or increasing temperatures causing increasing or decreasing occurrence of large basin area–normalized lake areas. In Figure 2C, we contour median (CDF = 0.5) normalized lake area to changes in precipitation and temperature. Assuming temperature estimates from other proxies for the western USA (Matsubara and Howard, 2009), we find that a majority of LGM lake levels are explained by moderate to large increases in precipitation (shaded blue IQR with precipitation factors of ~0.75–1.5 of modern; Matsubara and Howard, 2009; Ibarra et al.,

2014) accompanied by small decreases in evaporation. Further, decreased evaporative demand due to decreased temperature is of moderate importance for LGM lake areas when the distribution is adjusted to account for the observation that LGM stillstands were lower than the observed maximum highstands in the northern GB (Fig. DR3 in the Data Repository). In contrast, increased mid-Pliocene temperatures (Dowsett et al., 1994; Molnar and Cane, 2007) and the attendant increase in evaporative demand necessitate precipitation increases (Fig. 2C) to explain the distribution of lake areas, particularly when the southern GB is analyzed independently (shaded orange with IQR precipitation factor >1 ; Fig. 2D). Further, because the mid-Pliocene data have been derived primarily from basinal sedimentary deposits, which may have experienced subsequent erosion or burial, our distribution of mid-Pliocene areas may be an underestimate in precipitation increases.

Climate models and our proxy compilations demonstrate that LGM and mid-Pliocene precipitation and temperature changed in spatially heterogeneous ways, even in the sign of precipitation (cf. Molnar and Cane, 2007; Oster et al., 2015). For example, during the LGM, western USA precipitation exhibited a pronounced southwest-northeast dipole (Oster et al., 2015; Lora et al., 2017). When terminally draining basins in the southern portion of the GB are analyzed independently, large increases in precipitation ($1.3\times$ to $1.6\times$) are required to drive LGM lake levels because temperature decreased less than further-inland terminally draining basins (Fig. 2D). Further, within the southern GB domain, the distribution of midPliocene lakes (Fig. 1B) requires large precipitation increases ($1.6\times$ to $2.0\times$) (Fig. 2D).

Our sensitivity analyses do not account for spatially variable anomalies. Therefore, we carry out similar calculations using climate model output (Fig. 2B). There is significant spread in the forward-modeled lake area anomalies. Notably, some LGM models have CDFs similar to the ensemble average CDF for the mid-Pliocene, and a comparison of these results to the distribution of lake areas in Figure 2B shows agreement between the range of observations and the climate model output for both periods. However, because the region of interest is averaged over both terminally draining and open basins, and as the PMIP3 and PlioMIP climate model simulations do not yet parameterize permanent lakes in their boundary conditions (cf. Pound et al., 2014), the climate model distributions in Figure 2B show more heavily tailed distributions than the range of observations.

2.4 Implications

Hydroclimate in the western USA responded nonlinearly to past climatic forcings. Increased precipitation with reduced evaporative demand resulted in wetter conditions during colder-than-preindustrial periods. Further, increased moisture convergence may have been a mechanism for wetter conditions during warmer-than-preindustrial periods. Consequently, the interglacial western USA appears to represent a local aridity maximum that is transitional between two different wet states, resulting in the fewest and smallest lakes compared to geologically recent colder and warmer periods. Thus, past climatic change did not result in unidirectional changes in the regional water balance; rather, the interplay between thermodynamic and dynamic effects results in a more complex, nonlinear response. The mechanism of increased moisture convergence during the mid-

Pliocene is beyond the scope of this study. However, the existence of background El Niño-like conditions, driven by reduced meridional and zonal sea-surface temperature gradients (Burls and Fedorov, 2017), may have strengthened southwesterly moisture delivery (Molnar and Cane, 2007; Winnick et al., 2013; Haywood et al., 2013), resulting in greater wintertime precipitation that fed the southwest USA lakes. While the direct applicability of mid-Pliocene conditions to future warming scenarios remains unclear (Burls and Fedorov, 2017), our results suggest that if future warming results in similar El Niño-like tropical Pacific conditions, aridity may decrease in the western USA.

Our analysis demonstrates how differences in regional atmospheric moisture divergence and convergence, along with regional water and energy balances (e.g., Seager et al., 2014; Putnam and Broecker, 2017), are recorded by lake deposits. Future work to better constrain lake and terminally draining basin areas for underconstrained geologic time slices will provide new constraints on the terrestrial hydroclimate response to climatic change

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2.7 Figures

Figure 1. Maps of lakes and hydroclimate-sensitive proxies, western United States. A: Last Glacial Maximum (LGM) lake extents. B: Mid-Pliocene lake locations, from Pound et al. (2014) and from Macrostrat platform. Mid-Pliocene and LGM proxy networks are coded as indicating wetter, drier, or no change relative to modern. Dashed boxes denote analysis domains.

Figure 2 (next page). Climatic forcing and lake area changes, western United States. A: Scaling of modern climate distributions (cumulative distribution functions, CDFs) to linear changes in precipitation and temperature. Bold line is modern. B: Basin area–normalized lake area using climate model simulations relative to modern for western United States domain. C: Median basin area–normalized lake area (CDF = 0.5 from panel A) contoured for changes in precipitation and temperature for the western United States. Shaded regions are interquartile range (IQR) with thick median lines of observed lake areas and range of temperature change estimates relative to modern. D: Same as C, for southern Great basin domain. LGM—Last Glacial Maximum; A_L —lake area; A_B —terminal basin area; max.—maximum.

CHAPTER 3

Concentration-discharge relationships of monolithologic catchments and global rivers

Chapter Introduction

Quantifying the functional relationships between river discharge and dissolved weathering products places key constraints on our understanding of the coupling between weathering processes and climate. In this chapter I present two published manuscripts where I analyzed the concentration-discharge relationships of weathering products from geologically heterogeneous global rivers as well as smaller monolithologic catchments, which serve as lithological end-members representing basalt, granite, and carbonate. Concentration-discharge relationships are modeled with power-law and solute production equations to characterize the roles of weathering efficiency and thermodynamic limits to solute concentrations in controlling integrated solute fluxes. Weathering efficiency is quantified using Damköhler coefficients and power-law exponents, which describes the resistance of solute concentrations to dilution at high runoff. We find that Damköhler coefficient values derived for basaltic catchments are a factor of 2 to 6 higher than granitic catchments, accounting for a majority of the difference in increased area-normalized fluxes from mafic (basaltic) lithologies. In doing so we show that weatherability is runoff-dependent and increases with increasing runoff. For HCO_3^- and $\text{SiO}_2(\text{aq})$ fluxes, for modern global runoff, the derived mean basalt/granite weatherability is 2.2 (1.3–3.7, 2σ) and 1.7 (1.6–2.1, 2σ), respectively. Using a mix-lithology dataset

from global rivers we also demonstrate an inverse relationship between the power-law exponent and the Damköhler coefficient, which both increase and asymptote as catchments exhibit increasing chemostatic behavior. These two studies, focusing on monolithologic catchments (3.1; Ibarra et al., 2016, *Geochemica et Cosmochemica Acta*) and global rivers (3.2; Ibarra et al., 2017, *Acta Geochemica*) demonstrate the utility of long term monitoring networks providing discharge-resolved concentration datasets to quantify global weathering fluxes and the processes that control them.

3.1 Differential weathering of basaltic and granitic catchments from concentration-discharge relationships

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Abstract

A negative feedback between silicate weathering rates and climate is hypothesized to play a central role in moderating atmospheric CO₂ concentrations on geologic timescales. However, uncertainty regarding the processes that regulate the operation of the negative feedback limits our ability to interpret past variations in the ocean–atmosphere carbon cycle. In particular, the mechanisms that determine the flux of weathered material for a given climatic state are still poorly understood. Here, we quantify the processes that determine catchment-scale solute fluxes for two lithologic end-members—basalt and granite—by applying a recently developed solute production model that links weathering fluxes to both discharge and the reactivity of the weathering material. We evaluate the model against long-term monitoring of concentration–discharge relationships from basaltic and granitic catchments to determine the parameters associated with solute production in each catchment. Higher weathering rates in basaltic catchments relative to granitic catchments are driven by differing responses to increases in runoff, with basaltic catchments showing less dilution with increasing runoff. In addition, results from the solute production model suggest that thermodynamic constraints on weathering reactions could explain higher concentrations in basaltic catchments at lower runoff compared to granitic catchments. To understand how the response to changing discharge controls weathering fluxes under different climatic states, we define basalt/granite weatherability as the ratio of the basalt catchment flux to the granite catchment flux. This weatherability is runoff-dependent and increases with increasing runoff. For HCO₃[−] and SiO₂(aq) fluxes, for modern global runoff, the derived mean basalt/granite weatherability is 2.2 (1.3–3.7, 2σ) and 1.7 (1.6–2.1, 2σ), respectively.

Although we cannot determine the array of individual processes resulting in differences among catchments, the relative differences in certain model parameters that represent catchment-scale weathering fluxes of granitic and basaltic lithologies are robust. Our approach provides a mechanism that links runoff with the distribution of global sub-aerial silicate lithologies to understand how the basalt/granite weatherability of the Earth's surface may have varied on geologic timescales. The relationships between basalt/granite weatherability and runoff derived in this study could be used to parameterize the silicate weathering negative feedback to model past changes in $p\text{CO}_2$.

Keywords: *Silicate weathering; Solute fluxes; Geologic carbon cycle; Feedbacks*

3.1.1 Introduction

Global silicate weathering rates are thought to be modulated by the geographic distribution and areal extent of rock type, growth and decay of mountain ranges, the nature of biological activity, and the intensity of the hydrologic cycle (Berner, 1991; Kump and Arthur, 1997; Gibbs et al., 1999; Hartmann et al., 2009; Pagani et al., 2009; Banwart et al., 2009; Beerling et al., 2012; Kent and Muttoni, 2013; Maher and Chamberlain, 2014; Froelich and Misra, 2014). Understanding the factors that control global silicate weathering rates is fundamental to constraining the evolution of the Earth's carbon cycle over geologic timescales (Urey, 1952; Sagan and Mullen, 1972; Walker et al., 1981; Berner et al., 1983; Volk, 1987; Berner, 1991, 2006a; Caldeira and Kasting, 1992; Caldeira, 1992, 1995; Kasting, 1993; Berner and Caldeira, 1997; Gibbs et al., 1999; Kump et al., 2000; Berner and Kothavala, 2001).

One challenge for reconstructing past weathering rates is the considerable variability in the reactivity of the Earth's surface. For example, basaltic catchments weather faster than other silicates and account for approximately 20–35% of the modern global silicate weathering and CO₂ consumption flux, while occupying less than 5% of sub-aerial continental area (Gíslason et al., 1996, 2009; Louvat and Allègre, 1997; Dessert et al., 2001, 2003, 2009; von Blanckenburg et al., 2004; Rad et al., 2007; Hartmann et al., 2009; Schopka et al., 2011; Gaillardet et al., 2011a; Schopka and Derry, 2012; Moon et al., 2014; Balagizi et al., 2015). The higher weathering fluxes associated with basalt weathering have been explained by the high intrinsic reactivity of basaltic mafic mineral assemblages (Oelkers and Gíslason, 2001; Dessert et al., 2003; Gíslason and Oelkers, 2003), increased porosity in the basalt weathering zone (Navarre-Sitchler et al., 2009, 2013; 2015; Sak et al., 2010; Gleeson et al., 2011), and the importance of hydrologic fluctuations that moderate the water table depth and total stream discharge (Amiotte-Suchet and Probst, 1993; Bluth and Kump, 1994; Eiriksdottir et al., 2013, 2015; Balagizi et al., 2015; Dessert et al., 2015; Liu et al., 2015). Given the importance of basaltic weathering to total global solute fluxes, recent modeling studies that reconstruct weathering fluxes over the Cenozoic suggest that the weathering of mafic terrains may have been critically important in controlling past levels of atmospheric CO₂ (pCO₂) (Li and Elderfield, 2013; Kent and Muttoni, 2013; Molnar and Cronin, 2015; Jagoutz et al., 2016). However, scaling modern observations of weathering fluxes from catchments to both large spatial and temporal scales (e.g., Wallmann, 2001; Lefebvre et al., 2013; Li and Elderfield, 2013; Kent and Muttoni, 2008, 2013; Mills et al., 2014a; Li et al., 2016; Jagoutz et al., 2016; Cox et al., 2016) remains a challenge due to the lack of

phenomenological modeling frameworks that predict weathering fluxes at both catchment and global scales under different climate states.

To reconstruct changes in the geologic past, weathering fluxes are typically parameterized using modern solute flux data to derive a “weathering rate law.” These empirical laws are derived by fitting modern weathering rates to variables such as lithology, runoff, topographic slope, and temperature (Amiotte-Suchet and Probst, 1993; Bluth and Kump, 1994; White and Blum, 1995; Gaillardet et al., 1999; Dessert et al., 2001, 2003; Dupré et al., 2003; Navarre-Sitchler and Thyne, 2007; Hartmann et al., 2010, 2014a) and are often assumed to follow the form of either an exponential Arrhenius equation or power law (Velbel, 1993; White et al., 1999a; Gíslason and Oelkers, 2003; Carroll and Knauss, 2005; Gíslason et al., 2009; Eiriksdottir et al., 2013; Li and Long, 2014; Moon et al., 2014; Torres et al., 2015; Li et al., 2016). However, as discharge increases, solute concentrations decrease due to dilution, which results in an apparent plateau in weathering fluxes even as runoff increases (Godsey et al., 2009; Maher, 2011; Eiriksdottir et al., 2013; Maher and Chamberlain, 2014). Close examination of the catchment-scale weathering data on which these empirical weathering laws are derived (e.g., Bluth and Kump, 1994; Godsey et al., 2009; Gíslason et al., 2009; Clow and Mast, 2010; Maher, 2011; Eiriksdottir et al., 2013) demonstrates that the functional forms of the weathering rate laws (i.e., exponential Arrhenius or power-law) do not accurately reflect the decrease in concentration due to dilution with increasing runoff observed for individual catchments. Thus, existing frameworks do not capture the potential for weathering fluxes to plateau as runoff increases. Furthermore, if different lithologies

exhibit variable responses to changes in runoff, global weathering fluxes may show a complex behavior depending on the time-varying areal distribution of rock types.

Maher and Chamberlain (2014) recently developed a process-based solute production framework that links weathering fluxes to both runoff and the reactivity of the weathering zone. Given that this modeling approach contains both thermodynamic and kinetic constraints, as well as physical processes that govern the travel time of water through the subsurface, the solute production model could provide a useful alternative approach for parameterizing weathering fluxes because it allows for fluxes to plateau at sufficiently high runoff. However, this model has only been evaluated against single concentration–discharge pair values (i.e., time-averaged, flux-averaged, or single-samples) for global rivers (Maher and Chamberlain, 2014; von Blanckenburg et al., 2015) and long-term monitoring of $\text{SiO}_2(\text{aq})$ concentration–discharge patterns from a few small silicate bedrock catchments (Maher, 2011), and has not been systematically compared to rivers across gradients in lithology, climate, erosion rate, or basin size. As a consequence, it remains unclear whether such an approach could describe the variability in reactivity and hydrologic processes associated with individual catchments. Here, to isolate lithologic controls, we evaluate the ability of the solute production equations to capture patterns in concentration–discharge relationships exhibited by long-term monitoring of basaltic and granitic catchments (Fig. 1). In addition, we consider the extent to which concentration–discharge relationships can elucidate the differences in reactivity and composition that lead to large differences in area-normalized weathering fluxes between basaltic and granitic catchments.

By comparing basaltic and granitic catchments, we quantify patterns in observed concentration–discharge relationships for the two major silicate end-member lithologies responsible for terrestrial silicate weathering (Bluth and Kump, 1994; White and Blum, 1995; Kump and Arthur, 1997; Kump et al., 2000; Dessert et al., 2001; Berner, 2006b, 2008). We focus our analysis on two important parameters: (1) the degree to which solute fluxes from individual catchments resist dilution at high runoff and (2) the maximum solute concentrations. These two parameters determine the efficiency with which a catchment produces solute. We find that weathering fluxes from basaltic catchments are both more resistant to dilution at high runoff and have a greater maximum solute concentration, implying that basaltic catchments are more efficient at producing solute for a given climate. We further use these two parameters to show how the basalt catchment flux normalized to the granite catchment flux—the basalt/granite weatherability ratio—changes with runoff.

Earth surface weatherability is often treated as a tunable parameter in biogeochemical models (e.g., Kump and Arthur, 1997; Gibbs et al., 1999; Berner, 2006a, 2008; Mills et al., 2014a) because it determines the degree of coupling between climate and weathering. In turn, this coupling is a measure of the strength of the negative feedback between climate/atmospheric $p\text{CO}_2$ and silicate weathering. A weak coupling implies that weathering fluxes change little in response to changes in climate, whereas a strong coupling suggests that weathering responds rapidly to small changes in climate (West, 2012; Maher and Chamberlain, 2014; Goll et al., 2014; Caves et al., 2016). Our work demonstrates that weatherability cannot necessarily be treated as a constant, even over the short timescales that characterize rapid climate change in the geologic record.

Using these results, we propose a framework for linking basalt/granite weatherability to understand the behavior of the silicate weathering feedback over Earth history.

