A Stable Isotopic Study of Gnamma Hydrology in the Colorado Rocky Mountains

Johanne Albrigtsen
Johanne.Albrigtsen@Colorado.EDU

Follow this and additional works at: https://scholar.colorado.edu/honr_theses
Part of the Biogeochemistry Commons

Recommended Citation
https://scholar.colorado.edu/honr_theses/1683

This Thesis is brought to you for free and open access by Honors Program at CU Scholar. It has been accepted for inclusion in Undergraduate Honors Theses by an authorized administrator of CU Scholar. For more information, please contact cuscholaradmin@colorado.edu.
A Stable Isotopic Study of Gamma Hydrology in the Colorado Rocky Mountains

By

Johanne Marie Odasz Albrigtsen

Ecology and Evolutionary Biology, University of Colorado at Boulder

Defense Date:
April 9, 2018

Thesis Advisor:
Dr. Boswell Wing, Geological Sciences

Defense Committee:
Dr. Boswell Wing, Geological Sciences
Dr. Erin Tripp, Ecology and Evolutionary Biology
Dr. Barbara Demmig-Adams, Ecology and Evolutionary Biology (Honors Council Representative)
ABSTRACT

Gnammas are potholes in solid bedrock that periodically fill with rainwater to form ephemeral pools. In order to understand the ecological and evolutionary processes at play in these dynamic ecosystems, the spatial and temporal controls on gnamma hydrology must be constrained. Previous studies on the relationships between hydro-regime and biota in gnamma environments posit evaporation as the sole process of water loss. I evaluated this assumption about gnamma water balance via stable isotope analysis of gnamma waters in the Colorado Rocky Mountains. My study aimed to constrain the processes of water loss in gnmmas; that is, whether gnmmas lose water over time through evaporation, seepage through the rock substrate, or a combination of both processes. I conducted two week-long experiments with water samples taken from a suite of gnmmas of a variety of sizes. The stable isotope compositions of the water samples were interpreted with a derivation of Craig and Gordon’s (1965) evaporative fractionation model. Water loss in gnmmas was found to be attributable to a combination of both evaporation and seepage, with ~10 - 30% of water lost by means of evaporation. Although previously overlooked, water loss via seepage through the rock substrate plays a substantial role in the water balance of gnmmas. From this new understanding of gnamma water balance, I developed a conceptual model of gnamma development that highlights the importance of aridity and the residence time of water in the gnamma. This model also predicts that the environmental controls of gnamma development should vary as a function of gnamma size. The constraints provided here on gnamma hydrology should allow for the application of gnmmas as model systems to explore species richness-area relationships, insular biogeography concepts, and other geobiological hypotheses.
ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Boswell Wing for his invaluable guidance and enthusiasm throughout this project, in addition to inspiring me to creatively work through any challenges that arose. This thesis would not have come to fruition without his support. I would also like to acknowledge the additional members of my thesis committee: Dr. Barbara Demmig-Adams and Dr. Erin Tripp for their encouragement and participation in my defense. I extend thanks to Dr. Robert Anderson for the initial prospect of studying gnmmas and their potential as model systems. I would additionally like to thank Dr. Anderson and Rachel Glade for generating the aerial images and digital elevation model of my study site. Thanks to Peter Molnar and Sara Neustadt for generously allowing me to use their property as my field site.

I am grateful to the University of Colorado Undergraduate Research Opportunities Program for funding this research project. Additional thanks to the Institute of Arctic and Alpine Research Stable Isotope Laboratory, particularly Valerie Morris and Bruce Vaughn, for processing my water samples and providing the stable isotope data. I am also indebted to the Geomicrobial Physiology and Evolution Lab in the Department of Geology for allowing me to loan supplies for my field sampling. Lastly, I would like to thank my friends and family, especially my mother Dr. Ann Marie Odasz, for their encouragement, help with field work, and boundless support.
# Table of Contents

ABSTRACT.........................................................................................................................i

ACKNOWLEDGMENTS...........................................................................................................ii

I. INTRODUCTION..................................................................................................................1

II. BACKGROUND
   i. Biology of Ephemeral Waters......................................................................................3
   ii. Stable Isotope Analyses...........................................................................................4

III. METHODS
   i. Hydrology Model- Derivation of Isotope Mass Balance...............................6
   ii. Locality......................................................................................................................10
   iii. Hydrology Protocol..............................................................................................11

IV. RESULTS..........................................................................................................................13

V. DISCUSSION
   i. Hydrology Model....................................................................................................16
   ii. Conceptual Model of Gnamma Development....................................................18
   iii. Limitations and Future Applications.................................................................21

VI. REFERENCES....................................................................................................................24

VII. APPENDICIES
   i. Derivation of Isotope Mass Balance........................................................................27
   ii. Raw Data................................................................................................................30
   iii. Gnamma Photos....................................................................................................34
I. INTRODUCTION

Gnmamas, also known as weathering pits, potholes or rock holes, are erosional depressions in solid bedrock (c.f. Twidale and Corbin 1963; Timms and Rankin 2016). Filling ephemerally with rainwater, gnamma systems act as miniature aquatic ecosystems with complex interactions occurring among water, dissolved solutes, and the surrounding rock substrates (Domínguez-Villar et al. 2008; Hughes 2012). Gnmamas are found worldwide in many rock types, but generally form in granite (Migoń 2007). The morphology of gnmamas is broad; sizes range from a few centimeters up to tens of meters across and from millimeters to several meters deep (Twidale and Corbin 1963).