3.1.2 Background

Quantifying differences in concentration–discharge relationships among catchments of different lithologies may improve models for how weathering fluxes respond to changes at the Earth surface. We use a modeling framework outlined below that starts with the Damköhler number (Da), a dimensionless number that is the ratio of the fluid travel time (T_f [yr]) to the time required to reach equilibrium (T_{eq} [yr]) (Johnson and DePaolo, 1994; Steefel and Maher, 2009; Maher, 2010; Maher and Chamberlain, 2014; Li et al., 2014):

$$Da = \frac{T_f}{T_{eq}} = \frac{R_n L \phi}{q C_{max}} \quad (1)$$

where q [m/yr] is the flow rate (specific discharge), C_{max} [μmol/L] is the maximum solute concentration, R_n [μmol/L/yr] is the net mineral dissolution rate, and L [m] is the flowpath length, which is multiplied by ϕ (the effective porosity) to give the reactive flowpath length $L\phi$. A large Damköhler number ($Da > 1$) implies that reaction rates outpace advection such that local equilibrium within the weathering zone controls the solute concentrations (Sverdrup and Warfvinge, 1988; Steefel and Maher, 2009; Maher, 2010, 2011; Siirila and Maxwell, 2012; Maher and Chamberlain, 2014; Maher and Druhan, 2014; Li et al., 2014). Although the Da approach is widely used in reactive transport because it incorporates the balance between physical and chemical processes, the Damköhler number is non-unique when attempting to understand the importance of climatic versus lithologic controls on weathering, because changes in Da can be driven

by changes in travel time (T_f) or equilibrium time (T_{eq}), where the latter is set by the ratio between maximum solute concentrations and net dissolution rates ($T_{eq} = C_{max}/R_n$). For example, two catchments may have the same Da , but very different T_f or T_{eq} , meaning their response to changes in runoff (i.e., flow rate) will be very different (Fig. 2a). Thus, runoff can be factored out of Da to derive the Damköhler coefficient (Dw [m/yr] = $Da \times q = L\phi/T_{eq}$), which describes the reactivity of the material in the weathering zone over a given length scale, and modifies the relationship between concentration and discharge. The implication for concentration–discharge relationships is that Dw values describe the relative rate of increase in solute concentration for a given flowpath length. Thus, increased Dw values can result from either higher reaction rates or long flow paths (Maher and Chamberlain, 2014). Systems with high Dw values exhibit less dilution with increasing runoff compared to catchments with lower Dw values (Fig. 2a).

In this study, we focus on lithologic controls on Dw . We do not specifically evaluate the effect of erosion rates or differences in climate on Dw , although we do evaluate for relationships between Dw and temperature. Previous work with this solute production model has demonstrated that rapidly eroding mountain belts tend to have higher Dw values (Maher and Chamberlain, 2014). Accordingly, we expect the intra-lithology Dw distributions to be partially driven by these other factors. Given that the Dw value of a catchment reflects the ratio of the reactive flowpath length ($L\phi$) to the equilibrium time (T_{eq}), both of which may be impacted by erosion or climate, we thus emphasize how further stream measurements and upslope analyses might aid in deconvolving the derived concentration–discharge parameters presented below.

Solute production framework

Data from individual catchments display a range of solute concentrations (C [$\mu\text{mol/L}$]) as a function of discharge (Q [m^3/yr]) (i.e. C – Q relationships). The patterns in C – Q relationships that emerge in response to fluctuations in discharge are thought to indicate the processes that control the weathering flux. Thus, such patterns may inform the response of weathering rates to changes in the local climate (Godsey et al., 2009). Here, specific discharge or runoff (q [m/yr]) is defined as the instantaneous discharge (Q [m^3/yr]) divided by the catchment area (A [m^2]), and C [$\mu\text{mol/L}$] is the solute concentration (Fig. 1b). Below and for the remainder of the paper, we primarily discuss concentration-runoff (C – q) relationships because area normalization allows for direct comparison between catchments whose areal extents may differ by many orders of magnitude.

Maher and Chamberlain (2014) derived a framework for relating solute (C [$\mu\text{mol/L}$]) production to runoff (q [m/yr]):

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

where Dw [m/yr] is the Damköhler coefficient, C_0 is the initial solute concentration, and $C_{\max}$ is the maximum solute concentration, which may be associated with a “thermodynamic limit” imposed by approach to equilibrium with the primary and/or secondary mineral assemblages. Previous work with this solute production model (Maher and Chamberlain, 2014; von Blanckenburg et al., 2015) included a scaling factor (7.39) multiplied by the Dw coefficient that emerged from comparison between 1-dimensional reactive transport simulations and the analytical solution above (cf. Maher and Chamberlain, 2014). In the current work, we exclude the scaling factor from the analysis

since we make no comparison to reactive transport simulations and account for the scaling factor when comparing to previous results from von Blanckenburg et al. (2015) and Maher and Chamberlain (2014). Here, C_0 is the initial solute concentration, derived from atmospheric deposition and/or hydrothermal or deep groundwater inputs that mix with water in the weathering zone or the river and are independent of discharge. For most catchments, Eq. (2) can be simplified if C_0 is assumed to be zero (Maher and Chamberlain, 2014):

$$C = C_{\max} \frac{Dw / q}{1 + Dw / q} \quad (3)$$

Observations of constant concentrations with increasing discharge (i.e., “chemostatic” behavior) have demonstrated that $C_{\max}$ can vary among catchments (Godsey et al., 2009; Maher, 2011). The purpose of the C – q analysis carried out in this study is to derive $C_{\max}$ and Dw values for individual basaltic and granitic catchments, and determine trends between these two sample groups. Dw values derived from concentration-runoff data between catchments of comparable lithology allow for a direct, area-independent comparison of the efficiency of solute generation. At a given runoff, catchments with larger Dw values are more efficient at generating solute and hence more likely to approach the $C_{\max}$ concentration. For example, Fig. 2a demonstrates schematically how, for a given $C_{\max}$, a higher Dw results in a higher $\text{SiO}_2(\text{aq})$ concentration at a given runoff (yellow point ($Dw = 0.15$) vs. green point ($Dw = 1.5$)). Here, we use $\text{SiO}_2(\text{aq})$ to demonstrate these key concepts because it is a neutral species and closely tracks primary mineral silicate weathering (e.g., feldspar to a secondary clay mineral) although we do consider and analyze other major ions (HCO_3^- , Ca^{2+} , Mg^{2+} and Na^+) and measurements of chemical weathering in this paper.

The runoff value where dilution effects are observed varies by element (e.g., $\text{SiO}_2(\text{aq})$ dilution occurs at runoff values higher than for HCO_3^- ; Kump et al., 2000; Godsey et al., 2009; Moon et al., 2014). Dilution curves have been previously derived empirically assuming a power law relationship ($C = aQ^b$, where a and b are constants; Pokrovsky et al., 2005; Godsey et al., 2009; Moon et al., 2014). Chemostatic behavior has been traditionally defined as occurring when the power law exponent (b) approaches zero (e.g., Godsey et al., 2009; Moon et al., 2014; Torres et al., 2015). Previous work has demonstrated the importance of quantifying and understanding the mechanisms behind chemostatic concentrations of different elements observed in rivers for different lithologies and, most importantly, the extent to which maximum concentrations are associated with a thermodynamic limitation (White et al., 1996; Clow and Mast, 2010; Maher, 2011; Maher and Chamberlain, 2014; Maher and Druhan, 2014).

Finally, the equations presented above assume an idealized exponential transit time distribution of discharge, and thus concentrations represent the flux-weighted average concentration recorded by streams (cf. Małoszewski and Zuber, 1982; McGuire et al., 2005; McGuire and McDonnell, 2006; Steefel and Maher, 2009; Maher, 2011; Zapata-Rios et al., 2015), although observations and modeling of transit time distributions are complex and demonstrate fractal behavior (cf. Kirchner et al., 2000; Scher et al., 2002; Kollet and Maxwell, 2008; Kirchner and Neal, 2013; Maxwell et al., 2016). In our analysis we derive Dw values, which represent the balance of mean transit time to mean reaction rate to take into account permeability and flowpath heterogeneity (Maher, 2011; Maher and Druhan, 2014; Maher and Chamberlain, 2014; Li et al., 2014; Torres et al., 2015).

Catchment weathering potential

From Eq. (3), the area normalized weathering flux (W [t/km²/yr]) is obtained by multiplying the concentration (C) by the runoff (q):

$$W = qC_{\max} \frac{Dw / q}{1 + Dw / q} \quad (4)$$

and converting to mass using the appropriate atomic or molecular weight (g/mol) of the solute of interest. At higher runoff, solute fluxes from a given catchment or river basin plateau due to increased dilution, defining a maximum weathering flux ($W_{\max}$ in Fig. 2b). Higher Dw and $C_{\max}$ values result in a higher $W_{\max}$ value (the value as q approaches infinity; i.e., $W_{\max} = Dw \times C_{\max}$). For a given mean observed solute flux (W_{obs}), we can calculate the possible maximum increase in the weathering flux and the absolute weathering potential (ΔWP [t/km²/yr]) of a catchment, which is the difference between the $W_{\max}$ and the W_{obs} :

$$\Delta WP = W_{\max} - W_{\text{obs}} \quad (5)$$

To compare between catchments of different Dw values, this maximum weathering flux is expressed as the normalized weathering potential (WP_{norm} [%]):

$$WP_{\text{norm}} = \left(\frac{\Delta WP}{W_{\max}} \right) \cdot 100 \quad (6)$$

As shown schematically in Fig. 2b, for a given Dw and $C_{\max}$, the weathering potential for a chemostatic catchment (blue point) is higher than for a catchment located on the dilution curve (green and red points). Additionally, for a given runoff and $C_{\max}$, catchments with a higher Dw have a higher weathering potential (green point where $Dw = 1.5$ m/yr and $WP_{\text{norm}} = 93.3\%$) than catchments with a lower Dw (yellow point where Dw

= 0.15 m/yr and $WP_{norm} = 59.6\%$). The utility of this new metric is that it incorporates both D_w and C_{max} . Thus, we account for lithology-dependent variations and distributions in C_{max} values (e.g., Dessert et al., 2003; Dupré et al., 2003) when evaluating catchment weathering efficiency.

For catchments where C_0 is non-zero due to contributions from atmospheric deposition (e.g., soluble dust deposition or sea spray) or hydrothermal or deep groundwater inputs, Eq. (2) should be used to determine the catchment D_w . However, to represent only the silicate-weathering contribution to the solute flux, C_0 is subtracted from the dataset. Fig. 3 demonstrates how, within this solute production framework, there is no W_{max} when C_0 is non-zero because at high runoff the first term in Eq. (2) dominates, increasing the total solute flux proportional to increasing runoff. Therefore to calculate D_w and C_{max} values, and the resultant W_{max} values, we correct the flux vs. runoff relationships (as shown schematically in Fig. 3).

3.1.3 Methods

Data Sources

The concentration-runoff datasets considered in this study were compiled from locations where several years (>2 years) of data, comprising at least 20 solute concentration measurements, have been collected (Fig. 1a). Riverine solute data were compiled from (1) small (<10,000 km²) basaltic and granitic catchments from the U.S. Geological Survey National Water Information System (USGS NWIS) and used in three previous studies (Bluth and Kump, 1994; Dessert et al., 2003; Godsey et al., 2009); (2) basaltic catchments with sufficient concentration–discharge data from Iceland

(Eiriksdottir et al., 2013, 2015), and; (3) additional basaltic and granitic catchments (>90% single-lithology bedrock) identified from the Global River Chemistry Database (GlorRiCh) using the Global Lithologic Map (GLiM) lithology maps (Hartmann and Moosdorf, 2012; Hartmann et al., 2014b). Our dataset is restricted to sites with the paired runoff and solute data needed to constrain the weathering of primary silicate minerals to secondary minerals and to quantify the resulting solutes, total dissolved solids, and cation-equivalent ($\text{SiO}_2(\text{aq})$, Mg^{2+} , Ca^{2+} , K^+ , Na^+ and HCO_3^-) (e.g., Gaillardet et al., 1999; Dessert et al., 2003; Bouchez and Gaillardet, 2014). As noted by previous workers, it is difficult to fit statistically significant concentration–discharge relationships to datasets displaying minimal discharge variations (Godsey et al., 2009; Moon et al., 2014). Thus, we exclude catchment data showing minimal variations; of these, most were from catchments without sufficient temporal or seasonally representative coverage. In total, our compilation includes data from 44 basalt catchments, and 27 granite catchments (Table A1). In addition, we separate some of the basalt and granite catchments into sub-groups based on region (Iceland, Hawaii, Sierra Nevada, and the Pacific Northwest; Fig. 1, Table A1).

The analysis presented here utilizes some of the longest time-series available for studying riverine dissolved loads (e.g., Godsey et al., 2009; Maher, 2011; Eiriksdottir et al., 2013, 2015; Torres et al., 2015; Moquet et al., 2015), primarily from the USGS NWIS database. We are still limited by both the lack of spatial coverage of these long time-series datasets and by a lack of sampling at extreme runoff values (e.g., Dessert et al., 2015). However, our datasets allow to examine the influence of high runoff variability—particularly at extreme values and to accurately estimate C_{max} and C_0 values. To assess

whether using individual C - q pairs biases the dataset toward rare, extreme runoff values, or temporal sampling biases, we also evaluate our dataset by calculating flux-weighted average concentrations for each catchment and deriving Dw values from single concentration-runoff pairs (e.g., von Blanckenburg et al., 2015), assuming different C_{max} values for each sample group (basalt and granite).

Quantifying catchment-scale weathering efficiency from concentration-runoff relationship fitting

In order to quantify catchment-scale weathering efficiency, we first separate chemostatic and non-chemostatic catchments. For chemostatic catchments, we mathematically define with a power law b -value indistinguishable from 0 (within 95%, $p > 0.05$) (Godsey et al., 2009). Most of these catchments still likely fit the modeling framework employed in this study, but lack a sufficient number of concentration-discharge measurements at high runoff necessary to demonstrate dilution. For these catchments, we report C_{max} values as the median (and median absolute deviation) of all observed concentrations and do not quantify Dw values. For non-chemostatic catchments, we quantify catchment-specific Dw values using the paired concentration-runoff data and equations 1 and/or 2. We apply a non-linear least squares fitting to derive Dw and C_{max} values using the Gauss-Newton algorithm ('nls2' R package, Grothendieck, 2013) similar to the Newton methods employed by Godsey et al. (2009) and Moon et al. (2014) for power law fits. Finally, we calculate these fits for a variety of dissolved species, including $\text{SiO}_2(\text{aq})$, HCO_3^- (alkalinity), Mg^{2+} , Ca^{2+} , Na_* (Cl-corrected Na^+ ; $\text{Na}^* = \text{Na}^+ -$

Cl; cf. Moon et al., 2014), for cation-equivalent ($2\text{Mg}^{2+} + 2\text{Ca}^{2+} + \text{K}^+ + \text{Na}^+$ [$\mu\text{eq/L}$]), and for total dissolved solids (TDS; $\text{Mg}^{2+} + \text{Ca}^{2+} + \text{K}^+ + \text{Na}^+ + \text{SiO}_2(\text{aq})$ [mg/L]).

In Appendix B, we provide associated example code for fitting concentration-runoff relationships using the Maher and Chamberlain (2014) modeling framework. The Gauss–Newton method minimizes the sum of squares of the errors between the model prediction and input dataset. The advantage of this method is that because C_0 and C_{max} are unknown, we can simultaneously solve for all three required parameters given sufficient sample size (>20 paired data points). We only report concentration-runoff relationships that are statistically significant at 95% ($p\text{-value} < 0.05$ for all three parameters). If C_0 cannot be assumed to be zero (based on $p\text{-value} > 0.05$ for fitted Eq. (1) C_0 value), we correct for atmospheric, spring, and/or hydrothermal inputs by subtracting the calculated C_0 value from the concentration-runoff relationship as shown schematically in Fig. 3. TDS [mg/L] derived from the weathering of silicate rocks, which is a measure of total silicate chemical denudation, is calculated by weighting the concentrations by the molar mass of each major cation and SiO_2 (e.g., Bouchez and Gaillardet, 2014) and correcting the concentration-runoff relationship for C_0 . We also similarly calculate and correct concentration-runoff relationships for cation-equivalent (e.g., Gaillardet et al., 2011b), which is the charge-weighted concentration of positively charged cations (Mg^{2+} , Ca^{2+} , K^+ , and Na^+) and compare them to the HCO_3^- results.

We calculate the absolute weathering potential (ΔWP) and normalized weathering potential (WP_{norm}) using Eqs. (5) and (6). The observed weathering flux, W_{obs} , is determined using Eq. (4) where q is the median of the runoff distribution, with the range of weathering fluxes calculated for each catchment using the maximum and minimum

observed runoff values that are paired to solute concentrations. The maximum weathering flux, W_{max} , is determined as the product of C_{max} and Dw .

In addition to deriving Dw values from fitting concentration-runoff relationships from all available data, we also derive Dw values using single concentration-runoff pairs for each catchment. Maher and Chamberlain (2014) noted the lack of long-term monitoring available to fully constrain mechanisms driving the distribution of weathering efficiency (Dw values) in modern systems. Previous work using this solute production framework took the approach of assuming C_{max} values for global river datasets to derive flux-weighted Dw values from single concentration-runoff pairs (von Blanckenburg et al., 2015), assuming that time-averaging of discharge and concentrations in existing global river datasets were accurate (e.g., Gaillardet et al., 1999; Moon et al., 2014; Goldsmith et al., 2015). The advantage of using the single flux-averaged concentration-runoff pair for this analysis is that hysteresis (on storm event or seasonal timescales; e.g., Chanut et al., 2002; Moquet et al., 2015) is accounted for, rather than resulting in greater uncertainty around the solute production parameters derived from the concentration-runoff relationship fit (see above for fitting methods). However, recent work has shown, using an inverse modeling and bootstrapping approaches, that estimates of fluxes using datasets result in overestimation of global weathering fluxes (Moon et al., 2014, see their Fig. 8). Thus, we pair flux-weighted concentrations using all available data with average runoff values from each catchment. For each sample group, we calculate C_{max} as the 95th percentile (e.g., Dixon and von Blanckenburg, 2012; Maher and Chamberlain, 2014; von Blanckenburg et al., 2015). Assuming C_0 is zero, Eq. (3) is solved for flux-weighted Dw

values. The results from the single concentration-runoff pairs are compared to those derived by fitting concentration-runoff relationships.