The major source of environmental variation in gnamma systems is attributed to their cycles of water presence. Gnmamas periodically fill with rainwater and form ephemeral aquatic habitats. Ecological processes in ephemeral rock pools are constrained by their hydrologic regimes (the presence and duration of water in the system; Hulsmans et al. 2008). The hydro-regime of transient waters can exert significant selective pressure on the biota of the system (Hulsmans et al. 2008). In order to understand the ecological and evolutionary processes at play in these dynamic ecosystems, the spatial and temporal hydrological variation must be constrained. Previous studies on the relationships between hydro-regime and biota in rock pool environments consider evaporation as the sole process of water loss (Williams 1985; Hulsmans et al. 2008). This water balance assumption must be evaluated to gain better understanding of the implications of hydrologic variability and climate change for biotic communities in the pools created by potholes.
The controlled nature of gnamma systems allows for the potential development of a model experimental system for exploring geobiological processes and microbial ecosystem dynamics. Currently, studies of geobiological interactions are missing an *in vivo* model system that would enable long-term integrative monitoring of biogeochemical effects ‘in the wild’. Gnammas are “nano basins” that could be controlled and manipulated to investigate various biogeochemical processes on a small scale. In order to develop such a model system, the constraints and controls of the system must be understood. In many areas, numerous gnmmas occur in close proximity to each other; they all have developed in the same substrate and are exposed to equivalent abiotic variation. The major source of environmental variation is the wet-dry cycles that the gnmmas undergo (Twidale and Corbin 1963; Domínguez-Villar et al. 2008). Though it is understood that gnmmas are able to retain rainwater for varying lengths of time (Domínguez-Villar et al. 2008), the controls of the residence time of gnamma waters have not been thoroughly investigated. Previous studies assume that gnamma water levels are progressively reduced only due to evaporation processes (c.f. Domínguez-Villar et al. 2008; Hulsmans et al. 2008; Timms 2013) and fail to consider the role that seepage through the mineral may play in water loss. In order to understand the controls on residence time of gnamma water, this study aimed to determine if evaporation or seepage through the mineral was the primary process of water loss in gnmmas. The processes by which the systems lose water, either evaporation, seepage through the rock substrate, or a combination of the two, were explored via stable isotope analyses of the gnamma water over time.
II. BACKGROUND

i. Biology of Ephemeral Waters

Gnammas periodically and temporarily fill with rainwater, forming ephemeral aquatic habitats or rock-pools. These temporary waters are especially prevalent in semi-arid and arid regions (Williams 1985). Rock-pools have specific and seasonal environmental conditions consisting of multiple short and usually unpredictable hydroperiods (De Roeck et al. 2010). A hydroperiod is the duration of a single hydrocycle, from initial water input to the loss of the water from the system; in temporary waters, the variation, frequency, and periodicity of the hydrocycle are key structuring factors (Hulsmans et al. 2008). Hydrologic conditions are highly variable due to spatial and temporal variations in these habitats, this variation must be considered when investigating ecological processes in rock pools (Hulsmans et al. 2008).

The determinants of biology in temporary waters include the degree of predictability of water presence (Decksbach 1929) and salinity (Williams 1985). Topography is a major local determinant of fresh versus saline waters, with climate as the major regional determinant of water predictability in the pools (Williams 1985). The duration of time that pools contain water, their hydroperiod, is one of the most significant variables impacting biological populations and communities. Developmental rates and species richness of the biota in these environments depend on the residence time and rate of water loss as opposed to the original size of the pool, as biota perceive how fast the volume of water decreases rather than the actual volume of water present (Williams 1985; Tavernini et al. 2005). The hydro-
regime of transient waters can exert significant selective pressure on the biota of the system and influences the nature of their life-history adaptations (Williams 1985; Hulsmans et al. 2008; De Roeck et al. 2010). Due to their specific environmental conditions, temporary rock-pools are generally habituated by a small set of highly specialized species (De Roeck et al. 2010). Additionally, temporary pool ecosystems may be valuable indicators for climactic changes (Graham 1996). The implications of hydrologic variability and climate change for biotic communities in the pools created by potholes are understudied and warrant further exploration.

ii. Stable Isotope Analyses

Hydrogen occurs as three isotopes: $^1$H, $^2$H (deuterium), and $^3$H (tritium), however tritium is unstable and decays through beta decay and is thus not discussed further (Gat and Gonfiantini 1981). The most abundant hydrogen isotope, $^1$H, will be further designated as H and $^2$H, deuterium, will be referenced as D. Oxygen occurs as $^{16}$O, $^{17}$O, and $^{18}$O. Although there are various possible isotopic water species, only three main isotopic combinations - $H_2^{16}$O, $H_2^{18}$O, and HD$^{16}$O - are easily detectable in nature (Gat and Gonfiantini 1981; Rozanski et al. 2001). The abundance ratios of the isotopic pairs $^{18}$O/$^{16}$O and D/H will be considered in this investigation. The difference in the ratio of the heavy isotope to the light isotope of a water sample relative to a reference ratio is expressed as a delta (δ) value. The abundance ratios are referred to the internationally accepted water isotopic ratio standard, the Vienna Standard Mean Ocean Water, V-SMOW (Rozanski et al. 2001). This means that delta values, in per mil, are defined as the relative isotopic deviation.
of the sample from the standard as:

\[
\delta_{S/R} = \left( \frac{R_{\text{Sample}}}{R_{\text{Reference}}} - 1 \right) 1000
\]

where \(R_{\text{Sample}}\) is the isotopic ratio (\(^{18}\text{O} /^{16}\text{O}\) or \(\text{D/H}\)) in the sample and \(R_{\text{Reference}}\) the ratio in the standard, V-SMOW (Rozanski et al. 2001). Positive \(\delta\) values indicate that the sample is enriched in the heavy isotope species and negative values correspond to samples depleted in the heavy isotope, all relative to V-SMOW.

Stable isotope (\(\delta\text{D}\) and \(\delta^{18}\text{O}\)) compositions can be used as indicators to trace water flow through the hydrologic cycle and allow for the identification of evaporation processes and water sources (Kendall and McDonnell 1998). Evaporation and condensation processes define isotopic fractionation ratios between liquid and vapor phases (Rayleigh 1986) and establish the global meteoric water line (GMWL), \(\delta\text{D} = 8 \delta^{18}\text{O} + 10\%_0\) (Kendall and McDonnell 1998; Rozanski et al. 2001). The GMWL is used as a reference for processes influencing isotopic compositions in surface waters. Processes that don’t occur under equilibrium precipitation conditions will have differing isotopic fractionations traced through enriched or depleted isotopic ratios (Rayleigh 1986). Due to regional environmental differences, the relationships between water isotopes vary from the GMWL to form Local Meteoric Water Lines (LMWL), these regional lines have slightly different slopes than the GMWL and characterize isotopic compositions at the local scale (Kendall and McDonnell 1998; Rozanski et al. 2001). For the purpose of this project,
the Rocky Mountain Meteoric Water Line ($\delta D = 8.1 \delta^{18}O + 14.8\%$) is used as the LMWL (Dávila-Olmo 2011).

Phase transformations fractionate the isotopic components of water molecules and produce variations in the D and $^{18}O$ isotopic compositions of bodies of water (Singh and Kumar 2005). Due to these fractionation processes, mass differences allow the lighter isotopes, H and $^{16}O$, to evaporate faster than the heavier species, D and $^{18}O$ (Kendall and McDonnell 1998; Mazor 2004). Enrichment via evaporation is distinguished by ‘evaporation lines’ which have a lower slope than the meteoric water line (Gat and Gonfiantini 1981). Thus, evaporation processes favorably transform lighter isotopic species to the vapor phase, leaving the heavy species concentrated in the liquid phase. The residual volume of water is progressively enriched in the heavier isotopic species as evaporation progresses (Mazor 2004). This principle of differential isotopic fractionation will be applied in order to determine the major process involved in gnamma water loss.

III. METHODS

i. Hydrology Model – Derivation of Isotope Mass Balance

The interpretational framework for this project is a model derived from the conceptual evaporation model first presented by Craig and Gordon (1965) and further expanded by Benson and White (1994) and Gibson (2002). These previous studies investigated the influence of evaporation on variations of hydrogen and oxygen isotopic abundances in lakes. Equations from these studies attempted to model isotope mass balance in non-steady-state water balance scenarios. Balance
equations of the isotopic tracers $^{18}$O and D provide independent hydrological information that can be applied to estimate evaporation and other water balance parameters (Gibson 2002). The models are volume dependent as isotopic composition evolves in response to volume reduction. I applied these models to the gnamma systems in order to determine the hydrological processes involved in gnamma water loss. The models were applied under the assumption that gnamma hydrological processes are analogous to closed-basin lakes. The isotopic composition of a lake is given by

$$\frac{\delta (\delta V)}{\delta t} = (P\delta_p - E\delta_e)A + S_i\delta S_i - S_o\delta S_o + G_i\delta G_i - Q_0\delta Q_0$$  \hspace{1cm} (1)

Equation 1. Isotopic balance of a lake from Benson and White (1994).

where $t$ is time, $V$ is lake volume, $\delta$ represents either $\delta$D or $\delta$18O, $P$ is precipitation on the lake, $\delta_p$ is the isotopic composition of the precipitation, $E$ is the lake evaporation, $\delta_e$ is the isotopic composition of the evaporated water, $A$ is the surface area of the lake, $S_i$ is the surface water discharge to the lake, $\delta S_i$ is the isotopic composition of the surface water discharge to the lake, $\delta S_o$ is the isotopic composition of the surface water outflow, $S_o$ is surface water outflow, $\delta G_i$ is the isotopic composition of the surface water outflow, $G_i$ is the groundwater discharge to the lake, $\delta G_i$ is the isotopic composition of the groundwater discharge, $Q_0$ is groundwater outflow, and $\delta Q_0$ is the isotopic composition of the groundwater outflow (Benson and White, 1994). Like for closed-basin lakes, this equation was simplified for gnamma systems to only include evaporation and groundwater
outflow parameters giving

\[ \frac{\partial(\delta v)}{\partial t} = E\delta_e - Q\delta Q \] (2)

Equation 2. Gnamma/lake isotopic balance derived from equation (1)

I converted this equation from measured delta values to isotopic ratios. The isotopic ratios, indicated by \( R \), are defined as the heavy species relative to the light species. Converting equation (2) to be in terms of isotopic ratios gives

\[ \frac{\partial R_L v_L}{\partial t} = E R_e - Q R_q \] (3)

Equation 2. Gnamma/lake isotopic balance in terms of isotopic ratios or flux

where \( R_L \) is the isotopic ratio of the gnamma or lake, \( V_L \) is the volume of the lake, \( E \) is lake evaporation, \( R_e \) is the isotopic ratio of evaporated water, \( Q \) is groundwater outflow, and \( R_q \) is the isotopic ratio of outflow water. Since no fractionation occurs during outflow, seepage of water out of gnamma through the rock substrate, the isotopic ratio of the outflow water will be equal to that of the lake; \( R_q = R_L \). Also noting that \( \frac{\partial V}{\partial t} = -E - Q \), the following equation can be derived

\[ V \frac{\partial R_L}{\partial t} = -E(R_e - R_L) \] (4)

Defining the lake evaporation isotopic fractionation factor, \( \alpha_{e,L} \) as,

\[ \alpha_{e,L} = \frac{R_e}{R_L} \Rightarrow R_e = \alpha_{e,L} R_L \]

and substituting into equation (4), the normalized lake isotopic ratio can be defined after integration as a function of the fraction of water remaining, \( f \), in the gnamma

\[ \frac{R}{R_L} = f(\alpha_{e,L}^{-1})(\frac{E}{E+Q}) \] (5)
Equation (5) was applied to the gnamma systems to track changes in isotopic composition over time and as a function of the volume of water remaining in the gnamma. When the isotopic ratios were plotted versus the ln(f) the processes of water loss could be visualized for each experimental gnamma as the slope is equal to \((\alpha_{e,L} - 1) \left( \frac{E}{E+Q} \right)\).

![Figure 1](image)

Figure 1. Model of δD as a function of the natural log of f, the fraction of water left in the gnamma, applying my water balance model where \(\bar{K}_w = f^{(\alpha_{e,L} - 1)}(\frac{E}{E+Q})\). The upper solid line is a pure evaporation \([E/(E+Q) = 1]\) reference line and the lower solid line is the reference model for pure seepage processes \([E/(E+Q) = 0]\). The dashed lines represent models for varying levels of evaporation and seepage processes. The \(\alpha_{e,L}\) was set to 0.94 based on the control experiments conducted.