Statistics of sample groups

We report and illustrate the variability of C_{max} , C_0 -corrected C_{max} , Dw , and W_{max} values for each sample group of basalt and granitic catchments in Table and Figures. We use box and whisker plots with mean, median, interquartile range (IQR) and 95% confidence intervals. Summary statistics are necessary because (1) distributions in Dw and C_{max} are not normally distributed (typically positively skewed) within sample groups (Maher and Chamberlain, 2014), and the distribution in q observed within each catchment also tends to be non-normal; and (2) the rational forms of Eqs. (1) and (2) result in asymmetric propagated errors (cf. discussion in von Blanckenburg et al., 2015) when calculating W_{max} from derived values of C_{max} and Dw . It is notable that although we only include catchment fits with statistically significant Dw , C_{max} , and C_0 parameters (95%, $p > 0.05$), the estimated uncertainty for each parameter can vary by an order of magnitude or more depending on the goodness of fit and absolute values. Uncertainty in C_0 is propagated in quadrature when correcting the C_{max} values of concentration-runoff relationships for individual catchments.

Linear regressions between mean weathering temperature and the derived parameters (C_{max} and Dw) are illustrated for significant (p -value < 0.05) relationships only. We report coefficients of correlation, and slopes between C_{max} and temperature. The mean water temperature of the collected samples used to derive the concentration-runoff fits was selected to represent the mean weathering temperature of each catchment.

Saturation indices

To evaluate thermodynamic controls on C_{max} , we calculate the saturation index according to the ion activity product (IAP) and the equilibrium constant K (i.e., $\log(IAP/K)$) for calcium and sodium feldspar end-members and key secondary minerals. When $\log(IAP/K) = 0$, the fluid is in equilibrium with the mineral. When $\log(IAP/K) < 0$, the fluid is undersaturated relative to the mineral, and when $\log(IAP/K) > 0$, the fluid is supersaturated relative to the mineral. Saturation index calculations were performed in Geochemist's Workbench (Bethke and Yeakel, 2015) using the Thermoddem database (version: llvl2; Blanc et al., 2012; Marty et al., 2015) at the temperature of sample collection. Approximately 25% of the data considered in this study includes aluminum concentration data required for the speciation and saturation index calculations. Potassium feldspar saturation index calculations were not included due to a lack of potassium solute data (<8% of data). We include all available samples with pH and aluminum concentrations ($n = 1,952$) from the USGS NWIS database from basaltic and granitic catchments as well as from the Icelandic basaltic catchments (Eiriksdottir et al., 2013, 2015).

3.1.4 Results

Concentration-discharge relationships

Concentration-runoff ($C-q$) fits for all catchments in our compilation are illustrated in Fig. 4 and reported in Tables A2–A8. Many statistically significant $C-q$ relationships for HCO_3^- (51%, $n = 24$), Ca^{2+} (50%, $n = 24$), and Mg^{2+} (40%, $n = 18$) (and

by extension TDS and cation-equivalent) required C_0 corrections (Tables A3–A8). In contrast, proportionally fewer $\text{SiO}_2(\text{aq})$ (28%, $n = 12$) and Na^* (20%, $n = 8$) statistically significant relationships required a C_0 correction (Table A2). For the $\text{SiO}_2(\text{aq})$ C – q relationships, this likely reflects the fact that $\text{SiO}_2(\text{aq})$ is a primary recorder of silicate weathering (White and Blum, 1995; Waldbauer and Chamberlain, 2005; Maher and Chamberlain, 2014) with minimal C_0 contributions (Maher, 2011). Statistically significant C_0 values ($C_0 > 0$) for $\text{SiO}_2(\text{aq})$ and Na^* (Tables A2 and A5) proportionally account for less of the uncorrected C_{max} values relative to Ca^{2+} , Mg^{2+} and HCO_3^- (Tables A3, A4 and A6; see also Fig. 4). Because we are interested in analyzing the weathering zone component of the solute load, in particular apparent controls on W_{max} (e.g., Dixon and von Blanckenburg, 2012; Maher and Chamberlain, 2014), we focus below on the C_0 -corrected C – q fits illustrated in Fig. 5. In addition, Fig. 6 illustrates the derivation of the flux-weighted D_w values reported in Table A9 for single C – q pairs for each catchment, assuming sample group C_{max} values (95th percentiles) derived by calculating flux-weighted average concentrations for each catchment.

Chemostatic concentration (C_{max})

The distribution of C_{max} values demonstrates that the net weathering stoichiometry of the primary lithology plays a first order control on setting C_{max} (Fig. 5). To the right of each panel in Fig. 5 shows distribution of the C_{max} summary statistics for each group (Table 1). Also annotated for each dissolved species is the ratio of the mean basalt C_{max} to the mean granite C_{max} .

Based on a comparison of Dessert et al. (2003) and Gaillardet et al. (1999) datasets, Maher and Chamberlain (2014) estimated that basaltic C_{max} values are approximately 1.5 times greater than C_{max} values of large rivers, assuming similar Dw distributions (discussed below). The results presented in Fig. 5 (and Table 1) suggest that this estimate was of the correct magnitude and varies depending on the dissolved species considered. The mean C_{max} value for basaltic catchment $\text{SiO}_2(\text{aq})$ is 1.6 times higher than that of granite (324 vs. 209 $\mu\text{mol/L}$; Table 1), similar to the values derived for Na^+ (1.6), HCO_3^- (1.3), TDS (1.8), and cation-equivalent (1.8). The difference in C_{max} suggested by the $\text{SiO}_2(\text{aq})$ values is bracketed by Ca^{2+} (1.2) and Mg^{2+} (2.1), reflecting the mafic (i.e., Mg-rich) nature of basaltic bedrock and the net stoichiometry of the weathering reactions (discussed in detail below), or the secondary mineral assemblage (e.g., Bouchez and Gaillardet, 2014).

The $\text{SiO}_2(\text{aq})$ C_{max} values for both basalt (324 $\mu\text{mol/L}$) and granite (209 $\mu\text{mol/L}$) catchments are lower than the C_{max} value originally suggested by Maher and Chamberlain (2014), who used the 95th percentile of annually averaged datasets (Gaillardet et al., 1999) to infer a large river $\text{SiO}_2(\text{aq})$ C_{max} of 375 $\mu\text{mol/L}$. A population of annually averaged concentration data biases the apparent C_{max} values toward higher values because observations of lower concentrations at high runoff are sparse (*cf.* Godsey et al., 2009; Moon et al., 2014; von Blanckenburg et al., 2015; Dessert et al., 2015). Similarly, by calculating flux-weighted average concentrations for all catchments and deriving C_{max} values (using the 95th percentile; Table A9; Fig. 6) for each sample group, we find C_{max} values that are higher than those derived using the concentration–discharge relationships. However, based upon the flux-weighted concentrations, the apparent $\text{SiO}_2(\text{aq})$ C_{max} value

for basalt is 1.3 times that of granite (455 $\mu\text{mol/L}$ vs. 353 $\mu\text{mol/L}$; Table 1), which is of a similar magnitude to the mean C_{max} difference derived using the individual river concentration–discharge relationships. Importantly, this suggests that both methods produce comparable weatherability estimates at low runoff (discussed further below). Differences in C_{max} values between basalt and granite catchments of approximately a 1.3 to 1.9 factor remain for HCO_3^- (1.7), TDS (1.4), and cation-equivalent (1.7) using the flux-weighted concentrations (Table 1). The spread observed in basalt and granite catchments (Fig. 5) C_{max} values may be due to variations in soil $p\text{CO}_2$, bedrock age, temperature, effects of subsurface structure on flow regime, and additional geomorphic properties (Godsey et al., 2009; Clow and Mast, 2010; Maher, 2011; Moon et al., 2014; Torres et al., 2015).

The effect of temperature (Table A1) on C_{max} is assessed in Fig. 7. We find that only C_{max} values for $\text{SiO}_2(\text{aq})$ and Na^* (granite only) have statistically significant (p -values < 0.05) positive relationships with average water (i.e., weathering) temperature, with low coefficients of determination ($r^2 < 0.4$). The positive slopes of the temperature– C_{max} (C_0 -corrected C_{max}) relationship are reported in Fig. 7 and suggest a weak, but statistically significant temperature control for $\text{SiO}_2(\text{aq})$ and Na^* only. These trends are consistent with observations that dissolution rates increase with increasing temperature following Arrhenius-type relationships (e.g., Oelkers and Gíslason, 2001; Gíslason and Oelkers, 2003; Eiriksdottir et al., 2013; Li et al., 2016). Since solute fluxes are driven by runoff (Eiriksdottir et al., 2013), these results emphasize the importance of evaluating and considering concentration–discharge behavior in weathering flux datasets and compilations (e.g., Moon et al., 2014). Runoff and temperature are inherently positively

correlated in most datasets covering large ranges in latitudinal settings, such as those used to derive Arrhenius-type weathering relationships (e.g., Dessert et al., 2003; Li et al., 2016).

Lastly, we acknowledge that the C_{max} values from this analysis may not be directly applied to heterogeneous (non-monolithologic) catchments or global rivers (e.g., Gaillardet et al., 1999; Maher and Chamberlain, 2014; Moon et al., 2014) due to the same factors listed above and different proportions of silicate weathering. Further work with databases combining the areal extent of silicate bedrock with large river solute data including water temperature data (e.g., Moon et al., 2007; 2009; Jansen et al., 2010; Moosdorf et al., 2011; Hartmann and Moosdorf, 2011, 2012; Hartmann et al., 2014b) will allow for direct comparison between the apparent contribution (via inverse methods) to the dissolved load chemistry by the silicate lithologies and bedrock-based lithologic distributions within catchments.

Saturation indices of primary and secondary minerals

The trends between granitic and basaltic catchments in the C_{max} distributions (Fig. 5) may be controlled by the thermodynamics and the net stoichiometry of the primary silicate minerals (i.e., feldspars, olivine, and pyroxene) weathering to secondary minerals and generating solute (e.g., Schott et al., 2009; Navarre-Sitchler et al., 2013; Bouchez and Gaillardet, 2014). We propose that the dissolution of primary minerals and the approach to chemical equilibrium with secondary mineral assemblages formed in the weathering zone (e.g., Maher et al., 2009; Maher, 2010; Clow and Mast, 2010, 2011; Maher and Chamberlain, 2014; Li et al., 2014; Maher and Druhan, 2014) controls solute

concentration and C_{max} values for specific catchments. At present, few aluminum concentration data and/or bed-load X-ray diffraction data exist to determine the specific secondary minerals driving variations in C_{max} between lithologic groups and under different climatic conditions.

Here, we use aluminum concentration data as available for the catchments analyzed in this study to derive saturation indices of primary and secondary minerals. C_{max} values should reflect concentrations during base flow (i.e., low runoff), and the assumption that equilibrium with secondary phases is achieved given long flow paths (Maher, 2010, 2011). We also consider idealized end-member compositions whereas primary mineral compositions and assemblages can be highly variable, especially in catchments with hydrothermally altered bedrock. In addition, these speciation and saturation index calculations may be impacted by CO_2 evasion in the stream channel (e.g., Wallin et al., 2011; Lauerwald et al., 2015), emphasizing the need for upslope monitoring of soil and groundwater solute chemistry (e.g., Kim et al., 2014) to determine controls on C_{max} values for individual catchments.

In Fig. 8, we compare histograms of basalt and granite saturation indices for feldspar end-members, typical secondary weathering aluminosilicate minerals (halloysite, gibbsite, imogolite, smectites (Ca, Na and Mg end-members) and kaolinite), amorphous silica, and calcite. We separately show the chemostatic catchments as solid bars in Fig. 8. The histograms indicate that most samples are undersaturated with respect to end-member feldspars (albite and anorthite), amorphous silica and calcite, as well as for olivine and pyroxene minerals (not shown), in agreement with previous work (e.g., Bluth and Kump, 1994; Gíslason et al., 1996; Stefánsson and Gíslason, 2001; Stefánsson et al.,

2001; Oelkers and Gíslason, 2001; Jacobson et al., 2003; Eiríksdóttir et al., 2013, 2015). Chemostatic basalt catchments are most undersaturated with respect to feldspars compared to granitic catchments (discussed further below). This apparent higher degree of undersaturation observed for primary minerals (see feldspars in Fig. 8) in chemostatic catchments may suggest hydrologic thresholds on C_{max} concentrations (Chanat et al., 2002; Eiríksdóttir et al., 2013) as saturation state with respect to primary minerals tends to decrease with increasing discharge. Given this undersaturation with respect to primary minerals, the departure from equilibrium with respect to primary phases (feldspars (Fig. 8), as well as olivine and pyroxenes (not shown)), could be a factor in determining C_{max} concentrations, especially in granitic catchments. Despite this, as shown below, incorporation of elements into and equilibrium with secondary phases likely plays a controlling role on C_{max} concentrations.

Importantly, all samples are oversaturated with respect to the clay minerals (halloysite, imogolite, smectites, and kaolinite) and gibbsite. This saturation with respect to metastable aluminosilicate secondary clays is expected and has been observed in both stream/river waters (e.g., Gíslason and Eugster, 1987; Bluth and Kump, 1994; Stefánsson and Gíslason, 2001; Eiríksdóttir et al., 2013) and soils (Maher et al., 2009; White et al., 2009; Kim et al., 2014). Of the clay minerals, samples from both chemostatic and non-chemostatic catchments are closer to saturation ($\log(IAP/K) = 0$) with halloysite (and imogolite), and highly supersaturated with respect to kaolinite and the smectite end-members. Since halloysite and imogolite are thought to be metastable precursors (Stefánsson and Gíslason, 2001; Maher et al., 2009; White et al., 2009; Kim et al., 2014) and are closer to equilibrium compared to kaolinite or smectite (Fig. 8), this may justify

the use of halloysite (or imogolite) in reaction path reactive transport modeling instead of kaolinite or smectite (e.g., Maher, 2011). Field observations demonstrate that multiple different secondary clay minerals co-exist in typical weathering profiles (e.g., White et al., 2009; Maher et al., 2009). In Fig. 9, we illustrate activity diagrams of the Ca–Na and Ca–Mg systems with kaolinite and smectite stability fields (for different assumed $\text{SiO}_2(\text{aq})$ activities and the appropriate smectite end-members). We plot all of the basalt and granite data with available pH and sufficient solute data (anions, cations and $\text{SiO}_2(\text{aq})$) for speciation. The data for basalts and granites plot between the phase boundaries (Fig. 9), confirming previous work suggesting possible equilibrium between the more stable secondary phases of kaolinite and smectite (e.g., Bluth and Kump, 1994; Kump et al., 2000).

For feldspars, amorphous silica, and calcite, chemostatic basalt catchments are further from saturation compared to non-chemostatic catchments (filled red bars in histograms of Fig. 8). Whereas primary feldspars are not expected to be stable at surface temperatures, undersaturation of amorphous silica, and calcite is surprising given the high reactive surface areas of basaltic systems (Eiriksdottir et al., 2013). This may result from several factors, including the possibility that rapid weathering of basaltic catchments has reduced the amount of primary mineral (the reactant) in the weathering zone. In addition, some samples, mostly chemostatic granitic catchments, are near saturation with respect to calcite. This is not unexpected because trace calcite in granitic bedrock is commonly observed, as is new calcite precipitation in many seasonally arid/semi-arid granitic weathering systems (e.g., Wang et al., 1996; Amundson et al., 1996; Blum et al., 1998;

White et al., 1999b; Hartmann and Moosdorf, 2011; Kim et al., 2014; Jacobson et al., 2015).

Cumulatively, these observations corroborate observations of the mineral assemblages in weathering profiles from silicate dominated systems (*e.g.*, Eberl, 1984; Steefel and Van Cappellen, 1990; White et al., 1999a, 2009; Maher et al., 2009) and suggest that solute concentrations are influenced by the thermodynamic potential for primary mineral dissolution and secondary mineral precipitation – the stoichiometry of which consequently may determine the catchment C_{max} values for various solutes (Maher, 2011; Maher and Chamberlain, 2014). The nature of this analysis is preliminary given limited available datasets. Future acquisition of accurate aluminum concentration and pH data (*e.g.*, Eiriksdottir et al., 2013, 2015) is vital for speciation calculations of solute chemistry measurements in this manner and for informing further reaction path modeling of soil zone weathering (*e.g.*, Maher, 2011).

Comparison of Damköhler coefficients

The Damköhler coefficient (D_w) provides a metric to extract the resistance to dilution from the concentration–discharge relationship (Maher, 2011; Maher and Chamberlain, 2014). Higher D_w values would correspond to catchments that start to show dilution at higher discharge values, similar to more negative b -values in power-law C – Q relationships (*e.g.*, Godsey et al., 2009; Moon et al., 2014; Torres et al., 2015) (Fig. 2a). Due to different thermodynamic (*i.e.*, dissolution/precipitation) processes and stoichiometric constraints associated with C_{max} , along with kinetic effects at increasing runoff, D_w values should differ among elements. D_w values capture both the physical

length scale setting fluid residence times and the reactivity of the weathering reactions. Thus, D_w values have been linked to erosion rates, which determine the abundance of fresh minerals at the surface and hence the reactivity (Maher and Chamberlain, 2014). Increased erosion rates remove highly weathered material from the weathering zone, exposing new material at the surface and increasing reactive surface areas (e.g., Waldbauer and Chamberlain, 2005; West, 2012). Erosion may further alter the topography and drainage structure, resulting in different porosity and permeability distributions. Thus, the observed intra-lithology spread in D_w distributions may be driven by these variations in flow path porosity/permeability (e.g., White et al., 1996, 1999a, 2001, 2005, 2009, Jacobson et al., 2002; Maher et al., 2009; Navarre-Sitchler et al., 2009, 2011, 2013, 2015; Sak et al., 2010; Ryu et al., 2011; Parry et al., 2015) and/or erosion rates (e.g., Chamberlain et al., 2005; Waldbauer and Chamberlain, 2005; Hren et al., 2007; Porder et al., 2007; Eiriksdottir et al., 2008; Moon et al., 2011; West, 2012; Torres et al., 2015; Lee et al., 2015). Finally, on seasonal timescales ion-exchange on clay minerals or organic matter surfaces can serve as a temporary reservoir (Sverdrup and Warfvinge, 1988; White and Blum, 1995; Chorover and Sposito, 1995; Chorover et al., 2007; Clow and Mast, 2010; Andrews et al., 2016) and decouple the fluid residence times from the solute residence times, although for this study, we limit our dataset to sites with sufficient temporal coverage to negate seasonal biases.

In Fig. 10, we show cross-plots of D_w values for different solutes of individual catchments (for statistically significant $C-q$ relationships only). Plotted above and to the right are D_w distributions for each sample group as derived in Fig. 5. These results demonstrate that among all solutes the distribution of D_w values is positively skewed.

Observation of skewed distributions using the annually averaged Gaillardet et al. (1999) $\text{SiO}_2(\text{aq})$ data is consistent with previous work by Maher and Chamberlain (2014) and von Blanckenburg et al. (2015). However, because these studies used a C_{max} value of 375 $\mu\text{mol/L}$ for all catchments and used annually averaged datasets (see above), these studies underestimate absolute D_w values. Consequently, we find for basalt and granite catchments mean $\text{SiO}_2(\text{aq})$ D_w values of 3.47 m/yr and 1.49 m/yr, respectively (Table 1), compared to 0.21 m/yr for large rivers (cf. von Blanckenburg et al., 2015, their Table S6 corrected for the scaling factor). An additional, possible reason for this discrepancy may be that large rivers may not be merely a representation of mixing (and dilution) from small catchments for $\text{SiO}_2(\text{aq})$. Instead, processes in flood plains and modern dams/lakes may provide temporary storage (i.e., buffering the concentration) and/or sequestration (through biological sedimentation) of $\text{SiO}_2(\text{aq})$ (Admiraal et al., 1990; Dürr et al., 2011; Hartmann et al., 2011; Lupker et al., 2012; Bouchez et al., 2012; Lauerwald et al., 2013; Maavara et al., 2014). Further, changes in anthropogenic nutrient inputs (Hartmann et al., 2007) can cause $\text{SiO}_2(\text{aq})$ levels to vary with time when considering longer term as well as seasonal trends (Hartmann et al., 2011). Future longitudinal sampling campaigns along major rivers that integrate smaller silicate catchments may help explain this potential discrepancy (see Amazon River compilations by Bouchez et al., 2014; Torres et al., 2015; Moquet et al., 2015).

The cross-plots in Fig. 10 demonstrate that resistance to dilution is not uniform among solutes for a given catchment or within sample groups. The C – q relationships for $\text{SiO}_2(\text{aq})$ for both basalts and granites are characterized by higher D_w values for some catchments compared to the base cations (Mg^{2+} , Ca^{2+} , and Na^+) and HCO_3^- (Figs. 5 and

10a–d). This potential bias appears to be greatest among basaltic catchments (red basalt catchments in the lower right of Fig. 10a–d). However, a majority of catchments are within a factor of two of each other when comparing $\text{SiO}_2(\text{aq})$ -derived Dw values to other solutes (diagonal dashed lines in Fig. 10). The result that some catchments demonstrate higher $\text{SiO}_2(\text{aq})$ Dw values is consistent with power-law b -values from Moon et al. (2014) for large rivers, which had a median $\text{SiO}_2(\text{aq})$ value of -0.06 , compared to median values of -0.12 to -0.24 for other solute species (cations and HCO_3^-). Godsey et al. (2009) and Torres et al. (2015) also observed $\text{SiO}_2(\text{aq})$ relationships typically closer to chemostatic values (b -values approaching ~ 0).

Across all concentration–discharge fits, basaltic catchments typically have greater Dw values. Mean Dw values of basaltic catchments are two to five times higher than granitic catchments (Table 1). However, observed Dw values for Mg^{2+} and Ca^{2+} are similar, despite large differences in the Mg^{2+} and Ca^{2+} C_{max} values between basalts and granites (shown above) (Fig. 10g), suggesting similar behavior of these cations during primary mineral dissolution and secondary mineral precipitation, and dilution processes, despite differences in absolute values of C_{max} driven by the net stoichiometry of the weathering reactions. In addition, cation-equivalent and HCO_3^- , which may be influenced differently by ion exchange processes, have consistently similar Dw values, with only 8 of 37 catchments having Dw values that differ by more than a factor of two (Fig. 10f). Finally, we also analyzed the relationship between Dw and temperature. We find no statistically significant ($p < 0.05$) correlations for any solutes between Dw and the average weathering temperature, shown as scatterplots in Fig. 11.

Weathering potential

The results above demonstrate that basalt catchments, with higher Dw and C_{max} values than granite catchments, have a greater absolute capacity to increase weathering rates with increased runoff (i.e., larger ΔWP). This implies that increases in runoff result in much larger absolute increases in weathering fluxes in basaltic catchments (Fig. 2b). The absolute departure of catchment weathering fluxes from a theoretical maximum (i.e., $\Delta WP = W_{max} - W_{obs}$) is dependent on the derived Dw and C_{max} values, which combine to set W_{max} , and on the runoff distribution, which sets W_{obs} . Using $\text{SiO}_2(\text{aq})$ and HCO_3^- catchment fits, we show in Fig. 12 that basaltic catchments have a higher ΔWP relative to granitic catchments (y-axis). Basalts have higher and more positively skewed Dw and higher C_{max} distributions, resulting in higher W_{max} values (Fig. 12; Table 1), implying that both stoichiometric and thermodynamic effects and resistance to dilution result in a greater weathering potential for basalts. At equivalent runoff distributions, this results in basaltic catchments having a higher normalized weathering potential (WP_{norm}) due to higher W_{max} values than those in granitic catchments. Monitored basalt catchments included in this dataset are typically associated with higher Dw values, but also higher runoff distributions (Fig. 1) due to their proximity to coastal environments and potential for orographic effects (Bluth and Kump, 1994; Dessert et al., 2001, 2003; Hartmann et al., 2009; Gaillardet et al., 2011b; Maher and Chamberlain, 2014). Despite these effects, the fact that basaltic WP_{norm} values remain high at higher runoff illustrates the high reactivity of basalt catchments (Fig. 12).

These results imply that resistance to dilution at increasing runoff (higher Dw) and stoichiometric considerations (higher C_{max}) are lithology-dependent. Given that C_{max}

values between basalts and granites vary by <2 orders of magnitude and Dw values vary by 4-5 orders of magnitude (Figs. 5 and 10), the differences in observed (W_{obs}) and maximum weathering (W_{max}) fluxes from basalt catchments are primarily driven by differences in Dw . Although this dataset includes substantial variations in runoff, bedrock age, temperatures, and vegetation types within basalt and granite catchments, systematic testing of these two silicate lithology end-members under identical conditions is not yet possible (*cf.* Navarre-Sitchler and Brantley, 2007; Berner, 2008; Maher and Chamberlain, 2014). In Fig. 13a and b, we show the distribution of W_{max} values derived from the $C-q$ fits (Fig. 5) for $\text{SiO}_2(\text{aq})$ and HCO_3^- . The mean basalt $\text{SiO}_2(\text{aq})$ W_{max} is 3.6 times higher than for granites, whereas the mean basalt HCO_3^- W_{max} is 8.5 times higher than for granites (Table 1). These large differences in the $\text{SiO}_2(\text{aq})$ and HCO_3^- W_{max} values are driven by differences in Dw values, which are 2.3 and 6.7 times greater, respectively, rather than C_{max} concentrations, which are only 1.6 and 1.3 times greater, respectively (Table 1). Saturation state histograms shown in Fig. 8 demonstrate that basaltic catchments are closer to equilibrium (more oversaturated) with some secondary minerals such as the smectite end-members and kaolinite. Since $\text{SiO}_2(\text{aq})$ is involved in the dissolution of primary minerals and the precipitation and dissolution of secondary minerals (i.e., secondary phase buffering), this may result in more $\text{SiO}_2(\text{aq})$ removal relative to HCO_3^- in basaltic catchments compared to granitic catchments, driving the lower $\text{SiO}_2(\text{aq})$ Dw differences between catchment types.

If the W_{max} value is set by both thermodynamic and dilution effects at high runoff, this may provide a mechanism to explain lithologic differences in “maximum” fluxes or weathering speed-limits observed across silicate catchments (Dixon and von

Blanckenburg, 2012) (Fig. 13). However, for catchments that display near-chemostatic behavior, thermodynamic constraints (C_{max}) will control the chemical fluxes. Furthermore, there are very few datasets with concentration measurements at very high runoff, resulting in a large degree of uncertainty in the averaged W_{max} values for both sample groups presented in Fig. 13. Acquisition of new datasets that include storm event concentration–discharge pairs, such as recently published dataset by Dessert et al. (2015) from Guadeloupe, will provide further constraints on extrapolated W_{max} values.

3.1.5 Discussion

Runoff dependence of weatherability

The utility of the analysis presented in this paper is to derive the distribution of Dw and C_{max} values of the silicate end-member lithologies. Unlike previous parameterizations of weathering laws (e.g., Dessert et al., 2003), we use paired discharge and solute concentration measurements for individual catchments—rather than annually averaged datasets—to parameterize lithology-specific Dw and C_{max} values. Although we did not analyze a globally comprehensive dataset of basaltic and granitic catchments, the first-order lithological trends are robust. Our results demonstrate that higher weathering rates in basaltic catchments relative to granites are driven by differing responses to increases in runoff, with basaltic catchments showing less dilution with increasing runoff (higher average Dw). Further, the results suggest that thermodynamic constraints on weathering reactions, reflected in chemostatic concentrations (C_{max}) could explain higher concentrations in basaltic catchments at lower runoff compared to granitic catchments. For the remainder of the discussion, we primarily discuss the mean values derived from

the analysis of $\text{SiO}_2(\text{aq})$ and HCO_3^- concentration-runoff fits, and the 2σ uncertainty of these estimates is also reported.

We illustrate the annual modern global and regional runoff distributions in Fig. 14 by area-weighting the Dai and Trenberth (2002) global river discharge dataset.

Comparison of basalt and granite datasets within our solute production framework directly quantifies the relative weatherability between the two major end-member silicate lithologies responsible for terrestrial silicate weathering (Bluth and Kump, 1994; White and Blum, 1995; Kump and Arthur, 1997; Horton et al., 1999; Kump et al., 2000; Dessert et al., 2001; Berner, 2006b, 2008; Navarre-Sitchler et al., 2015). We demonstrate how the relative weatherability, the ratio between the basalt and granite fluxes, varies spatially along the latitudes based on global runoff distribution (Fig. 14d). These results suggest that the relative weatherability is runoff-dependent, which likely varies through geologic time depending on the area and location of granite vs. more reactive basalt, continental configuration, and spatial changes in the runoff distribution.

Modern weathering observations have defined the range of expected basalt/granite weatherability values, in some cases attempting to control for climate and other influences (i.e., bedrock age, slope etc.; Horton et al., 1999; Hartmann, 2009; Hartmann et al., 2010; Hartmann and Moosdorf, 2011). Flux-runoff relationships derived by Bluth and Kump (1994), also plotted in Fig. 13, suggest basalt/granite weatherability of ~ 1.5 (cf. Bluth and Kump, 1994, see Table 4; Kump et al., 2000), with slight variations with changing runoff. Similarly, synthesis of weathering fluxes from Japan suggests that the average basalt/granite weatherability is 1.67, ranging from ~ 1 to ~ 6 , corresponding to steep and flat slopes respectively (cf. Hartmann, 2009; Hartmann et al.,

2010; Hartmann and Moosdorf, 2011). By investigating proximal catchments with the same runoff distributions, Horton et al. (1999) suggested an andesite/granite weatherability of ~ 1.5 to 5.

In contrast, carbon cycle models have generally assumed invariant basalt/granite weatherability through time. For example, using data from Dessert et al. (2001), Berner (2006b) estimated that volcanic (basaltic) silicate weathering is ~ 5 times that of plutonic (granitic), with bounds of 2 to 10, as included into GEOCARBSULF (e.g., Royer et al., 2014). Subsequent sensitivity analysis of GEOCARBSULF indicated that the lower bound of ~ 2 is likely more realistic considering requirements for seawater composition and reconstructions of $p\text{CO}_2$ during the Mesozoic (Berner, 2008). Notably, the average flux-runoff curves from this analysis (solid red and blue lines in Fig. 13a,b) diverge from the Bluth and Kump (1994) relationships (dashed lines) at high runoff due to the mathematical formulation of the relationships (power-law vs. rational). Given that at an individual catchment scale, plateaus in weathering fluxes do occur at high runoff (e.g., Maher, 2011; Torres et al., 2015), the mathematical formulation of the solute production model employed here appears to capture both chemostatic and dilution processes adequately. As shown in Fig. 14a for HCO_3^- fluxes, because the modern global runoff distribution primarily lies between the end-members set by W_{max} and C_{max} , the derived weatherability is 2.2 at global mean runoff.

Higher area-normalized weathering rates and maximum limits on weathering fluxes for basaltic catchments, relative to granites (Fig. 13a,b), are primarily driven by higher D_w values and also higher C_{max} (see Results). Thus, depending on the underlying runoff distribution, weatherability is set by both C_{max} and W_{max} (Fig. 14a). For example, at

modern global mean runoff values of 0.344 m/yr (0.117–0.409, 2σ), basalt/granite weatherability is 2.2 (1.3–3.7, 2σ) for HCO_3^- fluxes and 1.7 (1.6–2.1, 2σ) for $\text{SiO}_2(\text{aq})$ fluxes (see red horizontal line in Fig. 9d). This difference is driven by a higher extrapolated weatherability (from derived W_{max} values) using HCO_3^- fluxes at high runoff. Notably, these calculations agree with basalt/granite weatherability calculated using the flux-weighted D_w values derived using the single C - q pairs (Fig. 6). That method suggests a global mean runoff basalt/granite weatherability is 2.3 (1.7–3.6, 2σ) for HCO_3^- fluxes and 1.7 (1.3–2.4, 2σ) for $\text{SiO}_2(\text{aq})$ fluxes (Table 1).

Under this framework end-member plateaus occur at both runoff extremes. At low runoff, weatherability is only set by the difference in chemostatic concentrations (C_{max}) shown in Fig. 5. The mean $\text{SiO}_2(\text{aq})$ and HCO_3^- basalt/granite weatherability at low runoff (approximately $q < 10$ – 2 m/yr) is 1.6 and 1.3, respectively (Table 1, Figs. 5 and 14a). In contrast, apparent mean W_{max} values suggest basalt/granite weatherability of 8.5 for HCO_3^- and 3.6 for $\text{SiO}_2(\text{aq})$ at very high runoff (approximately > 30 m/yr; Table 1, Fig. 14a). The higher basalt/granite weatherability at high runoff for HCO_3^- is primarily driven by the 6.7-fold difference between average basalt vs. granite D_w values, compared to a lesser 2.3-fold difference derived from $\text{SiO}_2(\text{aq})$ fluxes (Table 1). This inference of runoff-dependent basalt/granite weatherability presented in Fig. 14 implies that future carbon cycle modeling, in addition to influences of temperature (Li et al., 2016), should not necessarily assume invariant basalt/granite weatherability through time.

Dw, weatherability, and a variable silicate weathering feedback

Above, we demonstrate that the weatherability of the surface of the Earth is runoff-dependent under our modeling framework, with modern mean runoff primarily spanning the transition in weatherability between thermodynamic and kinetic limitations. To describe the functional form of the silicate weathering negative feedback, previous work has parameterized global terrestrial weatherability (Kump and Arthur, 1997) with adjustable parameters that relate the silicate weathering flux to climate, usually $p\text{CO}_2$ and runoff (e.g., Berner, 2006a, 2008; Zeebe, 2012; Royer et al., 2014; Mills et al., 2014b). These adjustable parameters determine the total weathering flux according to the strength of the silicate weathering negative feedback and the dependence on atmospheric $p\text{CO}_2$ and/or climate. Often, in 0-D models, global weathering fluxes (F_{sil}) are parameterized as proportional to climate through $p\text{CO}_2$; for example: $F_{\text{sil}} = k \times [p\text{CO}_2]^n$ (Uchikawa and Zeebe, 2008; Zeebe, 2012; Mills et al., 2014b), where k is the weathering time constant and n encapsulates a non-linear response to climate. Together, k and n modify the strength of the weathering feedback (Schwartzman and Volk, 1989; Mills et al., 2014a; Caves et al., 2016). Globally, although weathering fluxes are determined by runoff because weatherability is modified by the overlying runoff distribution (Fig. 14), the strength of the feedback (the k and n terms) is also dependent on runoff. To relate the weatherability framework developed here to global feedback parameters (calibrated values of k and n) requires knowledge of both the time-varying spatial distribution of silicate lithologies and changes in runoff patterns set by changes in atmospheric circulation and continental configuration. Assuming that increases in global runoff are positively correlated with increasing $p\text{CO}_2$ (Otto-Bliesner, 1995; Gibbs et al., 1999;

Pierrehumbert, 2002; Manabe et al., 2004), our solute production framework provides a quantitative method to parameterize formulations of the negative feedback in both 0-D carbon cycle models and spatially explicit weathering models. Thus, the strength of the negative feedback is set by the interaction between the Dw values of silicate bedrock catchments and the spatial runoff distribution.