For this model it is assumed that no isotopic fractionation occurs during water loss via seepage through the rock. As a result, pure seepage processes would produce a flat slope on a plot like figure 1. Pure evaporation would produce a maximum slope controlled by the fractionation factor of the system (Figure 1). If water is lost through a combination of evaporation and seepage the slope will fall...
somewhere between the bounds of the two pure processes (Figure 1). This model was used to interpret the measured isotopic data to determine the processes controlling water loss in gnmmas.

ii. Locality

The field site was located on private property three miles Northwest of Lyons, Colorado (40°16′ N 105°18′ W) in the foothills of the Rocky Mountains at approximately 1,637 meters (5,371 feet) above sea level. The study site consisted of large, homogenous slabs of the Silver Plume granite surrounded by a Ponderosa Pine forest (Punongbayan 1989). This site is typical for granite gnmmas in the Colorado Rocky Mountains and was chosen due to its accessibility and homogeneous substrate.

Figure 2. Ariel view of study site, three miles Northwest of Lyons, Colorado, 40°13′26″ N 105°16′8″ W (image courtesy of Rachel Glade and Robert Anderson).
iii. **Hydrology Protocol**

To investigate the hydrology of gnamma systems, water samples were taken over the course of multiple days to determine water stable isotope trends as a function of time and fraction of water left in the gnamma, \( f \). Two experiments were conducted. The first was a survey of ten natural gnammas, the second surveyed the same ten natural gnammas in addition to four controls for pure evaporation processes.

For both surveys, ten experimental gnammas were selected and labeled ‘A’ through ‘J’. All gnammas were chosen to fulfill the following criteria: undisturbed, unobstructed, and isolated (not connected to other gnammas). The physical characteristics (e.g. dimensions, shape/geometry, depth) of each gnamma were recorded. 20 liters of local well water were collected to fill the gnammas with and stored in an airtight carboy. Any water already present in the gnammas was removed with a syringe. Based on size, each gnamma was filled with between 100 mL to 2000 mL of water such that the entire floor of the gnamma was submerged in water at least a few centimeters deep. A Thermochron iButton was placed in the bottom of each gnamma to record temperature at five-minute intervals. In the larger potholes, two iButtons were placed to compare any differences in temperature within the system. The time and initial volume of added water was recorded for each gnamma. After filling, an initial sample of two milliliters was taken for each gnamma and kept in an airtight vial wrapped with parafilm to ensure no change in isotopic composition from the time of collection would occur due to evaporation.
Figure 3. Left: Ariel view of gnmmas A-E (image courtesy of Rachel Glade and Robert Anderson). Right: Control gmma M.

Sampling was continued periodically for four days. When water levels were very low, final volume and time measurements were taken. Using a syringe, the entirety of the water left in the gmma (including any rocks and sediment if necessary) was collected. The collected water was filtered through filter paper and collected in a graduated cylinder to measure total final volume. The final aliquot for isotope analysis was collected from the total final volume sample.

For the controlled experiment, the same protocol was followed as stated above but in addition to the ten experimental gnmmas, four control gnmmas, labeled ‘K’ through ‘N’, were assayed. The positive control gnmmas had their water loss constrained to a purely evaporative process. This was accomplished through isolating the gmma from the substrate rock with a water impermeable layer so that no water could be lost due to percolation through the mineral. A 4 mm thick, transparent polyethylene plastic tarp was used to cover the surface of each control gmma with generous edges to be secured around the perimeter (Figure 3, right).
Once secured, the control gnammas were filled in the same manner as the experimental sites and initial samples were taken.

All collected samples were filtered and then analyzed for \( \delta^D \) and \( \delta^{18}O \) values with a Piccaro Isotopic Water Analyzer by the Institute of Arctic and Alpine Research Stable Isotope Laboratory at the University of Colorado, Boulder (see appendix for raw data).

IV. RESULTS

The oxygen and hydrogen isotope results are reported in per mil (‰) relative to V-SMOW (Vienna Standard Mean Ocean Water). The Rocky Mountain Meteoric Water Line (Dávila-Olmo 2011) was used as the Local Meteoric Water Line (LMWL). \( \delta^D \) values versus \( \delta^{18}O \) values from both the natural and controlled experiments were plotted along with the LMWL (Figure 4). Data from both experiments deviate from the LMWL (Figure 4). The deviation corresponds to an evaporation trend where the remaining gnamma water is progressively enriched in heavier isotopes.
Figure 4. δD vs. δ¹⁸O for experimental data, plotted with the local meteoric water line (LMWL), δD = 8.1 δ¹⁸O + 14.8‰ (Dávila-Olmo 2011). The “Experiment with controls” data series represents the November experiment with natural and control gamma and the “Experiment without controls” data series represents the August experimental data from only natural gamma sampling.
Figure 5. $\delta D$ as a function of the natural log of $f$, the fraction of water left in the gnamma, applying my water balance model where $\bar{R}_L = f^{(\alpha_{e,L^{-1}})}(\frac{E}{E+Q})$. The points show the $\delta D$ values and measured water volumes from the various gnammas sampled in the controlled experiment. The orange points represent the pure evaporation control data and the blue points the experimental/natural gnammas. The upper solid line is a pure evaporation $[E/(E+Q) = 1]$ reference line based on the pattern of the control gnammas. The lower solid line is the reference model for pure seepage processes, $E/(E+Q) = 0$. The dashed lines represent models for varying levels of evaporation and seepage processes with the $\alpha_{e,L}$ set to 0.94.
Figure 5 depicts the data from the controlled experiment with $\delta D$ plotted as a function of the natural log of $f$, the fraction of water left in the gamma. Only the data from the controlled experiment are plotted. The orange points are the pure evaporation controls and the blue points are the natural gammas. The upper solid line is the reference model for pure evaporation processes where $E/(E+Q) = 1$. The lower solid line is the reference model for pure seepage processes, $E/(E+Q) = 0$. By applying the gamma water balance model to the control gammas, the average fractionation factor, $\alpha_{e,L}$, was determined as 0.94. This fractionation factor was then used for the subsequent reference models. The dashed lines represent model lines for trends with varying proportions of evaporation and seepage processes, with $E/(E+Q)$ values from 0.08 to 1. The natural gammas all fall between the reference lines of 0.08 and 0.30. Evaporation played a more substantial role in the water loss of smaller gammas, whereas larger gammas were controlled by seepage processes.