Given changes in continental configuration, eruptions of large igneous provinces, and changes in tectonic uplift, global Dw distributions must be non-stationary through geologic time. We propose here that a variable silicate weathering feedback may be driven by shifts in the Dw distribution of silicate catchments globally. Further, atmospheric circulation drives large variations in runoff across the Earth's surface today (Fig. 14c); thus, changes in climate that affect this circulation will vary the spatial pattern of runoff, further altering the strength of the negative feedback.

To demonstrate how the spatial distribution of lithology and runoff interact to determine basalt/granite weatherability, we plot in Fig. 14c, d the modern weatherability as a function of latitude. We calculate this for modern basalt catchments using the modern latitudinal runoff distribution from Dai and Trenberth (2002) (see Fig. 14 caption for details). In this figure, because runoff substantially varies latitudinally (Fig. 14c), weatherability also varies latitudinally and displays large, ~50% variability. Over geologic timescales, if the proportion of basalt relative to granite changes (black lines Fig. 14d), weatherability must also change, with the largest changes occurring in the tropics due to high runoff. Thus, for example, the eruption of a large igneous province in the tropics should have a much larger effect on global weathering than a similarly sized eruption in subsiding portions of Hadley cells (Kent and Muttoni, 2008, 2013). Similarly,

changes in climate that alter the distribution of runoff (such as Hadley cell expansion, shifting mid-latitude westerlies, etc.) would also produce changes in weatherability without necessarily a change in the areal distribution of lithologies. This view of weatherability contrasts with that presented in Fig. 14a. Here, we derive weatherability for global average runoff, which—due to energetic constraints (Pierrehumbert, 2002)—cannot change dramatically. Thus, 0-D models of weathering are potentially limited in their ability to capture large changes in weatherability due to changes in the spatial distribution of runoff and/or lithology, even if global averages remain constant.

Changes in global basalt/granite weatherability due to variations in runoff and in the distribution of bedrock silicate lithologies indicate that weatherability can change on both short and very long timescales (Fig. 14d). For example, basalt/granite weatherability increases at higher runoff; therefore, rapid climate change during greenhouse climates, such as in the early Eocene or Cretaceous, may cause pronounced changes in weatherability as runoff intensity and distribution changes (Fig. 14a). Thus, across a carbon-cycle perturbation such as the PETM—which witnessed large-scale changes in hydrology and runoff (Bolle and Adatte, 2001; Bowen et al., 2004; Pagani et al., 2006; Foreman et al., 2012) against a background greenhouse climate state—weatherability cannot be assumed constant. An increase in weatherability would tend to shorten the duration of the carbon cycle perturbation. Across such perturbations, globally averaged runoff may change, though likely not substantially (cf. Pierrehumbert, 2002; Manabe et al., 2004). However, if the spatial distribution of runoff changes dramatically (e.g., Pagani et al., 2006; Tipple et al., 2011; Foreman et al., 2012), this would drive larger

changes in the basalt/granite weatherability relative to changes expected based solely on globally-averaged runoff.

Similarly, on longer timescales, as continental configuration and climate change, the spatial interactions between these two effects will affect weatherability and, hence, the strength of the negative feedback. These effects are likely to be greater than those caused by changes in the global average runoff given that spatially runoff varies substantially. Indeed, previous studies have suggested that changes in global silicate weathering fluxes could be driven by the interaction of continental configuration and sea level with the overlying runoff distribution, as determined by atmospheric circulation, over both short (10^3 – 10^5 yr) and long ($>10^6$ yr) timescales (e.g., Gibbs and Kump, 1994; Gibbs et al., 1999; Ludwig et al., 1999; Munhoven, 2002; Donnadieu et al., 2004; Goddris et al., 2008; Kent and Muttoni, 2008; Le Hir et al., 2009; Mills et al., 2011, 2013; Jagoutz et al., 2016).

The spatial sensitivity of the weathering feedback points to the importance of further development of spatially explicit weathering models coupled to or driven by global climate models (e.g., Munhoven, 2002; Goddris et al., 2008; Lefebvre et al., 2013; Goll et al., 2014; von Blanckenburg et al., 2015) that will allow us to better quantify how the interaction between lithologic exposure, tectonic processes, configuration of continents, and climate sets the strength of the silicate weathering feedback through time. Though we have focused here on the role of lithology in determining the efficiency of silicate weathering, exposure of more rapidly eroding areas (e.g., higher D_w values) due to tectonic uplift (e.g., Waldbauer and Chamberlain, 2005; von Blanckenburg, 2005; West et al., 2005; Hilley et al., 2010; Norton and von

Blanckenburg, 2010; West, 2012) may also provide a mechanism for varying the strength of the silicate weathering feedback (Maher and Chamberlain, 2014; Caves et al., 2016).

Because the weatherability of the Earth's surface can vary through geologic time, paleogeographic and paleotopographic reconstructions are intrinsically important for placing bounds on the strength of the silicate weathering feedback. Constraining the strength of the silicate weathering feedback through time will require the use of paleoclimate model simulations to determine past runoff distributions under changing continental configurations (e.g. Gibbs et al., 1999; Munhoven, 2002; Goddris et al., 2008; von Blanckenburg et al., 2015), in combination with: (1) reconstructing the interaction of large orogenic belts with climate (e.g., Montgomery et al., 2001; Rowley and Currie, 2006; Mulch and Chamberlain, 2006; DeCelles et al., 2007; Garzione et al., 2008; Mix et al., 2011, 2016; Caves et al., 2014, 2015), (2) the inferred erosion rates of orogenic belts (e.g., Drever and Zobrist, 1992; Willett, 1999; Kirchner et al., 2001; Hilley et al., 2010; Willenbring and von Blanckenburg, 2010; Moon et al., 2011; Moore et al., 2013; Willett et al., 2014; Lee et al., 2015), (3) the spatial distribution and evolution of shielding soils (e.g., Taylor and Blum, 1995; Chamberlain et al., 2005; Porder et al., 2007; Goddris et al., 2008; Kent and Muttoni, 2013; Hartmann et al., 2014a; Minasny et al., 2015; St. Clair et al., 2015), (4) the interaction of climate and erosional processes on basin evolution to determine reactive flow path length and subsurface permeability (e.g., Rempe and Dietrich, 2014; St. Clair et al., 2015), and (5) the areal extent and spatial configuration of rapidly eroding areas (e.g., Bluth and Kump, 1991; Gibbs et al., 1999; Kent and Muttoni, 2008; 2013; Molnar and Cronin, 2015; Jagoutz et al., 2016; Cox et al., 2016) through geologic time.

3.1.6 Conclusions

We have shown using modern concentration-runoff relationships how hydrologic and lithologic controls combine to set weathering fluxes from catchments by applying the process-based model of Maher and Chamberlain (2014) to assess the weathering efficiency of individual catchments of the two silicate end-member lithologies, granites and basalts. Although our analysis is limited to the Northern Hemisphere and primarily mid-latitude North America, the dataset shows first-order trends in weathering efficiency and lithological controls. We find that the relative weatherability of basalt compared to granites is runoff dependent due to both the plateaus in weathering fluxes caused by dilution of solutes at high runoff and the thermodynamic controls at lower runoff. As a consequence, the weatherability of basalt relative to granites has likely not been constant over geologic time—as runoff and lithologic exposure changes spatially—and is perhaps not constant even on shorter timescales. In addition, when more directly comparable modern data becomes available, weatherability can be assessed under constant climate, soil age, and vegetation parameters using the framework presented in this paper. Finally, if the differences in bedrock weatherability can be extrapolated to the geologic past as presented here, then determining the global distribution and geographic configuration of lithologies, in addition to the interaction of topography with atmospheric circulation changes, will be essential in constraining the variable strength of the silicate weathering negative feedback and its role in controlling past atmospheric $p\text{CO}_2$.

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3.1.9 Tables

The following table is included in the appended excel workbook

“Ibarra_Chapter3_Tables.xlsx” and was published with the original publication (Ibarra et al., 2016).

Table 1. Summary statistics for concentration-runoff fits and flux-weighted data

3.1.10 Figures

Figure 1. Location of datasets and conceptual model for concentration-runoff processes.

(a) Map of catchments included in this analysis. For overlapping sites the numbers are listed by group (e.g., 10 $\times$) (see Table A1). PNW – Pacific Northwest, SN – Sierra Nevada. (b) Catchment-scale conceptual model used to illustrate fluxes shown in Eqs. (2) and (3), and the framework presented in Fig. 2. In this study we only analyze concentration-runoff relationships of end-member silicate catchments. Analysis of concentration-runoff relationships of large rivers by Maher and Chamberlain (2014) and von Blanckenburg et al. (2015) was carried out on datasets from heterogenous, mix-lithology datasets (e.g., Gaillardet et al., 1999; Moon et al., 2014).

Figure 2 (next page). Framework for evaluating catchment solute production. (a) $\text{SiO}_2(\text{aq})$ concentration as a function of runoff (Eq. (3)). Illustrated catchments types are from Maher (2011). Constant Damköhler numbers (Da) are denoted as horizontal dashed lines of constant concentration. Note log-scale runoff axis. (b) $\text{SiO}_2(\text{aq})$ fluxes as a function of runoff and illustration of weathering potential (WP) (Eqs. (4)-(6)). Weathering potential is expressed in percent ($WP_{norm}[\%]$). Note that both axes are on log-scales.

Figure 3 (next page). Illustrative correction of concentration-runoff relationship for non-zero C_0 within the solute production framework; solid lines are a hypothetical observed concentration-runoff relationship and the dashed lines are the silicate weathering component only. Log-scale axes are as in Fig. 2. (a) $\text{SiO}_2(\text{aq})$ concentration as a function of runoff (Eqs. (2) and (3)). Values of C_{max} and C_0 are annotated. (b) $\text{SiO}_2(\text{aq})$ fluxes as a function of runoff showing that the correction for C_0 contributions results in a plateau of the weathering flux (W_{max}). Chemostatic portions of the curve are annotated.

a **b**

Figure 4 (next page). Concentration-runoff fits for catchments; plotted as concentration as a function of runoff (Eqs. (1) and (2)) for (a) $\text{SiO}_2(\text{aq})$ ($\mu\text{mol/L}$), (b) Mg^{2+} ($\mu\text{mol/L}$), (c) Ca^{2+} ($\mu\text{mol/L}$), (d) Na^+ ($\mu\text{mol/L}$), (e) HCO_3^- ($\mu\text{mol/L}$), (f) cation-equivalent ($\mu\text{eq/L}$), and (g) total dissolved solids (mg/L). The median sampled runoff is denoted by dots (diamonds for chemostatic catchments and circles for catchments demonstrating dilution) and lines are plotted for the full range of paired runoff and solute observations from each catchment. Note that both axes are log-scaled.

Figure 5 (next page). C_0 -corrected concentration-runoff fits and C_{max} distributions.

Concentration-runoff fits are displayed as in Fig. 4, corrected for C_0 (as demonstrated in Fig. 2) for (a) $\text{SiO}_2(\text{aq})$ ($\mu\text{mol/L}$), (b) Mg^{2+} ($\mu\text{mol/L}$), (c) Ca^{2+} ($\mu\text{mol/L}$), (d) Na^+ ($\mu\text{mol/L}$), (e) HCO_3^- ($\mu\text{mol/L}$), (f) cation-equivalent ($\mu\text{eq/L}$), and (g) total dissolved solid (mg/L). C_{max} distributions are displayed with summary statistics (mean (diamonds), median, interquartile range (IQR) and 95% range) color coded by catchment type (granite or basalt). Also shown (e.g., 1.50 $\times$) is a comparison of the mean basalt C_{max} to the mean granite C_{max} value.

Figure 6 (next page). Flux-weighted concentration pairs. Fluxed weighted concentration-runoff relationships. Each point represents a single catchment. C_{max} values, denoted in square brackets, are determined from the 95th percentile of concentrations for each catchment type (granite or basalt) following Maher and Chamberlain (2014) (see their Fig. S3 and Table S1). Dw values contoured here, and reported in Table A9, assume the 95th percentile C_{max} value.

Figure 7 (next page). Concentration-runoff derived maximum concentration (C_{max}) vs. water temperature. Scatter plots of average water temperature vs. concentration-runoff derived C_{max} values (C_0 -corrected C_{max} values) for (a) $\text{SiO}_2(\text{aq})$ ($\mu\text{mol/L}$), (b) Mg^{2+} ($\mu\text{mol/L}$), (c) Ca^{2+} ($\mu\text{mol/L}$), (d) Na^+ ($\mu\text{mol/L}$), (e) HCO_3^- ($\mu\text{mol/L}$), (f) cation-equivalent ($\mu\text{eq/L}$), and (g) total dissolved solid (mg/L). Temperature is the average of the water temperature during sample collection, not the air temperature. C_{max} errors (reported in Tables A2–A8) are 1σ . For clarity temperature errors are not included, but are reported in Table A1. Linear regressions are individually calculated for each sample group (basalts and granites), using the C_{max} and temperature population statistics (mean and errors). Only statistically significant regressions are illustrated and reported ($p\text{-value} < 0.05$). The temperature-concentration relationships (dC/dT) are reported for the statistically significant regressions and 95% confidence intervals are shaded.

Figure 8 (next page). Histograms of saturation indices (i.e., $\log(IAP/K)$) for select primary and secondary minerals. Saturation index calculations carried out in Geochemist's Workbench (Bethke and Yeakel, 2015) using the Thermoddem database (version: llvl2; Blanc et al., 2012; Marty et al., 2015). Here we include all available samples with aluminum concentrations ($n = 1952$) from the USGS NWIS database from basaltic and granitic catchments as well as from the Icelandic catchments (Eiriksdottir et al., 2013, 2015). Data from chemostatic catchments are highlighted as solid bars. For smectite we use the end-member half reactions for Na, Ca and Mg (Smectite-Na = $\text{Na}_{0.34}\text{Al}_{2.34}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2$; Smectite-Ca = $\text{Ca}_{0.17}\text{Al}_{2.34}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2$; Smectite-Mg = $\text{Mg}_{0.17}\text{Al}_{2.34}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2$). The “Albite (High)” histogram uses thermodynamic data for the highly disordered albite end-member more typically found in basalts (*cf.* Stefánsson et al., 2001).

Figure 9. Activity diagrams of the smectite-kaolinite system for Ca–Mg and Ca–Na.

Following Bluth and Kump (1994) activity diagrams were constructed assuming that $\log [\text{SiO}_2(\text{aq})] = 10^{-3}$ to $10^{-3.7}$ and temperature = 15 °C. Brackets denote activity. All available data from the USGS NWIS database from basaltic and granitic catchments as well as from the Icelandic catchments (Eiriksdottir et al., 2013, 2015) were speciated using Geochemist’s Workbench (Bethke and Yeakel, 2015) using the Thermoddem database (version: llvl2; Blanc et al., 2012; Marty et al., 2015) to calculate $\log [\text{Ca}^{2+}]/[\text{H}^+]^2$ (n = 7853), $\log [\text{Na}^+]/[\text{H}^+]$ (n = 8031), and $\log [\text{Mg}^{2+}]/[\text{H}^+]^2$ (n = 7835).

Figure 10 (next page). Concentration-runoff derived Damköhler coefficient (Dw) cross-plots. Comparison of concentration-runoff derived Dw values for basalts (red) and granites (blue) derived using different solutes. Diagonal solid lines are the 1:1 line, and the parallel dashed lines are a factor of two envelope ($2\times$ and $0.5\times$ the 1:1 line). Note both axis scales are equivalent and are log-scaled. Dw distributions are displayed with summary statistics (mean (diamonds), median, interquartile range (IQR) and 95% range) color coded by catchment type (granite or basalt). Plots compare (a) $\text{SiO}_2(\text{aq})$ vs. Mg^{2+} , (b) $\text{SiO}_2(\text{aq})$ vs. Ca^{2+} , (c) $\text{SiO}_2(\text{aq})$ vs. HCO_3^- , (d) $\text{SiO}_2(\text{aq})$ vs. Na^+ , (e) $\text{SiO}_2(\text{aq})$ vs. TDS, (f) cation-equivalent vs. HCO_3^- , and (g) Mg^{2+} vs. Ca^{2+} .

Figure 11. Concentration-runoff derived Damköhler coefficients (D_w) vs. water temperature. Scatter plots of average water temperature vs. concentration-runoff derived D_w values for (a) $\text{SiO}_2(\text{aq})$, (b) Mg^{2+} , (c) Ca^{2+} , (d) Na^+ , (e) HCO_3^- , (f) cation-equivalent, and (g) total dissolved solid. As in Fig. 9, temperature errors are not included but are reported in Table A1. No statistically significant regressions (p -value < 0.05) exist between D_w and temperature in this dataset.

Figure 12. Weathering potential. Maximum weathering potential (ΔWP) vs. the median normalized weathering potential (WP_{norm}) for basalts (red) and granites (blue) derived for (a) $\text{SiO}_2(\text{aq})$ and (b) HCO_3^- . Note the log-scale for ΔWP (y-axis). Error bars for ΔWP are the minimum and maximum range of observations. Error on WP_{norm} are not shown for clarity but can be calculated using the minimum and maximum runoff values given in Tables A2 and A6. Linear regressions with confidence intervals are individually illustrated for each sample group (basalts and granites).

Figure 13 (next page). $\text{SiO}_2(\text{aq})$ and HCO_3^- fluxes. (a) $\text{SiO}_2(\text{aq})$ fluxes ($\text{t}/\text{km}^2/\text{yr}$) and (b) HCO_3^- fluxes ($\text{t}/\text{km}^2/\text{yr}$). Note both axes are log-scales. Heavy plotted lines are the mean fluxes (granite–blue; basalt–red) based on the C_{max} and Dw distributions (Fig. 5, Table 1) derived from the granite (thin lighter blue) and basalt (thin lighter red) catchments (see text). W_{max} distributions are displayed with summary statistics (mean (diamonds), median, interquartile range (IQR) and 95% range) color coded by catchment type (granite or basalt). Previously derived flux-runoff relationships by Bluth and Kump (1994) are also plotted for reference.

Figure 14 (next page). Weatherability of basalt vs. granite catchments. (a) Basalt/granite weatherability, calculated from the average area-normalized basalt/granitic fluxes derived from the average C_{max} and Dw values (Table 1, Fig. 9a,b) for $\text{SiO}_2(\text{aq})$ (thick black line), and HCO_3^- (thick gray line) as a function of runoff. Errors associated with the parameters used to calculate the weatherability curves are reported in Table 1. Global average runoff (thick red horizontal line) is calculated from Dai and Trenberth (2002) (panel c) with an uncertainty band assuming a 10% increase/decrease in runoff for a doubling of global $p\text{CO}_2$ (based on Manabe et al., 2004) up to a five times doubling. (b) Range of weatherability from previous studies (Horton et al., 1999; Berner, 2006b, 2008; Hartmann, 2009; Hartmann et al., 2010; Hartmann and Moosdorf, 2011). (c) Area-weighted global river runoff distribution (mean and 95% range) binned by latitude (3° bins) derived from the volumetric discharge and variance of observations from the 200 largest rivers reported by Dai and Trenberth (2002). Calculated by area-weighting and combining the binned northern and southern hemisphere runoff averages. (d) Mean basalt/granite $\text{SiO}_2(\text{aq})$ weatherability (mean and 95% range) vs. latitude (binned at 3° latitude bands) based on the modern runoff distribution. Calculated by area-weighting the binned northern and southern hemisphere runoff averages (panel c) and multiplying by the $\text{SiO}_2(\text{aq})$ runoff-dependent weatherability relationship (panel b) assuming 100% basalt proportion relative to granites.

0-D Models

Spatially Explicit Models

3.2 Concentration-discharge patterns of weathering products from global rivers

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Abstract

Quantifying the functional relationships relating river discharge and weathering products places key constraints on the negative feedback between silicate weathering and climate. In this study we analyze the concentration–discharge relationships of weathering products from global rivers using previously compiled time-series datasets for concentrations and discharge from global rivers. To analyze the nature of the covariation between specific discharge and concentrations, we use both a power law equation and a recently developed solute production equation. The solute production equation allows us to quantify weathering efficiency, or the resistance to dilution at high runoff, via the Damköhler coefficient. These results are also compared to those derived using average concentration–discharge pairs. Both the power law exponent and the Damköhler coefficient increase and asymptote as catchments exhibit increasingly chemostatic behavior, resulting in an inverse relationship between the two parameters. We also show that using the distribution of average concentration–discharge pairs from global rivers, rather than fitting concentration–discharge relationships for each individual river, underestimates global median weathering efficiency by up to a factor of ~ 10 . This study demonstrates the utility of long time-series sampling of global rivers to elucidate controlling processes needed to quantify patterns in global silicate weathering rates.

Keywords: Concentration-discharge, Rivers, Silicate weathering, Solutes

3.2.1 Introduction

Silicate weathering is hypothesized to impose a variable negative feedback on the evolution of Earth's carbon cycle over geologic time (François and Walker, 1992; Kump and Arthur, 1997; Caves et al., 2016). Thus, understanding the functional relationships that couple climate and weathering is critical to modeling how atmospheric CO₂ has varied in the past (Kump et al., 2000; Maher and Chamberlain, 2014; Caves et al., 2016). In this study, we compare two such functional relationships relating the covariation of discharge and weathering products using a recently compiled time-series comprising 43 global rivers (Moon et al., 2014). We fit concentration-discharge (C-q) relationships using both a power-law equation (e.g., Bluth and Kump, 1994; Godsey et al., 2009; Moon et al., 2014; Torres et al., 2015) and a solute production model (Maher, 2011; Maher and Chamberlain, 2014; Ibarra et al., 2016).

3.2.2 Framework and Methods

The C-q datasets considered in this study is a dataset of 43 large rivers with 3,843 measurements [United Nations Environment Programme (UNEP) - Global Environment Monitoring System (GEMS/Water) supplemented by the Environmental Research Observatory (HYBAM)] compiled by Moon et al. (2014). Our dataset is restricted to sites with the paired runoff and solute concentration (C) data needed to constrain the weathering of primary silicate minerals to secondary minerals [SiO₂(aq), Mg²⁺, Ca²⁺, Na⁺, Cl⁻, and HCO₃⁻]. Na* is equal to Na⁺ - Cl⁻ following Moon et al. (2014). All discharge data are normalized by watershed area to calculate changes in specific discharge or runoff (q , [m/yr]), which allows for direct area-normalized quantification of

solute production over orders-of-magnitude differences in discharge. We also compare our weathering efficiency results to the average C - q pair data from Moon et al. (2014) (their Table 2) and Gaillardet et al. (1999) (their Table 1).

We briefly describe the equations used to fit the data and the numerical Gauss-Newton method used for fitting the C - q relationships. Many studies of modern weathering use power-law relationships (PLM hereafter) between concentration and runoff or discharge (e.g., Bluth and Kump, 1994; Godsey et al., 2009; Moon et al., 2014; Torres et al., 2015). Following previous work, we use the form:

$$C = aq^b \quad (1),$$

where C is the solute concentration [$\mu\text{mol/L}$], q is the paired instantaneous runoff, and a and b are the fitted parameters. For weathering solutes, b is typically less than 1, resulting in a convex-up dilution relationship (decreasing concentration with increasing runoff). Numerous models have been proposed to explain the observation that power-law relationships are observed across an array of catchments (*cf.* Godsey et al., 2009; Torres et al., 2015).

The process-based solute production equation (SPM hereafter) for C - q derived by Maher and Chamberlain (2014) relates concentration (C) to specific discharge (runoff) (q):

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

where Dw [m/yr] is the Damköhler coefficient, C_0 is the initial solute concentration, and $C_{\max}$ is the maximum theoretical solute concentration, thought to be set by equilibrium among the primary and secondary mineral assemblages (Maher, 2010, 2011). A higher Dw value reflects more efficient generation of solutes and a system more resistant to

dilution (Maher and Chamberlain, 2014). C_0 is the initial solute concentration, derived from atmospheric deposition and/or hydrothermal or deep groundwater inputs and is independent of discharge. Equation 2 can be simplified if C_0 can be assumed to be zero (Maher and Chamberlain, 2014):

$$C = C_{\max} \frac{Dw / q}{1 + Dw / q} \quad (3).$$

From equations (2) and (3), the fitted C - q relationships parameters from long-term monitoring are Dw , $C_{\max}$ and C_0 .

Following our previous work (Ibarra et al., 2016), we only report C - q relationships with statistically significant parameter fits ($p < 0.05$) and > 20 C - q pairs/river (Table S1). To fit both the PLM (equation 1) and the SPM (equations 2 and 3) we apply a non-linear least squares method to derive the fitted parameter values using a Gauss-Newton algorithm [‘nls2’ R package; Grothendieck (2013)]. If the b -value derived using equation 1 is insignificant ($b = 0$) the C - q relationships is assumed to be chemostatic (e.g., Godsey et al., 2009), and we do not fit the SPM. We fit equation 2 for the SPM and use equation 3 if the C_0 value derived from equation is statistically insignificant or less than zero ($C_0 \leq 0$). Finally, we calculate Dw values, denoted hereafter as Dw_{avg} , using average C - q pair datasets (Moon et al., 2014; Gaillardet et al., 1999) for each individual river by rearranging equation (3) and assuming $C_{\max}$ values as the 95th percentile for each weathering solute following methods used in von Blanckenburg et al. (2015) and Ibarra et al. (2016). Note that in Ibarra et al. (2016) the discharge-weighted mean concentrations were used, rather than arithmetic mean concentrations as used in von Blanckenburg et al. (2015), although the results presented below are not influenced by this assumption.

3.2.3 Results and Discussion

Here we report the results of fitting C - q relationships using time-series data, and compare these results to those derived from average C - q pairs (Table S1; Figure 2). Following this, we directly compare C - q fit dilution parameters, SPM Dw values with PLM b -values.

Distributions of fitted dilution parameters

The distributions reported in Table S1 are comparable in magnitude and range to those derived for small granite catchments in Ibarra et al. (2016). Further, the distribution in b -values and magnitude of higher b -values for $\text{SiO}_2(\text{aq})$ corroborates the results of Moon et al. (2014) using this same dataset, and demonstrates a much wider range of b -values observed for global rivers here compared to the 59 small US catchments analyzed in Godsey et al. (2009). Slopes of the PLM fits were mostly negative, indicating dilution, with some b -values near zero. $\text{SiO}_2(\text{aq})$ displayed b -values close to chemostatic with the corresponding highest Dw values. Na^+ displayed the lowest b -values, however HCO_3^- displayed the lowest Dw values.

Comparison of Dw values derived here to those using average C - q pairs (Dw_{avg}) is substantially different. We find that the median Dw , when considering all solutes evaluated, is 6.2 times greater using the C - q fits than using average C - q pairs for the Gaillardet et al. (1999) dataset, and 9.8 times greater for the Moon et al. (2014) average dataset (Figure 2B). This appears to be because averaging the concentrations (Figure 1) results in C - q pair values lower (in concentration and runoff) than the SPM fit, giving a

lower Dw_{avg} value. In Figure 2A, we show that this is the case for a majority of catchments (all but 3 catchments with significant fits), and can result in a bias up to 100 fold in some cases. An additional bias is that this method assumes a global C_{max} value for each solute rather than variable C_{max} values for each individual river, which likely change with soil pCO_2 , lithology, and other geomorphic and catchment properties (*cf.* Maher, 2011; Ibarra et al., 2016).

Relationship between b values and Damkohler coefficients

In Figure 2C, we cross plot all C - q fit-derived Damköhler coefficients (Dw) with power law b -values. We find that both parameters increase as b -values asymptote to chemostatic values (note that Dw values cannot be calculated for chemostatic catchments). This asymptotic behavior suggests that the form of equation 3, when equated to equation 1, results in an inversely proportional relationship. Broadly this relationship would take the form $b = -k/Dw$, where, based on the data, the constant of proportionality (k), is less than 1 among the data presented here (grey contours in Figure 2C). As b -values approach complete dilution ($b = -1$, note that we found no b -values less than -0.7) the relationship with Dw follows k value contours of 0.1 to 0.3.

This analysis demonstrates the fundamental difference between fitting the PLM compared to the SPM derived by Maher and Chamberlain (2014). A dilution relationship with a b -value between -1 and 0 is exclusively convex up in C - q space (dashed grey lines in Figure 1); however, because of the lack of further fitted parameters when fitting a power law relationship there is no turnover and plateau at lower runoff (e.g., Figure 1A). In contrast, the functional form of the SPM allows for both a convex down relationship at

low runoff and a convex up relationship at high dilution. This difference in the form of these relationships results in increasing spread among the dilution parameters (b -values and D_w values) closer to chemostatic behavior (Figure 2C). This may be due to different carbonate vs. silicate weathering contributions (e.g., Moon et al., 2014) and/or seasonal mixing from different sources (e.g., Torres et al., 2017) during baseflow compared to peak flow regimes.

3.2.4 Conclusion

This study provides the first comparison between process-based modeling framework derived by Maher and Chamberlain (2014) and the traditionally used power-law relationship. We propose an inversely proportional relationship between the solute production dilution parameter and power-law b -values that converge at near chemostatic relationships. In addition, we demonstrate that using average C-q pairs results in an underestimate in the SPM dilution parameter (D_w). These results demonstrate the value and necessity for time-series sampling of global rivers to better constrain the functional relationships that couple weathering rates and climate.

3.2.5 Acknowledgements

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3.2.7 Figures

Figure 1. Example $C-q$ fits for two global rivers. (A) HCO_3^- vs. runoff from the Narmada River. (B) Ca^{2+} vs. runoff from the Pechora River. Solid lines are the SPM fits and dashed lines are the PLM fits. Large grey dots are the mean runoff and discharge-weighted mean concentration.

Figure 2 (next page). (A) Dw_{avg} values compared to Dw values (Figure 1) using the dataset from Moon et al. (2014). Both axes are log-scale. Grey lines indicate factor of 10 and 100 envelopes around the 1:1 line (bold). Errors are the standard error of the parameter estimate. (B) Box-and-whisker plots of Dw and Dw_{avg} values from: 1) fitted $C-q$ relationships (Figure 1); 2) average $C-q$ pairs from Moon et al. (2014); and 3) average $C-q$ pairs from Gaillardet et al. (1999). Thick grey lines are the median value for each dataset (see text for values). (C) Dw values versus power law b -values. Errors are the standard error of the parameter estimates. Grey contours are for a general inversely proportional relationship $b=k/-Dw$ for different scaling values of k . (D) Same as (B) for power law b -values using only fitted $C-q$ relationships.

APPENDICES

APPENDIX A

Supplemental Figures for Chapter 1

Figure A1 (next page). Schematic of HyBIM model structure. The model structure uses a matrix inversion to solve a system of three equations ($x = A^{-1}b$) implemented at each time step to calculate changes in lake volume (from the combined evaporation and inputs) and basin average air temperature. After smoothing and interpolating to an even time series, the input dataset (time series of $\delta^{18}O$, Mg/Ca and Sr/Ca from biogenic carbonate), given a set of adjustable input parameters (right side of the fig.; table 1), is first placed in lake water composition ($\delta^{18}O$, [Mg] and [Sr] Lake Water). The first derivative of the lake water time series is inputted as the b vector at each time step ($d(\delta^{18}O)$, $d[Mg]$ and $d[Sr]$). The partial derivatives that make up the A matrix are substituted at each time step using mixing equations and evaporation equations (eqs 5 to 9 for F_{evap} and F_{input} derivatives), or estimated for temperature (the T derivatives) based on the geographic location (see text for details). For each Monte Carlo iteration the model produces a time series of the x solution vector. To provide summary statistics after combining the evaporation and lake input variables to calculate changes in volume we calculate the median and 95% range (as in figs. 3 and 4).

Figure A2. Annual weighted precipitation $\delta^{18}\text{O}$ and mean annual temperature from the Global Network in Precipitation Data (GNIP) as compiled by the Stable Water Isotope Intercomparison Group (SWING). Following Rozanski and other (1993) we calculate slope of the temperature vs. weighted precipitation $\delta^{18}\text{O}$ for the mid and high latitude ($> 23^\circ$) sites (gray), and tropics (black). We only use the empirical regression (slope and uncertainty) for the tropics in modeling of Lake Miragoane temperature changes. For the Songliao Basin we use the original regression of Rozanski and others (1993) of $0.58\text{‰}/^\circ\text{C}$.

APPENDIX B

Supplemental Text, Figures and Tables for Chapter 2

Date Repository Contents:

- Scaling of potential evapotranspiration with surface temperature
- Processing of climate model output and NARR dataset
- Dataset Treatment
- Figures DR1-DR3
- Links to databases used for this study
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- DR References

Scaling of potential evapotranspiration with surface temperature

We use climate model experiments to estimate how net surface radiation (R_N) and potential evapotranspiration (E_p) scale with temperature (Equation 4). To do so we sum the radiation fluxes (Equation 4) to obtain the annual net surface radiation (R_N) and calculate average annual temperature for all land grid cells in our domain of interest (30-45 °N, 102-121 °W). We then calculate domain average temperature and R_N anomalies for the LGM and Pliocene using the PMIP3 and PliMIP output (Table DR5) relative to the preindustrial control experiments (see next section). We also include 25 CMIP5 climate models using 30-year averages from the historical (1976-2005) and RCP 8.5 (2070-2099) simulations (where the historical period is taken as the control point). The R_N anomalies are calculated as a percentage change relative to the control.

The potential evapotranspiration calculated from the net surface radiation scales with surface temperature at a rate of 1.6%/K (Figure DR1). For this study we use the net-radiation formulation of potential evapotranspiration (Roderick et al., 2014) and thus use the scaling factor of 1.6%/K for the NARR sensitivity analyses. This regional result derived using the CMIP5, PMIP3 and PlioMIP models is similar to previous work using CMIP3 and CMIP5 models which suggest empirical scalings of R_N to temperature of ~ 0.9 to 1.5 %/K (Milly and Dunne, 2016; Scheff and Frierson, 2014; Roderick et al., 2014; 2015).