V. DISCUSSION

i. Hydrology Model

The deviation of both the experiments from the LMWL suggests that some process is controlling the change in isotopic fractionation (Figure 4). All data for both experiments fall below the LMWL indicating an enrichment pattern that corresponds to evaporation processes. When evaporation occurs in surface waters, lighter isotopes preferentially form into the vapor phase and leave the remaining water enriched in heavy isotopes, D and $^{18}$O (Mazor 2004). Enrichment trends correspond to evaporation.
The parallel evaporative trends indicate that analogous evaporation processes are acting in the gnamma systems, and thus the experiment without controls can be interpreted in the context of the controlled experiment (Figure 4). Rain has differing starting isotopic compositions, but in each rain event, water is affected by the same processes. Multiple rain events during the sampling period for the experiment without controls contribute to the scatter of the dataset. Rain has inherent isotopic variability which shifts the data and results in a broader range. The trends of both data sets support prior assumptions that evaporation is a contributing factor to gnamma water loss. However, the role of seepage processes must still be explored.

Through my derivation of Benson and White’s (1994) hydrology model, the change over time of gnamma isotopic compositions could be explored. My model assumes that no isotopic fractionation occurs during water loss via seepage through the rock. Theoretically pure seepage processes will produce a flat slope and pure evaporation will produce a maximum slope controlled by the fractionation factor of the system. If water is lost through a combination of the two processes, the slope will fall somewhere between the bounds of the two pure processes. The fractionation factor of the system was determined by the trends of the control gnammas which were considered the upper limit for pure evaporation processes. This fractionation factor was then applied to other proportions of evaporation and seepage to constrain the processes occurring in the natural gnammas. As shown in Figure 5, there is a clear difference between pure evaporative controls (orange points) and all experimental gnammas (blue points), this indicates that some other
process, besides evaporation, is responsible for water loss. The control gnammas are clustered and exhibit comparable trends, while the natural gnammas exhibit more variation but similar overall trends compared to the controls (Figure 5). The experimental gnammas appear to lose the majority of their water via seepage through the mineral substrate, with only 8 – 30% of water loss attributable to evaporation (Figure 5). Additionally, the experimental gnammas provided evidence of the natural variability present in gamma hydrology.

ii. Conceptual Model of Gamma Development

After the formation of the initial depression, by lichen bioweathering or other weathering processes, gnammas are further weathered by water and wind (Twidale and Corbin 1963). Stages of gmma development roughly correspond to size; young pothole stages are relatively small and shallow and more developed stages are deeper and larger (Chan et al. 2005). Small gnammas, in early stages of development, likely have higher evaporation to seepage ratios than larger gnammas. The following model predicts that evaporation plays a more substantial role in younger gnammas with seepage processes greatly dominating the water balance of larger gnammas.
Figure 6. Conceptual model of gnamma development over time with upwards arrows indicating evaporative processes (E) and downwards arrows indicating seepage (Q) through the fractures (curved lines) in the mineral substrate. Time progresses from the top of the diagram, $t_{\text{initial}}$, to the bottom, $t_{\text{final}}$. Initially, when the gnamma is small and undeveloped, water loss is dominated by evaporation. As water evaporates, dissolved solute concentrations increase in the remaining water and contribute to salt weathering. Salt weathering accelerates dissolution of the rock surface and leads to enhanced permeability, indicated by the curved lines in the floor of the gnammas. As time proceeds, the rock becomes increasingly more permeable and water can leave the system via seepage. Gnamma size increases due to weathering and as the gnamma becomes more developed more water is lost through seepage. Seepage surpasses evaporation and becomes the major process of water loss in gnammas of late developmental stages.
Evaporation of water molecules results in increased solute concentrations in the remaining gnamma water. Higher solute concentrations can accelerate mineral dissolution, which in turn leads to enhanced permeability of rock surfaces. These connections led to the generation of my conceptual model of gnamma development which relates gnamma size, and state of development, to water loss processes (Figure 6). Early potholes are small and loose water predominantly through evaporation processes (E>Q). As water evaporates, the system becomes increasingly more saline. The increased concentration of solutes over time, along with freeze thaw processes, contributes to enhanced permeability of the mineral surface and the formation of fractures in the mineral base of the gnamma. Water can now be discharged from the gnamma through the mineral substrate via seepage processes. As the gnamma is further weathered and grows in size, the system enters a stage where water loss through evaporation is approximately equal to that of seepage (E ≈ Q). Fractures propagate, and mineral dissolution further enhances the permeability of the floor of the gnamma. As time proceeds, the gnamma eventually develops to a point where seepage processes are the predominate means of water loss (E<Q). These gnammas no longer accumulate solutes in such high concentrations since seepage exceeds evaporation and solutes can exit the system.

The model presented in Figure 6 emphasizes the relationship between the state of gnamma development and the hydrology of the system. In small gnammas salinity is a large factor, and potential constraint, on the biology of the system since water is predominantly lost through evaporation. However, in large gnammas salinity is not a strong selective force because most water is lost through seepage.
and thus solute concentrations don’t progressively increase as water is lost. Large gnmmas are more controlled by aridity than salinity. Broadly, environmental change differs across gnamma size classes due to their differential hydrology. Thus, the state of gnamma development controls the factors that are the main selective pressures on the biology of the systems.

This model presents predictable relationships between gnamma development and the environmental change imposed on pothole ecosystems. Applications of this model to future studies of gnamma biology could alleviate potential confounding of size effects and salinity, by accounting for differential processes of water loss. By understanding the parallel between gnamma size and environmental change, the controls of gnamma systems are more constrained. Gnammas can be used as model systems which will allow other biogeochemical relationships and theories to be more accurately investigated.

**iii. Limitations and Future Applications**

The gnamma model system could be applied to investigate the potential biogeochemical feedbacks between gnamma formation and characteristics, and lichen colonization. Lichen-mineral interactions are known to play a role in the initial development of gnammas due to the biological weathering capabilities of lichen (Twidale and Corbin 1963). However, comprehensive studies on the continued role of lichens in gnamma systems are lacking. The lichen-gnamma interface provides an ideal environment to study biological weathering due to substantial chemical and physical activity. Despite lichen-dominated vegetation composing around 8% of the terrestrial surface of the Earth (Larson 1987), lichen-
mineral interactions are relatively understudied. Lichen-mineral associations have the potential to cause geochemical change, which can in turn largely influence global biogeochemical cycles through biotic amplification of weathering rates (Taylor et al. 2009; Porada et al. 2014). The gnamma model system could be applied to explore the lichen-mineral interface and potential relationships between lichen community composition and gnamma distribution. Two hypotheses could be considered, (1) larger gnammas are more susceptible to lichen colonization and lichen mediated mineral weathering reactions because they have longer lived rock-water-lichen interfaces than smaller gnammas and (2) smaller gnammas are more susceptible to lichen colonization and lichen mediated mineral weathering reactions because they experience greater evaporation and higher concentrations of secondary metabolites. Gnammas would be used as a model system to test these hypotheses under controlled environmental conditions in the field.

The gnamma model could also be applicable to studies of island, or insular, biogeography, the power law that relates species richness and area size through the study of isolated natural communities. Recent studies have investigated this species-area relationship for microbes with differing results (Bell et al. 2005). This discordance indicates that the current understanding of natural microbial community dynamics must be reevaluated (Bell et al. 2005). Gnamma model systems would provide the ideal conditions for further study of microbial populations in the natural environment and how they fit into the species-area law.

Chan et al. (2005) proposed that microbial mats may aid in maintaining water in potholes by sealing the mineral grains. Their studied pothole systems were
in sandstone and they found that the mats may slow the percolation of water through the porous sandstone matrix. The role of microbial mats in granite pothole systems should be further investigated, especially since the sealing ability of microbial mats contrasts the bioweathering role of microbes in accelerating weathering reactions that contribute to gnamma development.

In future studies, the hydrology of gnamma systems should be compared across differing climates (i.e. arid versus semi-arid, and desert versus montane environments) and various mineral substrates (i.e. sandstone and other granites). The seasonality of gnamma hydrology should also be investigated; does the ratio of evaporation to seepage have seasonal variation?

Overall, the controls of gnamma systems have been relatively well constrained and can be applied to various biogeochemical processes. Gnamma model systems will aid in further understanding ecological and evolutionary processes in ephemeral rock pools and the selective pressures exerted on the biota in these systems. Gnamma systems provide a valuable, controllable framework for investigating environmental processes in vivo.
VI. REFERENCES


Tavernini S, Mura G, Rossetti G. 2005. Factors Influencing the Seasonal Phenology and Composition of Zooplankton Communities in Mountain Temporary


VII. APPENDICIES

i. Derivation of Isotope Mass Balance

\[ R_e = \alpha_{\text{kin}} \left[ \frac{R_L - RHR_v}{\alpha_{\text{eq}} - RH} \right] \]

Equation 1. Evaporative flux equation from Benson and White (1994) where:

- \( R \) = ratio of heavy/light isotopes
- \( RH \) = relative humidity, how far from equilib (0-1)
- \( R_e \) = evaporative flux
- \( \alpha_{\text{kin}} \) = alpha kinetic, light isotopes move faster and diffuse

\[ \frac{\partial R_L V}{\partial t} = E R_e - Q R_q \]

E= evaporative flux  \( E = \frac{\text{mol} 18O}{\text{mol} 16O} \frac{L^3}{t} \)
Q= outflow flux

\[ R_L \frac{\partial V}{\partial t} + V \frac{\partial R_L}{\partial t} = E R_e - Q R_d \]

Note that: \( R_q = R_L \) and \( \frac{\partial V}{\partial t} = -E - Q \)

\[ R_L (-E - Q) + V \frac{\partial R_L}{\partial t} = -E R_e - Q R_L \]

\[ V \frac{\partial R_L}{\partial t} = -E(R_e - R_L) \]

\( V(t) \) changes over time due to evaporation

\[ \frac{\partial V}{\partial t} = -E - Q \]

\( V(t) = \int -(E + Q) t = -(E + Q) t + C \)
$V_0 = C$ thus substitute $V(t) = V_0 - (E + Q) t$ for $V(t)$ from above to account for volume as a function of time

$$[V_0 - (E + Q) t] \frac{\partial R_L}{\partial t} = -E(R_e - R_L)$$

$\alpha_{e,L} = \text{fractionation factor}$

$$\alpha_{e,L} = \frac{R_e}{R_L} \therefore R_e = \alpha_{e,L} R_L$$

$$[V_0 - (E + Q) t] \frac{\partial R_L}{\partial t} = -E(\alpha_{e,L} - 1)R_L$$

Integration:

$$\frac{\partial R_L}{-E(\alpha_{e,L} - 1)R_L} = \frac{\partial t}{[V_0 - (E + Q) t]}$$

$$\int \frac{1}{-E(\alpha_{e,L} - 1) R_L} \, \frac{\partial R_L}{\partial R_L} = \int \frac{1}{-E(\alpha_{e,L} - 1) \ln R_L} \, \ln |V_0 - (E + Q) t|$$

Thus,

$$\frac{1}{-E(\alpha_{e,L} - 1) \ln R_L} = \frac{1}{-E(\alpha_{e,L} - 1) \ln |V_0 - (E + Q) t|} + C$$

$$\ln \left( R_L^{-E(\alpha_{e,L} - 1)} \right) = \ln |V_0 - (E + Q) t|^{-1} - (E + Q) + C$$

$$R_L^{-E(\alpha_{e,L} - 1)} = |V_0 - (E + Q) t|^{-1} - (E + Q) * C$$

Note: $\frac{V_0 - (E + Q) t}{V_0} = f \therefore f = 1 - \frac{(E + Q) t}{V_0}$

$$\left[ R_L^{-E(\alpha_{e,L} - 1)} \right]^{-E(\alpha_{e,L} - 1)} = \left[ f^{-\alpha_{e,L} - 1} \right]^{-E(\alpha_{e,L} - 1)}$$
Normalized lake isotope ratio:

$$R_L = f \frac{-E(a_{e,L}-1)}{-E+Q} \ast C$$

Note: $R_L(f = 1) = C$

$$R_L(f) = R_L(f = 1)f^{\frac{-E(a_{e,L}-1)}{-E+Q}}$$

$$R_L(f) = R_L(f = 1)f^{(a_{e,L}-1)(\frac{E}{E+Q})}$$

$$R_L > R_e \therefore \alpha > 1$$

Relative isotopic change:

$$\delta_L = \left( \frac{R_L(f)}{R_L(f = 1)} - 1 \right) \times 1000$$

Gamma isotopic ratio as a function of the fraction of water remaining ($f$):

$$\overline{R_L} = f^{(a_{e,L}-1)(\frac{E}{E+Q})}$$

Note: slope of line when graphed = $(a_{e,L} - 1)(\frac{E}{E+Q})$

Can convert between fraction of water remaining and time:

$$f = \frac{V_0 - (E + Q)t}{V_0} \therefore t = \frac{V_0(f - 1)}{-(E + Q)}$$
### ii. Raw Data

Table 1. Collection dates, times, and water volumes for samples from August 10 – 14, 2018.