Processing of climate model output and NARR dataset

To carry out our lake area modeling (Equations 2 and 3), we use monthly average output from the North American Regional Reanalysis (NARR) (Mesinger et al., 2006), the Paleoclimate Model Intercomparison Project 3 (PMIP3) ensemble and the Pliocene Model Intercomparison Project (PlioMIP) ensemble (Braconnot et al., 2012; Haywood et al., 2011; 2013). PlioMIP conducted two distinct simulations; we choose to use Experiment 2, which is the full ocean-atmosphere climate model simulations of the mid-Pliocene (*cf.* Haywood et al., 2013), making them more directly comparable to the LGM model output from PMIP3. We only use the archived energy and precipitation fields for forward modeling lake area distributions (Equation 2), and follow Roderick et al. (2014) by also using evapotranspiration (ET) fields to derive estimates of the regional ω parameters used in the Budyko equation (Equation 3). The models used in this study (Table DR4) are a subset of the PMIP3 and PlioMIP ensembles that included all of the necessary surface energy and water flux variables necessary to carry out our calculations.

Because of different model resolutions we re-grid all model data prior to further analysis using the ‘fields’ package in R (Nycha et al. 2016).

We use the methods outlined by Roderick et al. (2014) and process the NARR and climate model output by calculating the annual sum of potential evapotranspiration (E_p) as the liquid water equivalent of the net irradiance (Equation 4 in main text). Further, annually summed precipitation (P) and evapotranspiration were tabulated from monthly averages. We use all of the land-grid cells where ET does not exceed P annually to fit the Budyko relationship (Equation 3 in main text) using the ‘nls2’ package in R (Grothendieck, 2013). The derived ω values are reported in Table DR5. The median change in E_p/P vs. ET/P for all grid cells in the domain for each model is shown in Figure DR2 with the mean ω value over all models contoured. We plot the median change of E_p/P vs. ET/P , rather than mean changes, for each individual model because the spatial distributions of E_p , P and ET are skewed in the modeling domain of interest. To avoid potential biases in absolute precipitation amount simulated by different models, we plot the anomaly relative to the pre-industrial control simulation in the predicted lake surface area change in Figure 2B rather than the absolute value. Further, since our objective is to model trends and lake area distributions, we determine E_L using the Priestley-Taylor equation (Priestley, 1959; Priestley and Taylor, 1972; Sumner and Jacobs, 2005):

$$LE = \alpha \frac{\Delta}{\Delta + \gamma} R_N$$

(DR1)

where LE is the latent heat flux that is related to lake evaporation (E_L in equation 3 in the main text) by the latent heat of vaporization, $\alpha=1.25$ is an empirically determined dimensionless correction, Δ is the slope of the saturation vapor-pressure curve, which is temperature dependent, γ is the psychrometric constant, which is elevation dependent, and R_N is the net downward radiation at the surface (see equation 4). Use of more complex evaporation equations would require additional parameters that are difficult to estimate or measure in the past (e.g., Linacre, 1977).

To carry out the NARR sensitivity analyses (Figure 2A, 2C, 2D and DR3), we scale precipitation linearly using a scaling factor as described in the main text. Temperature is scaled linearly to scale R_N (equation 4) by 1.6%/K (see previous section). Further, because we use the Priestley-Taylor equation (Priestley, 1959; Priestley and Taylor, 1972; Sumner and Jacobs, 2005) to approximate lake evaporation (E_L in equation 2 in the main text) changes in temperature change the slope (Δ) of the saturation vapor-pressure curve. For the NARR sensitivity analyses, we use the US catchment median value of $\omega = 2.6$ (Greve et al., 2015). If we were to use a lower ω value (see for example PMIP3/PlioMIP control simulations in Table DR5), as suggested by maps of modern catchment derived ω values in Greve et al. (2015), the effect of decreasing evaporative demand on increasing LGM lake levels would be greater, suggesting lower precipitation scaling factors (Figure 2C and 2D). Conversely, the increase in precipitation needed to drive Pliocene lake areas would be lower, but greater than pre-industrial. However, a majority of the models suggest a decrease in ω for the LGM but not the Pliocene (Table DR5).

Dataset Treatment

LGM Normalized Lake Areas. LGM lake areas were compiled from the tables and maps of the sources listed in Table DR1 (Allen, 2005; Reheis, 1999; Orme, 2008; Grayson, 2011; *Natural Earth* database; Soller et al., 2009; Williams and Bedinger, 1984; Mifflin and Wheat, 1979). We assume no major watershed boundary and basin configuration changes since the LGM. We paired the lake areas in ArcGIS 10.0 with the LGM lake areas with modern watershed boundaries from the *HydroSHEDS*, *HydroBASINS*, and *HydroLAKES* (Lehner et al., 2008; Lehner and Grill, 2013; Messenger et al., 2016) databases (<http://www.hydrosheds.org/>). Further assumptions were:

- Average normalized areas were calculated across all available estimates (rightmost column of Table DR1).
- For Figure DR3 northern Great Basin lakes ($> 39^{\circ}\text{N}$) areas were reduced by 50%, based on work from smaller lakes such as Lake Surprise (Ibarra et al., 2014), Lake Franklin (Munroe and Laabs, 2013), and a review by Reheis et al. (2014).

Mid-Pliocene Normalized Lake Areas. Lake areas were only derived from the compilation in Pound et al. (2014). We only paired lakes in the compilation from Pound et al. (2014) to modern drainage basins (Table DR3) if the following criteria were met:

- It was clear that the lake was terminal based on the lacustrine sedimentology, topography and drainage network (cf. Table 2 in Pound et al. (2014)).

- The lake area did not span multiple modern watersheds over large drainage divides nor did it appear to be influenced by large tectonic drainage reconfigurations (cf. Adam et al., 1990; Thompson, 1992; Reheis et al., 2002; Knott et al., 2008; Phillips, 2008; Pound et al., 2014).

Given that extension in the Basin and Range has been ongoing since the Miocene (e.g., Colgan et al., 2006), it is likely that the many terminal basins created by Basin and Range faulting were filled by lakes during wet intervals such as the mid-Pliocene. Since the Pound et al. (2014) dataset is primarily derived from basinal sedimentary deposits, which may have undergone unquantifiable erosion or burial since Pliocene deposition the A_I/A_B calculations may be underestimates which would necessitate even larger increases in precipitation relative to present day during the mid-Pliocene. However, if additional extension has occurred since the Pliocene these estimates may be overestimates. Examples of lakes in Table DR 3 from the Pound et al. (2014) compilation for which normalized lake areas were not calculated include Tule Lake (Adam et al., 1990), which has evidence for a sill indicating that the lake overflowed into the Klamath River basin (cf. Figure 1 of Adam et al., (1990)), and Glenn's Ferry (Smith, 1981; Thompson, 1992), due to possible drainage to the southwest (Thompson, 1992).

Macrostrat lacustrine data are only used as supporting evidence plotted on Figure 1B. The *Macrostrat* database does not provide individual lakes, rather the database contains aggregates of stratigraphic datasets grouped into polygons of differing areas. However, given the relatively high resolution of the *Macrostrat* polygons the distribution of mid-Pliocene lacustrine sediments suggests that many areas of modern terminally draining basins had lakes during the mid-Pliocene (Fig. 1B).

The calculation of lake area, A_L represents the maximum expansion of lakes in a given basin during the time intervals of interest. A complication for both the LGM and mid-Pliocene lake areas is the “Manly Group”, which contain multiple higher elevation fill and spill sub-basins that eventually flowed to Lake Manly (Death Valley). For ease of analysis we choose to group these sub-basins into one large terminal basin (see Table DR1 and DR3) although this treatment may result in an underestimate in A_L/A_B . Similarly, Lake Lahontan and Lake Bonneville integrated multiple sub-basins but were fully connected at their highstand elevations (Reheis et al., 2014). As such, we combined areas for all sub-basins in the Lahontan and Bonneville watersheds in Table DR1.

Temperature Estimates. Independent estimates of temperature changes (relative to modern) (x-axis of Figures 2C, 2D and DR3) are as follows:

- Figure 2C we plot the full range of temperature estimates for the LGM (-13 to -2.75 °C (median = -7.5°C) based on tables in: Matsubara and Howard, 2008; Grayson, 2011).
- In Figure 2D depressions are observed to be less depressed in this region than further inland. Thus, we plot a reduced range of temperature estimates for the LGM (-10 to -2.75 °C based on tables in: Matsubara and Howard, 2008; Grayson, 2011).
- For Figures 2C and 2D we plot the full range of temperature estimates for the mid-Pliocene (0 to +6 °C based on tables in: Dowsett et al., 1994; Molnar and Cane, 2007)

Figure DR1. Empirical scaling of potential evapotranspiration with surface temperature based on PMIP3, PlioMIP and CMIP5 simulations (see DR text above).

Figure DR2. A: Budyko framework – median changes in E_p/P vs. ET/P calculated from LGM climate model simulations. Dashed lines connect simulations from the same models. Colored curves and symbols are the LGM simulations. Solid lines are the ensemble averages (Table DR5). See climate model processing methods for more details.

B: Same as A for mid-Pliocene simulations.

Figure DR3 (next page). Effect of adjusting northern Great Basin lake areas. Median calculated lake level from NARR data (black lines) and original LGM distributions (blue shading and lines) are the same as Figure 2C. Shown in red is the adjusted distribution of LGM lake areas (see Table DR1) assuming ~50% smaller lakes in the northern Great Basin (lakes north of 39 °N). Many lakes in the northern Great Basin stood at prominent but lower stillstands during the LGM than the post-LGM highstands (Munroe and Laabs, 2013; Ibarra et al., 2014; Reheis et al., 2014). As in Figure 2B we plot the full range of temperature estimates for the LGM (-13 to -2.75 °C (median = -7.5°C) based on tables in: Matsubara and Howard, 2008; Grayson, 2011).

Links to online databases for geospatial and climate data used for this study

- *HydroSHEDS/HydroBASINS/HydroLAKES* (Lehner et al., 2008; Lehner and Grill, 2013; Messenger et al., 2016): <http://www.hydrosheds.org/>
- *Natural Earth* pluvial lakes database:
<http://www.naturalearthdata.com/downloads/10m-physical-vectors/10m-lakes/>
- *Macrostrat* database: <https://macrostrat.org/>
- “Extent of Pleistocene Lakes in the Western Great Basin”, by Reheis (1999):
<https://geo-nsdi.er.usgs.gov/metadata/map-mf/2323/metadata.faq.html>
- “Map Database for Surficial Materials in the Conterminous United States”, by Soller et al. (2009): <https://pubs.usgs.gov/ds/425/>
- NCEP North American Regional Reanalysis (NARR):
<https://www.esrl.noaa.gov/psd/data/gridded/data.narr.html>
- Paleoclimate Modelling Intercomparison Project 3 (PMIP3):
<https://pmip3.lsce.ipsl.fr/>
- PlioMIP1 output was distributed by Alan Haywood, Aislin Dolan, Daniel Hill and Steven Pickering (personal communication, 2016)

Table DR1 (next page) – Compilation of late Pleistocene (~LGM) lake areas and modern watershed areas. All areas are in km².

References: (1) *HydroSHEDS/HydroBASINS/HydroLAKES* (Lehner et al., 2008; Lehner and Grill, 2013; Messenger et al., 2016), (2) Allen (2005), (3) Reheis (1999), (4) Orme (2008), (5) Grayson (2011), (6) *Natural Earth* database, (7) Soller et al. (2009), (8) Williams and Bedinger (1984), (9) Mifflin and Wheat (1979). Average normalized areas are calculated using the *HydroBASINS* (Lehner and Grill, 2013) basin areas and stream networks with all available lake area estimates (columns 2b, 3a, 4-9). Agreement of lake areas between publications is <5% for most basins. Allen (2005) basin areas (column 2a) are for comparison only. Reheis (1999) maximum lake areas (column 3b) are not used as they represent post-LGM highstand areas or pre-MIS 2 highstands. Latitude and longitude values are for reference only and correspond to the centroid for each terminal basin. Soller et al. (2009), Reheis (1999) and the *Natural Earth* pluvial lakes database are mapped in Figure 1A. Adjusted normalized distributions (shown used in Figure DR3) assumes that LGM lake areas were ~50% maximum highstands for watersheds north of 39 °N (polygon centroid's location) to account for post-LGM highstands observed in the northern Great Basin (Munroe and Laabs, 2013; Ibarra et al., 2014; Reheis et al., 2014). Unnamed basins were assigned numbers: UN-GB# – Unnamed-Great Basin; UN-SW# – Unnamed-Southwest.

Lake Name	Latitude	Longitude	Basin Area (1)	Basin Area (2a)	Lake Area (2b)	Lake Area (3a)	Maximum Lake Area (3b)	Lake Area (4)	Lake Area (5)	Lake Area (6)	Lake Area (7)	Lake Area (8)	Lake Area (9)	Average Normalized Area (%)
Acme	38.55	-118.32	351.45							7.40				2.10
Alford	42.18	-118.68	7031.36			1153.62		1270.00	1269.10	947.19		1217.30		16.66
Alkali	43.04	-120.06	1375.20					550.00	590.52	565.90				41.36
Animas	32.29	-108.85	5607.00	5670.00	374.00						313.38			5.59
Antelope	39.85	-114.31	874.68			140.15			124.32	127.12		124.32	124.32	14.64
Bonneville	40.18	-112.67	134131.13					51700.00	51864.55	51956.71		51644.40	51644.40	38.59
Bonnie Claire	37.33	-117.11	3526.21							142.63				4.04
Bristol	37.96	-114.76	2334.47						90.65	77.33		90.65		3.69
Buffalo	40.50	-117.32	1284.38			66.55			199.43	195.25		199.43		12.86
Cactus Flat	38.13	-116.80	6100.73					344.47		374.97				5.90
Cahuilla	33.00	-115.80	20050.8									7769.97		38.75
Carpenter	38.51	-114.57	1432.29			121.93			347.06	358.10		347.06	347.06	21.24
Catlow	42.52	-119.20	4850.63					900.00	898.73	905.54		1152.55		19.88
Cave	38.57	-114.85	930.13			121.29			178.71	180.27		178.71	178.71	18.01
Cedar	37.62	-113.17	374.57							18.55				4.95
Chewaucan	42.68	-120.51	3385.35					1200.00	1243.20	1194.08		1243.20		36.04
Chochise	32.15	-109.84	4357.00								545.79	621.60		13.40
Clayton	37.71	-117.60	1437.76							85.14				5.92
Clover	40.85	-114.83	2665.56			743.21	1094.25	890.00	890.96	913.81		911.68	911.68	32.90
Cloverdale	31.36	-108.85	467.80	460.00	102.00						82.52	77.70		17.12
Coal	38.00	-115.41	2487.57						178.71	188.33		178.71	178.71	7.28
Colombus	37.79	-118.00	3532.12			141.45			139.86	365.10		204.61	204.61	5.98
Coyote	42.38	-118.19	1789.45			317.39				125.90				12.39
Cuddeback	35.31	-117.47	555.31									90.65		16.32
Deep Spring	37.36	-118.08	519.42						44.03	25.33		44.03		7.28
Delamar	37.44	-114.87	926.74							26.49				2.86
Desatoya	39.29	-117.57	1490.65			397.51			435.12	442.13		435.12	435.12	28.78
Diamond	39.40	-116.38	8018.15			1021.21	2283.22	760.00	758.87	1023.04		1015.28		11.42
Dixie	39.80	-117.84	5410.24			798.63	2394.69	1090.00	1090.39	721.47		714.84	766.64	15.96
Eagle	40.64	-120.89	1123.78			126.84			160.58	145.49				12.84
Edwards	39.58	-117.69	1078.89			287.10			264.18	266.36		264.18	264.18	24.95
Encino	34.60	-105.60	644.20	620.00	96.00						56.77	310.80		28.53
Estancia	34.67	-105.96	5733.70	5050.00	1125.00						1084.76	2330.99		29.79
Fort Rock	43.28	-120.89	6403.89						1945.08	1564.66		2343.94		30.47
Franklin	40.37	-115.23	3345.89			947.49		1220.00	1219.89	1248.19		1250.97	1250.97	35.55
Fred	39.77	-119.82	47.73							7.90				16.56
Frenchman	36.85	-115.96	1180.75							20.05				1.70
Gabbs	38.85	-118.09	3319.81							312.43				9.41

Gale	39.83	-115.09	1912.71			168.82			411.81	431.64		411.81		18.61
Garfield	38.36	-118.32	246.58						7.77	17.47		7.77	8.55	4.21
Gilbert	39.84	-116.71	1540.94			392.61		540.00	538.72	398.62		401.45		29.48
Gold Flat	37.50	-116.50	1791.85						67.34	66.76		67.34	67.34	3.75
Goldfield	37.85	-117.29	826.72							17.75				2.15
Goodsight	32.50	-107.33	532.20	590.00	65.00							38.85		7.30
Granite Springs	40.25	-118.89	2518.64						103.60	109.41		103.60	103.60	4.17
Groom	37.31	-115.86	1717.34						93.24	74.32		93.24		5.06
Groom	37.23	-115.41	2575.13							133.60		93.24		4.40
Guano	42.00	-119.48	2124.41							172.02				8.10
Harper	35.06	-117.33	1871.58									139.86		7.47
High Rock	42.02	-119.16	194.06							13.95		31.08		11.60
Hubbs	39.76	-115.37	1666.22			532.16	619.98	530.00	530.95	521.93		505.05	505.05	31.26
Huntoon	38.11	-118.58	318.05							5.39				1.69
Indian Springs	36.68	-115.73	1719.03							168.33				9.79
Jakes	39.30	-115.27	1102.26			213.14			163.17	155.12		163.17	163.17	15.56
Kawich	37.49	-116.22	947.41						56.98	49.12		56.98	56.98	5.81
Kumiva	40.43	-119.12	853.07						38.85	45.10		38.85	38.85	4.74
Labou	39.23	-118.27	790.86			35.64			51.80	50.69		51.80	51.80	6.11
Lahontan	40.36	-118.09	105613.36			21906.48	30917.97	22300.00	22004.56	23368.63		21859.52	23478.78	21.29
Laughton	39.68	-119.97	81.36						18.13	10.87		18.13		19.31
Lemmon	39.67	-119.87	247.58						33.67	37.94		33.67	33.67	14.03
Little Fish	38.84	-116.42	1055.41							12.67				1.20
Lunar Crater	38.66	-115.98	1291.56							16.17				1.25
Luning	38.46	-118.10	637.12							30.56				4.80
Macy	41.97	-119.66	76.41							20.35		23.31		28.57
Madeline	40.89	-120.38	2167.64					780.00	777.00	763.23		777.00		35.72
Malheur	43.44	-119.11	13083.89					2380.00	2380.20	2432.95		2460.49		18.45
Manly Group	36.20	-117.16	51541.38						4169.88	5004.85				8.90
Maxey	38.76	-114.42	1370.13			210.87			209.79	211.83		209.79	209.79	15.36
Meinzer	41.59	-119.73	1870.75			923.61		920.00	919.45	992.93		890.96	890.96	49.34
Monte Cristo	38.34	-117.80	720.59							14.26				1.98
Mormon	36.84	-115.40	973.54							70.35				7.23
Newark	39.38	-115.82	3604.16			816.84	986.44	930.00	795.13	805.90		782.18	782.18	22.72
Otero	32.86	-106.36	9556.70	12600.00	745.00						409.94	466.20		4.58
Pahrump	36.05	-115.81	3748.99							657.73				17.54
Papoose	37.08	-115.81	256.83							27.20				10.59
Penoyer	37.74	-115.79	1819.15							59.39				3.26
Pine	38.45	-113.74	1898.09				922.41		106.19	116.43				5.86

Pinos Wells	34.46	-105.60	589.90	560.00	82.00						49.11	207.20		21.72
Playas	31.86	-108.57	1135.60	1120.00	49.00						16.72	259.00		12.14
Railroad	38.65	-115.67	5518.75			864.43		1360.00	1359.74	980.86		971.25	971.25	19.65
Reveille	38.22	-116.22	4346.40			146.20			106.19	103.75		106.19	106.19	2.62
Rhodes	38.25	-118.11	520.42						33.67	29.66		33.67	33.67	6.28
Sacramento	32.46	-105.66	1397.40	780.00	86.00									6.15
Saline	36.78	-117.78	1928.51							83.93				4.35
San Agustin	33.85	-108.15	3046.90	3880.00	786.00						513.47	1129.24		26.96
Snyder	38.84	-116.07	163.65							38.98				23.82
Spring	39.45	-114.47	2949.98			617.85		870.00	870.24	640.32		603.47	603.47	23.76
Stonewall	37.63	-116.94	938.60							49.80				5.31
Surprise	41.35	-119.98	3840.91			1477.95		1310.00	1310.53	1475.66		1471.11	1484.84	37.01
Teel	38.13	-118.37	810.54							42.30				5.22
Thompson	34.92	-118.02	9115.90					950.00	950.53			556.85		8.99
Toiyabe	39.10	-117.02	3411.50			421.96		650.00	650.09	573.98		525.77	525.77	16.35
Tonopah	38.42	-117.51	5294.27			277.56			233.10	264.91		233.10	233.10	4.69
Trinity	33.55	-106.56	4524.50	4240.00	207.00						134.57	199.43		3.69
UN-GB1	35.76	-116.83	43.73							3.73				8.53
UN -GB2	35.70	-116.77	360.86							2.72				0.75
UN -GB3	37.14	-117.22	249.07							4.34				1.74
UN-GB4	37.17	-117.83	1540.52							6.55				0.43
UN-GB5	36.76	-117.53	162.92							6.25				3.84
UN-GB6	35.55	-116.69	402.92							4.78				1.19
UN-GB7	35.44	-113.80	3674.90								300.82			8.19
UN-SW1	34.14	-107.61	882.90								49.73			5.63
UN-SW10	33.47	-102.49	936.20								20.46			2.19
UN-SW11	33.76	-102.52	702.40								54.71			7.79
UN-SW12	33.98	-102.55	200.50								19.16			9.56
UN-SW13	33.89	-102.98	1653.40								51.41			3.11
UN-SW14	33.68	-103.68	82.80								15.54			18.77
UN-SW15	34.85	-103.99	49.30								14.32			29.05
UN-SW2	31.77	-102.88	2437.20								19.49			0.80
UN-SW3	31.50	-102.67	340.80								15.02			4.41
UN-SW4	31.47	-102.52	696.00								17.44			2.51
UN-SW5	31.68	-101.88	202.60								14.15			6.99
UN-SW6	32.39	-102.66	103.70								32.83			31.66
UN-SW7	32.91	-102.29	421.70								35.39			8.39
UN-SW8	33.13	223.12	222.00								47.14			21.23
UN-SW9	33.44	-102.07	688.90								19.94			2.89
Waring	40.00	-114.65	8566.76			1375.87		2520.00	1331.25	1686.23		1401.18	1401.18	18.90
Warner	42.40	-119.90	4804.82			1331.27		1250.00	1250.97	1202.50		1307.94		26.40
Yahoo	39.47	-116.09	44.62						5.18	6.97		5.18	5.18	12.61
Yucca	37.09	-116.08	777.53							12.39				1.59

Normalized Area (%) Distribution	
Median	9.20
Q1	4.62
Q3	19.17
Max	49.34
Adjusted Normalized Area (%) Distribution	
Median	7.30
Q1	4.32
Q3	13.62
Max	38.75
South Great Basin (%) Distribution	
Median	5.06
Q1	2.62
Q3	8.53
Max	23.82

Table DR2 –Area of modern lakes (>1km²) found in terminal watersheds. Data derived from the HydroSHEDS/HydroLAKES/HydroBASINS database (Lehner et al., 2008; Lehner and Grill, 2013; Messenger et al., 2016) intended to represent maximum possible sizes by including seasonal playa lakes.

Lake Name	Basin Area	Total Lake Area	Normalized Area (%)	Notes
Alkali	1375.20	14.97	1.09	3 unnamed seasonal playa lakes
Alvord	7031.36	5.49	0.08	Seasonal playa lake
Bonneville	134131.13	8923.51	6.65	Maximum size: Great Salt Lake, Bonneville Salt Flats, Bear Lake and other playa lakes
Chewaucan	3385.35	285.86	8.44	Lake Abert and Summer Lake
Clover	2665.56	5.13	0.19	Playa Lake
Fort Rock	6403.89	8.24	0.13	Seasonal playa Lake
Franklin	3345.89	13.17	0.39	3 playa/marsh lakes
Lahontan	105613.36	954.70	0.90	Pyramid and Walker Lakes (historic areas) plus playa lakes
Malheur	13083.89	422.28	3.23	2 playa lakes
Manly Group	51541.38	238.52	0.46	Includes area of Mono Lake (Pleistocene Lake Russell) and seasonal playa lakes in all following sub-basins: Owens, Searles, Panamint, Manly
Meinzer	1870.75	56.33	3.01	Numerous small seasonal playa lakes
Spring	2949.98	4.07	0.14	Playa lake
Surprise	3840.91	255.13	6.64	3 seasonal playa lakes
Warner	4804.82	130.15	2.71	Numerous small seasonal playa lakes
Area Normalized (%) Distribution				
Median				1.00
IQR1				0.24
IQR3				3.17
Max				8.44

Table DR3 – Compilation of mid-Pliocene (early Piacenzian, ~2.9 to 3.3 Ma) lake deposits. P2014 – Pound et al. (2014). We consider all continuous formations that span the Piacenzian in *Macrostrat*. Pliocene lake areas are only paired to basin areas when it is clear that the lake was terminal, does not span multiple modern watersheds over large drainage divides, and have not been greatly influenced by tectonic drainage reconfiguration.

Name of Lake/Formation	Latitude	Longitude	Reference	Age minimum (Ma)	Age maximum (ma)	Thickness (m)	Unit ID	Section ID
Palouse Loess	46.56	-117.2	Macrostrat	0	3.3	100	7460	1968
	36.42	-115.43	Macrostrat	0	5.3	10	14059	3727
	38.08	-113.78	Macrostrat	0	17.1	1000	14212	3774
Santa Fe Gp	35.46	-106.08	Macrostrat	0	14.4	1000	14906	3965
Paso Robles Fm	35.39	-120.29	Macrostrat	0	5.3	200	17724	4603
Santa Fe Gp	34.15	-107.28	Macrostrat	0.7	4.9	470	2187	356
Santa Fe Gp	33.81	-106.8	Macrostrat	0.7	4.9	130	2214	362
Glenns Ferry Fm	43.56	-115.92	Macrostrat	0.7	5.8	300	7488	1975
	40.71	-118.24	Macrostrat	0.7	4.9	300	13530	3584
Atherton Fm	38.63	-87.07	Macrostrat	1.5	5.1	50	11687	3158
Fort Hancock Fm	31.91	-106.5	Macrostrat	1.9	3.6	10	1889	292
Santa Fe Gp	33.05	-105.61	Macrostrat	1.9	19.3	10	2275	383
Paso Robles Fm	35.46	-120.68	Macrostrat	1.9	8.3	120	17735	4605
Paso Robles Fm	36.48	-121.74	Macrostrat	1.9	8.3	155	17753	4612
Blanco Fm	33.73	-99.98	Macrostrat	2.6	3.3	24	2575	469
Hungry Valley Fm	34.67	-118.66	Macrostrat	2.6	4.9	2000	6314	1522
Palm Spring Fm	33.57	-115.85	Macrostrat	2.6	3.3	1500	6544	1598
Salt Lake Fm	41.95	-113.76	Macrostrat	2.6	8.7	800	14128	3752
	40.03	-113.9	Macrostrat	2.6	17.1	1000	14210	3773
Salt Lake Fm	41.71	-111.59	Macrostrat	2.6	17.1	1000	14476	3839
Salt Lake Fm	40	-112.03	Macrostrat	2.6	10.5	1500	14565	3863
	40.55	-112.3	Macrostrat	2.6	17.1	10	14626	3885
Salt Lake Fm	40.98	-111.62	Macrostrat	2.6	19.3	2000	14722	3909
Salt Lake Fm	40.25	-111.54	Macrostrat	2.6	17.1	4000	14727	3910
Bidahochi Fm	35.95	-109.91	Macrostrat	2.6	5.3	272	14987	3988
Bug Fm	42.05	-106.49	Macrostrat	2.6	4	37	15759	4174
Tule Gp	34.43	-101.83	Macrostrat	2.8	2.9	10	2528	458
Gila Conglomerate	32.48	-108.26	Macrostrat	2.8	4	10	1855	271
Sunshine Ranch Mbr of Saugus Fm	34.3	-118.53	Macrostrat	2.8	3.1	915	6344	1529
	46.66	-122.88	Macrostrat	2.8	13.3	350	7257	1896
Glenns Ferry Gp	43.23	-114.67	Macrostrat	2.8	8.3	300	13673	3622
	39.18	-112.25	Macrostrat	2.8	12.2	1000	14570	3864

Thousand Creek Beds	41.46	-119.04	Macrostrat	2.9	8.3	130	13454	3543	
Name of Lake/Formation	Latitude	Longitude	Reference	Basin Area (km ²)	Basin Area Notes	Outcrop or Lake Area (km ²)	Normalized Area (%)	Age minimum (Ma)	Age maximum (ma)
Glenn's Ferry, ID	43.50	-116.30	P2014		Not terminal	22144		2.4	3.8
Tule Lake	41.98	-122.05	P2014		Not terminal?	6291.45		2.6	3
Rhodes-Clayton-Fish Valleys, NV	38.00	-118.00	P2014		Watershed unclear	10800		2.6	3.4
Owens Lake	36.55	-118.00	P2014		Larger Manly Basin	1500		2	3
Lake Manly	36.55	-117.05	P2014		Larger Manly Basin	1300		2	3
Panamint Lake	35.95	-117.20	P2014		Larger Manly Basin	276		2	3
China-Scarles Lake	35.55	-117.40	P2014		Larger Manly Basin	800		2	3
Kochn Lake 1	35.18	-117.85	P2014		Larger Manly Basin	40		2	3
Kochn Lake 2	35.15	-117.40	P2014		Larger Manly Basin	12.5		2	3
Kochn Lake 3	35.10	-117.10	P2014		Larger Manly Basin	16		2	3
Lake Russell	38.00	-119.00	P2014		Mono and Lake Russell listed separately by P2014	2800		2	2.8
Mono Lake	38.00	-118.55	P2014		Mono and Lake Russell listed separately by P2014	1125		2	3
All Manly Basin with Lake Russell Area			P2014	51541		6744.5	13.09		
Harper 1	34.65	-118.00	P2014		Watershed unclear	25		2	3
Harper 2	34.65	-117.90	P2014		Watershed unclear	4		2	3
Harper 3	34.70	-117.80	P2014	750	Assumed separate from Harper 4	60	8.00	2	3
Harper 4	34.45	-117.50	P2014	1027	Assumed separate from Harper 3	10	0.97	2	3
South Mojave	34.30	-117.00	P2014	11237		4	0.04	2	3
Lake Tecopa	35.75	-116.25	P2014	14129		112	0.79	2	3
Lake Mojave	35.05	-116.10	P2014	8219	Assume that Mojave separate from Manly group during Pliocene	120	1.46	2	3
Lake Manix	34.85	-116.40	P2014	1041	Assume that Manix separate from Manly group during Pliocene	50	4.80	2	3
Bristol Lake	34.30	-115.65	P2014	1285		84	6.54	2	3
Cadiz Lake	34.15	-115.40	P2014	967		55	5.69	2	3
Danby Lake	34.05	-115.15	P2014	1120		72	6.43	2	3
Rita Blanca	35.72	-102.39	P2014	1738		54.39	3.13	3	3.6
Hueco Bolson, TX	30.90	-105.30	P2014		Not terminal?	5780		1.8	4.8
						Normalized Area (%) Distribution			
						Median	4.80		
						Q1	1.22		
						Q3	6.48		
						Max	13.09		

Table DR4 – Climate models used in this study.

Model	Organization, Country	Atmospheric Resolution (#lat x lon x levels)	References
PMIP3 LGM Ensemble			
CNRM-CM5	CNRM-CERFACS, France	256x128 x L31	Voldoire et al. (2013)
COSMOS-ASO	Freie Universität Berlin, Germany	96x48 x L19	Zhou et al. (2014)
CCSM4	National Center for Atmospheric Research, USA	288x192 x L26	Gent et al. (2011); Brady et al. (2013)
MRI-CGCM3	Meteorological Research Institute, Japan	320x160 x L48	Yukimoto et al. (2012)
IPSL-CM5A-L	Institute Pierre Simon Laplace, France	96x95 x L39	Kageyama et al. (2013); Dufresne et al. (2013)
MPI-ESM-P	Max Planck Institute for Meteorology, Germany	196x98 x L47	
MIROC-ESM	Model for Interdisciplinary Research on Climate, Japan	128x64 x L80	Sueyoshi et al. (2013)
PlioMIP (Experiment 2) Ensemble			
CCSM4	National Center for Atmospheric Research, USA	288x192 x L26	Rosenbloom et al. (2013)
MRI-CGCM 2.3	Meteorological Research Institute and University of Tsukuba, Japan	128x64 x L30	Kamae and Ueda (2012)
NorESM-L	Bjerknes Centre for Climate Research, Norway	96x48 x L26	Zhang and Yan (2012); Zhang et al. (2012)
HadCM3	Hadley Centre for Climate Prediction and Research/Met Office, UK	96x73 x L19	Bragg et al. (2012)
IPSL-CM5A	Institute Pierre Simon Laplace, France	96x95 x L39	Contoux et al. (2012)
COSMOS	Alfred Wegener Institute, Germany	96x48 x L19	Stepanek and Lohmann (2012)

Table DR5 – Regional fitted Budyko parameters

Model	LGM ω value	PI Control ω value
CNRM-CM5	1.82	2.08
COSMOS-ASO	1.98	2.30
CCSM4	1.98	2.44
MRI-CGCM3	1.97	2.57
IPSL-CM5A-L	1.69	2.21
MPI-ESM-P	1.82	2.31
MIROC-ESM	1.76	2.60
	Pliocene ω value	PI Control ω value
CCSM4	2.25	2.60
MRI-CGCM 2.3	2.31	2.27
NorESM-L	1.98	2.18
HadCM3	1.99	1.90
IPSL-CM5A	2.04	2.24
COSMOS	2.64	2.51

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APPENDIX C

Supplemental Tables for Chapter 3

The following tables are included in the appended excel file

“Ibarra_Chapter3_Tables.xlsx” and have been published as supplementary files with the original publications (Ibarra et al., 2016; Ibarra et al., 2017).

Chapter 3.1 (Ibarra et al., 2016, *Geochemica et Cosmochimica Acta*)

Table A1. Summary of compiled datasets

Table A2. SiO₂(aq) concentration-runoff results

Table A3. Mg²⁺ concentration-runoff results

Table A4. Ca²⁺ concentration-runoff results

Table A5. Na⁺ concentration-runoff results

Table A6. HCO₃⁻ concentration-runoff results

Table A7. Catio-equivalent concentration-runoff results

Table A8. TDS concentration-runoff results

Table A9. Flux weighted concentrations and *D_w* values

Chapter 3.2 (Ibarra et al., 2017, *Acta Geochemica*)

Table S1. Average concentration-runoff pair and full concentration-runoff fitted parameters.