<table>
<thead>
<tr>
<th>Site</th>
<th>Initial Volume (mL):</th>
<th>Initial Date/Time:</th>
<th>Sample 1 D/T:</th>
<th>Sample 2 D/T:</th>
<th>Sample 3 D/T:</th>
<th>Sample 4 D/T:</th>
<th>Sample 5 D/T:</th>
<th>Sample 6 D/T:</th>
<th>Sample 7 D/T:</th>
<th>Sample 8 D/T:</th>
<th>Final Volume (mL):</th>
<th>Final Date/Time:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30</td>
<td>8/10/17 11:10</td>
<td>8/10/17 13:23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>8/10/17 12:05</td>
<td>8/11/17 9:18</td>
<td>8/11/17 18:19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>250</td>
<td>8/10/17 12:41</td>
<td>8/11/17 8:45</td>
<td>8/11/17 18:28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>150</td>
<td>8/10/17 12:55</td>
<td>8/11/17 8:52</td>
<td>8/11/17 18:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Collection dates, times, and water volumes for samples from November 23 – 26, 2018.

<table>
<thead>
<tr>
<th>Site</th>
<th>Initial Volume (mL)</th>
<th>Initial Date/Time</th>
<th>Sample 1 D/T:</th>
<th>Sample 2 D/T:</th>
<th>Final Volume (mL)</th>
<th>Final Date/Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>250</td>
<td>11/23/17 12:19</td>
<td></td>
<td></td>
<td>0</td>
<td>11/24/17 11:00</td>
</tr>
<tr>
<td>H</td>
<td>150</td>
<td>11/23/17 12:28</td>
<td></td>
<td></td>
<td>0</td>
<td>11/24/2017 time uncertain</td>
</tr>
<tr>
<td>J</td>
<td>200</td>
<td>11/23/17 12:34</td>
<td>11/24/17 11:06</td>
<td></td>
<td>0</td>
<td>11/24/17 14:00</td>
</tr>
</tbody>
</table>
Table 3. δ¹⁸O and δD values in per mil (‰) relative to V-SMOW (Vienna Standard Mean Ocean Water) for samples from August 10 – 14, 2018.

<table>
<thead>
<tr>
<th>Gnamma Sample:</th>
<th>δ¹⁸O (‰)</th>
<th>δD (‰)</th>
<th>Gnamma Sample:</th>
<th>δ¹⁸O (‰)</th>
<th>δD (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Initial</td>
<td>-4.31</td>
<td>-40.18</td>
<td>G1</td>
<td>-7.38</td>
<td>-50.10</td>
</tr>
<tr>
<td>A#2 Initial</td>
<td>-4.13</td>
<td>-41.13</td>
<td>G2</td>
<td>-2.68</td>
<td>-31.69</td>
</tr>
<tr>
<td>A#2 1</td>
<td>-5.88</td>
<td>-44.12</td>
<td>G3</td>
<td>-1.16</td>
<td>-23.80</td>
</tr>
<tr>
<td>B Initial</td>
<td>5.38</td>
<td>-18.61</td>
<td>G4</td>
<td>0.79</td>
<td>-14.90</td>
</tr>
<tr>
<td>B1</td>
<td>-0.88</td>
<td>-32.69</td>
<td>G5</td>
<td>2.36</td>
<td>-6.07</td>
</tr>
<tr>
<td>B2</td>
<td>-4.30</td>
<td>-37.31</td>
<td>G6</td>
<td>-2.80</td>
<td>-27.70</td>
</tr>
<tr>
<td>B3</td>
<td>-2.06</td>
<td>-27.75</td>
<td>G7</td>
<td>-2.55</td>
<td>-24.32</td>
</tr>
<tr>
<td>B4</td>
<td>-1.13</td>
<td>-24.01</td>
<td>G8</td>
<td>0.98</td>
<td>-8.31</td>
</tr>
<tr>
<td>B5</td>
<td>2.11</td>
<td>-6.94</td>
<td>H Initial</td>
<td>-3.44</td>
<td>-38.13</td>
</tr>
<tr>
<td>B6</td>
<td>-2.80</td>
<td>-26.33</td>
<td>H1</td>
<td>-7.41</td>
<td>-49.78</td>
</tr>
<tr>
<td>B7</td>
<td>-2.22</td>
<td>-22.79</td>
<td>I Initial</td>
<td>-3.60</td>
<td>-37.72</td>
</tr>
<tr>
<td>B8</td>
<td>1.15</td>
<td>-7.54</td>
<td>I1</td>
<td>-6.60</td>
<td>-46.51</td>
</tr>
<tr>
<td>C Initial</td>
<td>-5.01</td>
<td>-44.34</td>
<td>I2</td>
<td>-2.05</td>
<td>-28.63</td>
</tr>
<tr>
<td>C1</td>
<td>-7.26</td>
<td>-49.93</td>
<td>I3</td>
<td>-0.71</td>
<td>-21.88</td>
</tr>
<tr>
<td>C2</td>
<td>-4.30</td>
<td>-38.72</td>
<td>I4</td>
<td>1.61</td>
<td>-12.73</td>
</tr>
<tr>
<td>C3</td>
<td>-3.14</td>
<td>-32.61</td>
<td>I5</td>
<td>17.43</td>
<td>32.74</td>
</tr>
<tr>
<td>C4</td>
<td>-2.02</td>
<td>-28.60</td>
<td>I6</td>
<td>-2.74</td>
<td>-27.08</td>
</tr>
<tr>
<td>C5</td>
<td>1.03</td>
<td>-13.86</td>
<td>I7</td>
<td>-1.17</td>
<td>-17.91</td>
</tr>
<tr>
<td>C6</td>
<td>-1.16</td>
<td>-21.39</td>
<td>I8</td>
<td>5.19</td>
<td>13.80</td>
</tr>
<tr>
<td>C7</td>
<td>-1.08</td>
<td>-20.25</td>
<td>J Initial</td>
<td>-3.68</td>
<td>-36.86</td>
</tr>
<tr>
<td>C8</td>
<td>1.10</td>
<td>-9.79</td>
<td>J1</td>
<td>-7.67</td>
<td>-51.04</td>
</tr>
<tr>
<td>D Initial</td>
<td>-3.37</td>
<td>-35.52</td>
<td>J2</td>
<td>-0.91</td>
<td>-23.74</td>
</tr>
<tr>
<td>D1</td>
<td>-6.82</td>
<td>-48.26</td>
<td>Hail 1</td>
<td>-11.12</td>
<td>-67.78</td>
</tr>
<tr>
<td>E Initial</td>
<td>-4.36</td>
<td>-41.17</td>
<td>Rain 1</td>
<td>-9.38</td>
<td>-56.70</td>
</tr>
<tr>
<td>E1</td>
<td>-6.40</td>
<td>-45.50</td>
<td>Rain 2</td>
<td>-6.35</td>
<td>-37.62</td>
</tr>
<tr>
<td>F Initial</td>
<td>-2.33</td>
<td>-30.20</td>
<td>Rain 3a</td>
<td>-8.35</td>
<td>-49.89</td>
</tr>
<tr>
<td>F1</td>
<td>-7.17</td>
<td>-48.37</td>
<td>Rain 3b</td>
<td>-8.23</td>
<td>-49.87</td>
</tr>
<tr>
<td>G Initial</td>
<td>-4.13</td>
<td>-38.23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4. $\delta^{18}$O and $\delta$D values in per mil (‰) relative to V-SMOW (Vienna Standard Mean Ocean Water) for samples from November 23 – 26, 2018.

<table>
<thead>
<tr>
<th>Gnamma Sample</th>
<th>$\delta^{18}$O (‰)</th>
<th>$\delta$D (‰)</th>
<th>Gnamma Sample</th>
<th>$\delta^{18}$O (‰)</th>
<th>$\delta$D (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Initial</td>
<td>-13.09</td>
<td>-95.84</td>
<td>K Initial</td>
<td>-13.47</td>
<td>-96.87</td>
</tr>
<tr>
<td>A1</td>
<td>-2.52</td>
<td>-56.25</td>
<td>K1</td>
<td>-7.95</td>
<td>-77.36</td>
</tr>
<tr>
<td>B Initial</td>
<td>-13.11</td>
<td>-96.13</td>
<td>K2</td>
<td>-6.05</td>
<td>-69.20</td>
</tr>
<tr>
<td>B1</td>
<td>-5.41</td>
<td>-67.55</td>
<td>K3a</td>
<td>-4.04</td>
<td>-61.17</td>
</tr>
<tr>
<td>B2</td>
<td>-1.45</td>
<td>-53.09</td>
<td>K3b</td>
<td>-4.26</td>
<td>-61.15</td>
</tr>
<tr>
<td>C Initial</td>
<td>-12.31</td>
<td>-93.17</td>
<td>L Initial</td>
<td>-13.02</td>
<td>-95.27</td>
</tr>
<tr>
<td>C1</td>
<td>-4.67</td>
<td>-63.56</td>
<td>L1</td>
<td>-7.65</td>
<td>-76.58</td>
</tr>
<tr>
<td>C2</td>
<td>-1.39</td>
<td>-51.20</td>
<td>L2</td>
<td>-6.04</td>
<td>-70.54</td>
</tr>
<tr>
<td>D Initial</td>
<td>-13.18</td>
<td>-96.07</td>
<td>L3a</td>
<td>-4.09</td>
<td>-62.16</td>
</tr>
<tr>
<td>E Initial</td>
<td>-13.10</td>
<td>-95.48</td>
<td>L3b</td>
<td>-4.11</td>
<td>-62.11</td>
</tr>
<tr>
<td>E1</td>
<td>-0.97</td>
<td>-51.68</td>
<td>M Initial</td>
<td>-13.13</td>
<td>-95.99</td>
</tr>
<tr>
<td>F Initial</td>
<td>-12.99</td>
<td>-95.19</td>
<td>M1</td>
<td>-4.21</td>
<td>-65.52</td>
</tr>
<tr>
<td>G Initial</td>
<td>-13.30</td>
<td>-96.83</td>
<td>M2</td>
<td>-1.11</td>
<td>-52.88</td>
</tr>
<tr>
<td>G1</td>
<td>-5.48</td>
<td>-67.57</td>
<td>M3a</td>
<td>0.10</td>
<td>-46.12</td>
</tr>
<tr>
<td>H Initial</td>
<td>-13.04</td>
<td>-94.80</td>
<td>M3b</td>
<td>0.61</td>
<td>-44.05</td>
</tr>
<tr>
<td>I Initial</td>
<td>-13.13</td>
<td>-95.87</td>
<td>N Initial</td>
<td>-13.00</td>
<td>-95.37</td>
</tr>
<tr>
<td>I1</td>
<td>-5.41</td>
<td>-66.79</td>
<td>N1</td>
<td>-8.14</td>
<td>-79.05</td>
</tr>
<tr>
<td>I2</td>
<td>-0.92</td>
<td>-48.74</td>
<td>N2</td>
<td>-6.29</td>
<td>-71.85</td>
</tr>
<tr>
<td>J Initial</td>
<td>-13.08</td>
<td>-95.29</td>
<td>N3a</td>
<td>-4.70</td>
<td>-64.93</td>
</tr>
<tr>
<td>J1</td>
<td>-5.91</td>
<td>-69.04</td>
<td>N3b</td>
<td>-4.70</td>
<td>-64.56</td>
</tr>
</tbody>
</table>
iii. Gnamma Photos

Gnamma A:  

Gnamma B:  

Gnamma C:  

Gnamma D:  

Gnamma E:  

Gnamma F: