2012-2013 PROJECTS

TECTONIC EVOLUTION OF THE CHUGACH-PRINCE WILLIAM TERRANE: SHUMAGIN ISLANDS AND KENAI PENINSULA, ALASKA
Faculty: JOHN GARVER, Union College, CAMERON DAVIDSON, Carleton College
Students: MICHAEL DELUCA, Union College, NICOLAS ROBERTS, Carleton College, ROSE PETTIETTE, Washington & Lee University, ALEXANDER SHORT, University of Minnesota-Morris, CARLY ROE, Lawrence University.

LAVAS AND INTERBEDS OF THE POWDER RIVER VOLCANIC FIELD, NORTHEASTERN OREGON
Faculty: NICHOLAS BADER & KIRSTEN NICOLAYSEN, Whitman College.
Students: REBECCA RODD, University of California-Davis, RICARDO LOPEZ-MALDONADO, University of Idaho, JOHNNY RAY HINOJOSA, Williams College, ANNA MUDD, The College of Wooster, LUKE FERGUSON, Pomona College, MICHAEL BAEZ, California State University-Fullerton.

BIOGEOCHEMICAL CARBON CYCLING IN FLUVIAL SYSTEMS FROM BIVALVE SHELL GEOCHEMISTRY - USING THE MODERN TO UNDERSTAND THE PAST
Faculty: DAVID GILLIKIN, Union College, DAVID GOODWIN, Denison University.
Students: ROXANNE BANKER, Denison University, MAX DAVIDSON, Union College, GARY LINKEVICH, Vassar College, HANNAH SMITH, Rensselaer Polytechnic Institute, NICOLLETTE BUCKLE, Oberlin College, SCOTT EVANS, State University of New York-Geneseo.

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Faculty: ZEB PAGE, Oberlin College, EMILY WALSH, Cornell College.
Students: MICHAEL BARTHELMEs, Cornell College, WILLIAM TOWBIN, Oberlin College, ABIGAIL SEYMOUR, Colorado College, MITCHELL AWALT, Macalester College, FREDY, AGUIRRE, Franklin & Marshall College, LAUREN MAGLIOZZI, Smith College.

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Faculty: MARTIN WONG, Colgate University, PHIL GANS, University of California-Santa Barbara.
Students: EVAN MONROE, University of California-Santa Barbara, CASEY PORTELA, Colgate University, JOSEPH WILCH, The College of Wooster, JORY LERBACK, Franklin & Marshall College, WILLIAM BENDER, Whitman College, JORDAN ELMIGER, Virginia Polytechnic Institute and State University.

THE ROLE OF GROUNDWATER IN THE FLOODING HISTORY OF CLEAR LAKE, WISCONSIN
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Students: NICHOLAS ICKS, Northern Illinois University, GRACE GRAHAM, Beloit College, NOA KARR, Mt. Holyoke College, CAROLINE LABRIOLA, Colgate University, BARRY CHEW, California State University-San Bernardino, LEIGH HONOROF, Mt. Holyoke College.

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Students: SARAH SHACKLETON, Wesleyan University, LAURA HAYNES, Pomona College, ALYSSA DONOVAN, Amherst College.

INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT, FRONT RANGE, COLORADO
Faculty: David Dethier, Williams College, Will Ouimet, U. Connecticut.
Students: CLAUDIA CORONA, Williams College, HANNAH MONDRACH, University of Connecticut, ANNETTE PATTON, Whitman College, BENJAMIN PURINTON, Wesleyan University, TIMOTHY BOATENG, Amherst College, CHRISTOPHER HALCSIK, Beloit College.

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Faculty: David Dethier, Williams College, Will Ouimet, U. Connecticut.

GEOCHEMICAL RESPONSE OF TWO ADJACENT ALPINE STREAMS IN GREEN LAKES VALLEY, COLORADO, IN A LOW-SNOW YEAR
CLAUDIA CORONA, Williams College
Research Advisor: Dr. David P. Dethier

HILLSLOPE SEDIMENT ANALYSIS USING FALLOUT RADIONUCLIDES, COLORADO FRONT RANGE
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TIMOTHY BOATENG, Amherst College
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INVESTIGATING LATE PLEISTOCENE AND ANTHROPOCENE FLOOD DEPOSITS ALONG CARIBOU AND NORTH BOULDER CREEK, COLORADO FRONT RANGE
CHRISTOPHER R. HALCSIK, Beloit College
Research Advisor: Sue Swanson
INTRODUCTION

The Critical Zone, the topmost part of the earth’s crust where rock materials interact with the biosphere, atmosphere, and hydrosphere, influences stream chemistry (Anderson et al., 2007). Processes in this zone include any interactions occurring between the top of the vegetation canopy to the base of groundwater. Complex processes cause minerals to weather, creating the substrates needed to support microbial, floral, and faunal activity. Specifically, the Critical Zone includes the solar radiation and tectonism which provide the system with energy to drive the chemical and physical weathering of bedrock, interactions with precipitation, and interactions with the stream water that travels through the unsaturated and saturated zone (Anderson et al., 2008). However, which relationships influence the rates of change in the Critical Zone, and how these relationships vary at multiple spatial and temporal scales, is still not well understood (Anderson and Anderson, 2010).

Hydrologic inputs and biogeochemical reactions occurring within a watershed influence spatial variations of stream solute concentrations (Asano et al. 2009; Zimmer, 2010). Concentration patterns of solutes differ from sample site to sample site and are representative of water interacting with geologic or biologic riparian features within the basin (Acuna and Dahm, 2007). The representative elementary area (REA) proposes a threshold for which average hydrochemical response for a catchment can be predicted based on its watershed area (Wolock et al., 1997). Previous studies used thresholds in spatial stream chemistry to describe the watershed area necessary to separate chemical variation of headwaters due to local processes and chemistry variation of higher-order streams as a result of larger, regional controls (Asano et al. 2009, Zimmer, 2010,). Literature-calculated REA values are between 10 and 1500 hectares (0.1-15.0km²) and incorporate 4th and 5th order streams. Fine scale sampling at a headwater catchment of ~25 ha (0.25km²), encompassing zero order ephemeral and intermittent streams, can test if the REA concept applies to the smaller-end of catchment areas (Zimmer, 2010). Analyzing stream chemistry and its spatial concentration patterns helps explain the influence of local conditions, its interaction with the mixing of different hydrologic inputs, and its overall importance in the Critical Zone.

This study examines water quality in Saddle and Martinelli, two snowmelt-dominated alpine sub-catchments in the Green Lakes Valley to: (1) account for spatial variation and temporal trends of chemical constituents; (2) compare and contrast adjacent, similarly sized sub-catchments with different vegetation; (3) test the REA concept in two small-scale catchments and (4) relate chemical concentrations to physical and geochemical processes occurring within the Critical Zone.

SETTING/LOCATION

Martinelli and Saddle are small, alpine catchments supporting seasonal, late-lying snowfields situated on the south-facing slope of the lower Green Lakes Valley along Niwot Ridge (Fig. 1a). Previous studies identified the small alpine catchment as a nivation hollow (Thorn, 1976). Most snow at Martinelli accumulates through drifting; thick accumulation may result in persistent snowfields from year to year (Caine
and Thurman, 1990). Measured at the Martinelli and Saddle gages, these adjacent catchments have drainage areas of 0.25km², and both extend from ~3420m to ~3560m in elevation. Average annual precipitation is ~130cm (NADP meteorological station, CO02).

**GEOLOGY**

The upper part of the catchments is composed of Tertiary syenite (Ts) and Tertiary or Quaternary diamicton (QTd). The lower part of the catchments is monzonite (Tm) and Holocene colluvium (Qc). Monzonite dikes in the area cross cut metasedimentary rocks (biotite schists and gneisses) of Precambrian age, which extend into the upper Green Lakes Valley. Though the lower part of the catchment is composed of quartz monzonite (Tm), much of Niwot Ridge is covered by surficial deposits (Qc) of Holocene and upper Pleistocene age. The catchments lie above the highest extent of recent glaciations in the Green Lakes Valley. Vegetation in the Saddle watershed consists of alpine tundra and soils are cryochrepts developed in a ~2m thick diamicton of granitic parent material (Williams et al., 2001). Martinelli has a poorly developed soil structure, little vegetation, and alpine grass and colluvium as covering.
DATA COLLECTION/METHODS

Melting snow during the warm months of the year create seasonal streams that drain the Martinelli and Saddle catchments. The Niwot Ridge Long-Term Ecological Research (NWLTER) Project has collected discharge data at stream gages in the Martinelli catchment for 28 years, and in Saddle, T. Nelson Caine has collected data for 18 years.

This study reflects field and lab work from the summer and fall of 2012 and winter of 2013. In addition, I include stream chemistry data from 2011 collected by James Winkler (Keck Student, 2011-2012), and 2010 data collected by Reese Lyerly (Keck Student, 2010-2011), who used similar methods to those discussed here. Data are compared to long-term discharge and stream chemistry records managed primarily by Nel Caine (UC Boulder) and the NWTLTER. Details on NWTLTER’s data collection methodology are located on their website (Niwot Ridge LTER, 2012).

FIELD

126 water samples were collected from study sites between July 12th and August 7th 2012. Collection methods remained consistent between July-August 2011 and 2010. All samples were collected directly into Nalgene polyethylene 125mL sampling bottles. Sample bottles were cleaned with deionized water and then rinsed 3 times with water from their respective sample locations before the final sample was collected. Water samples were suction-filtered by hand through a 0.45 micron Nuclepore filter, refrigerated at 5°C in the dark, and shipped back to Williams College for further analysis. About 80% of samples were suction-filtered and refrigerated within 12 hours of collection; the other 20% were completed within 36 hours of sample collection. Sample sites were spread throughout the Saddle and Martinelli catchment to allow for maximum representation of different drainage areas, influences of snowmelt and groundwater/subsurface inputs, lithology, and vegetation. A Garmin eTrex handheld device (3-5 meter accuracy) recorded the location of all water sampling sites and locations with measured stream discharge and/or water temperature.

LABORATORY

Sample chemistry was measured at the Environmental Analysis Laboratory, Williams College (Williamstown, MA), after the field season. I used automated colorimetry to measure concentrations of dissolved silica and ammonium using a Technicon AutoAnalyzer. Atomic absorption spectrometry using a Perkin-Elmer AAnalyst 300 analyzed major cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺). Ion chromatography examined concentrations of major anions (Cl⁻, SO₄²⁻, and NO₃⁻). A Fisher Accumet pH meter 10 and Orion PerpHect Low Maintenance pH Electrode measured sample acidity and was recalibrated after every 10 samples. The acid neutralizing capacity (ANC), reported in mg/L of bicarbonate ion (HCO₃⁻) was determined by titration, using a Hach digital titrator with 0.16N H₂SO₄.

RESULTS

Alpine catchments, relatively pristine environments, clearly show stream solute concentration changes over time. I first discuss precipitation and runoff amounts for the 2010, 2011 and 2012 water years for Saddle and Martinelli catchments. Then I describe the ion concentrations for Martinelli from the highest measured sample point at the snowfield (M-9) to the stream gage (M-4) on 7/17/12, as well as the ion concentrations for Saddle from the highest measured sample point (S-5) to a point below the stream gage (S-1).

The 2012 water year was about average for precipitation and had early snowmelt, whereas the 2011 water year was well above average with late snowmelt, and the 2010 water year was slightly below average. Water year precipitation totals, measured at University Station were ~95cm for 2012, ~126.2cm for 2011 and ~79.5cm for 2010.

The Saddle stream gage recorded a total flow of 52,200m³ over a period of 95 days for 2010, a total flow of 93,800m³ for 102 days during 2011, and a total flow of 8,400m³ over a period of 97 days for 2012 (Fig. 1b). The Martinelli stream gage recorded a total flow of 67,000 over a period of 105 days for 2010, 99,300 m³ over a period of 55 days for 2011, and a total flow...
Table 1. Area, average field discharge, pH, and average solute concentrations for stream locations sampled over the 2012 field season from July 12th to August 7th. Areas were derived from watershed modeling of LiDAR data.

<table>
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<th>Site</th>
<th>Area (km²)</th>
<th>Q (l/s)</th>
<th>Ca²⁺ (μeq/L)</th>
<th>Mg²⁺ (μeq/L)</th>
<th>Na⁺ (μeq/L)</th>
<th>K⁺ (μeq/L)</th>
<th>NH₄⁺ (μeq/L)</th>
<th>HCO₃⁻ (μeq/L)</th>
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<th>Cl⁻ (μeq/L)</th>
<th>NO₃⁻ (μeq/L)</th>
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Figure 2. Spatial changes in solute concentrations for Martinelli stream for the 2012 field season. a. Cations and contributing catchment area from the highest point at the Martinelli snowfield (M-9, 3510m elevation) to the Martinelli stream gage (M-4, 3427m elevation) measured day 2 of sampling, 7/17/12. b. Anions and contributing catchment area from the highest point (M-9) to the stream gage (M-4).
of 26,000 m³ over a period of 97 days for 2012 (Fig. 1c). The 2012 value for Saddle represents the second lowest flow rate ever recorded for a water year since monitoring began in 1999; 2001 is the lowest thus far with a total flow of 4,045 m³ over a period of 93 days. Average annual flow at Saddle from 1999-2012 is ~56,000 m³ over a period of ~106 days. Average annual flow for Martinelli (1982-2012) is ~76,000 m³. Interestingly, discharge from 1999-2010 was similar at Saddle and Martinelli; annual totals were within 30% of each other.

Figure 3. Spatial changes in solute concentrations for Saddle stream for the 2012 field season. a. Cations and contributing catchment area from the highest point (S-5, 3500 m elevation) to the lowest consistently measured point (S-1, 3397 m elevation) measured day 3 of sampling, 7/19/12. b. Anions and contributing catchment area from the highest point (S-5) to the lowest consistently measured point (S-1).

Overall, water samples (Table 1) have low ionic concentrations and near-neutral pH. For both Martinelli and Saddle, calcium (Ca⁺) is the dominant cation and bicarbonate (HCO₃⁻) the dominant anion. Excluding ammonium (NH₄⁺) and nitrate (NO₃⁻), which had average concentrations of 0 mg/L at both Saddle and Martinelli, concentrations measured at the stream gages are ~2-3 times greater at Saddle (S2:a-h) than at Martinelli (M4:a-h).

Downstream changes of ion concentrations show the combined effects of increasing drainage area and longer contact times. For Martinelli, I plotted the changes in ionic concentrations from M-9 (uppermost sample point) to M-4, the stream gage (Fig. 2a). Here, cation concentrations ranged from 0-140 μeq/L and anion concentrations range from 0-55 μeq/L. Cation concentrations show no consistent pattern with increasing drainage area. For example, plotting the data from 7/19/12 (day 3 of sampling) shows that for Martinelli, Ca and Mg concentrations increase with increasing drainage area. Potassium concentrations remain between 0-3 μeq/L, sodium decreases from the

Figure 4. Percent of Martinelli and Saddle basin outflow provided by precipitation measured from 1984-2010 (Martinelli) and 1999-2010 (Saddle) by the LTER and Nel Caine. The mean concentrations are discharge-weighted and in mg/L except for Si, which is in mmol/L. The mean annual LTER precipitation for the period record was ~1200 mm and ~895 at the University Station. Si values are from Caine and Thurman (1990).
snowfield (uppermost point) to a point below lower Martinelli, and then increases again as it continues downstream to the gage (M-4). Silica increases from the snowfield to M-2, but then stabilizes and remains at a constant concentration tens of meters downstream at the gage (M-4).

Anions measured in Martinelli stream exhibit a different pattern downstream (Fig. 2b). Sulfate concentrations increase by ~70% from the uppermost point (M-9) at 16.71 μeq/L to M-2, then decrease by ~50% from M-2 to the Martinelli gage (M-4), where the concentration is ~24 μeq/L. Chloride concentrations at the snowfield are ~7 μeq/L, and downstream, to ~5 μeq/L at M-2 and ~1 μeq/L at the gage. Nitrate follows the same pattern as sulfate, where it starts at ~2 μeq/L at the snowfield, increases greatly to ~20 μeq/L at M-2 and decreases to 0 μeq/L by the time stream water reaches the Martinelli gage.

The data from 7/17/12 (day 2 of sampling) shows that cation concentrations were greater for Saddle than they were for Martinelli, but anion concentrations, except for HCO$_3^-$, were lower at Saddle than at Martinelli. Cation concentrations along Saddle stream ranged from 0 to 225 μeq/L and anion concentrations ranged from 0 to 35 μeq/L (Fig. 3a). Overall, neither the cation concentrations nor the anion concentrations exhibited persistent patterns with increasing drainage area. For example, the cations Mg$^{2+}$ and K$^+$ had little concentration change from the highest point at S-5 to the lowest at S-1. In contrast, calcium and silica steadily decreased from 211 to 159 μeq/L and 154 to 114 μeq/L. Sodium steadily increased from 12 to 52 μeq/L.

At Saddle, anion concentrations were more variable than cations. Sulfate increased and decreased from site to site ending at 38 μeq/L from a starting point at the top of the catchment where the measured concentration was 12 μeq/L (Fig. 3b). Nitrate concentrations were variable but low, between 0-4 μeq/L. Chloride increased steadily with increasing catchment area, but then decreased sharply, starting at 0 μeq/L, increasing to 8 μeq/L (at the stream gage) and decreasing by half (~4 μeq/L) by S-1.

From the stream geochemistry and discharge data collected at the stream gages, we calculated the discharge-weighted mean concentration of ions (in mg/L, μmol/L for Si) for the Saddle stream from 1999 to 2010 and the Martinelli stream from 1984-2010 and then the ion concentration flux for Saddle and Martinelli (in kg). Combining this data and elemental deposition data from the National Atmospheric Deposition Program (NADP) and assuming conservation of Cl, we calculated that Martinelli effectively drains ~7.55 ha and Saddle drains ~5.26 ha of the ~25 ha catchments.

From these calculations, we combined the data for Saddle and Martinelli and took their averages in order to identify the total flux of solutes. We found that cations derive mainly from weathering and anions are provided by precipitation (Fig. 4). Precipitation introduces 329% of nitrate (NO$_3^-$) to the basin, and 71% of sulfate (SO$_4^{2-}$) and 24% of calcium (Ca$^{2+}$) leaves the basin from precipitation. In addition, 19% of potassium (K$^+$), 13% of magnesium (Mg$^{2+}$) and 13% of sodium (Na$^+$) are due to precipitation. Almost 99% of the silica (Si) in Martinelli and Saddle stream water derives from weathering.

DISCUSSION

The spatial variations of ion concentrations indicate hydrologic mixing of source waters and unique local conditions, and are influenced by the seasonal variations in stream flow. At the scale of my study (km$^2$), cation concentrations along Saddle stream show a decrease in variability with increasing drainage area (Fig. 2a), as shown by previous hydro-chemical research (Asano et al., 2009). Cation concentrations along Martinelli show some variability (Na$^+$), but anions are the most spatially and temporally variable (Fig. 2b, 3b).

According to Caine and Thurman (1990), at all sites in the Green Lakes Valley, the dominant cations were calcium (Ca$^{2+}$) > sodium (Na$^+$) > potassium (K$^+$) = magnesium (Mg$^{2+}$), with sulfate (SO$_4^{2-}$) and bicarbonate (HCO$_3^-$) as the dominant anions. My data show nearly the same pattern in decreasing concentration, except magnesium is 5-10 times higher than potassium, each day at each sample site. One explanation could be the local bedrock geology. Magnesium is a major constituent of the dark-colored
ferromagnesian minerals like pyroxene, amphiboles, and biotite (Hem, 1985). The high concentration of magnesium in the Martinelli and Saddle basins may be due to the composition of the underlying Tertiary syenite (Ts) and monzonite (Tm), whose primary minerals include dark amphiboles, biotite (Ts) and dark pyroxenes, hornblende, and biotite (Tm).

Samples from the Saddle gage travel further from snow to gage than samples from the Martinelli gage. Uptake by biologic activity and weathering and exchange processes favored by subsurface contact increase downstream (Caine and Thurman, 1990), a possible reason why NO$_3^-$ is not present or significant at the Saddle gage. In addition, wetland vegetation directly below Saddle snowfields may uptake and remove nitrate. Potassium, another ion strongly involved in the biosphere, decreases in concentration along Saddle from the highest sampling site at $\sim$7 μeq /L (S-5) to $\sim$2 μeq /L at the stream gage (S-2), and suggests ion uptake.

Martinelli water samples have consistently higher average values of ammonium (NH$_4^+$) and nitrate (NO$_3^-$) ions (Table 1) than Saddle. This implies a greater atmospheric influence and less biological activity in the Martinelli catchment.

The lower average ionic concentrations from Martinelli show a greater snowmelt dilution signal than samples taken along the Saddle stream. The lower average ionic concentrations indicate lower annual solute yield for weathering related constituents: Si, Na, Mg, and Ca. Current estimates of catchment area and annual flow are similar for both basins, which implies that total solute removal is less from Martinelli than from Saddle. Saddle and Martinelli flux calculations show higher solute yield for all ions except chloride and nitrate in Saddle than in Martinelli during recorded years.

The idea that there exists a threshold for which average hydro-chemical response for a catchment can be predicted based on its watershed area, known as the representative elementary area (REA) concept, has the potential to separate catchment areas in such a way to differentiate between local processes and regional controls dominating the stream water chemistry (Wolock, 1997). Temnerud and Bishop (2005) argue that an REA value of 1500 ha ($\sim$15km$^2$) is indicative of constant solute concentrations, while Asano et al. (2009) suggests 10-150 ha ($\sim$0.1-1.5km$^2$) and Zimmer (2010) suggests 0.6 ha ($\sim$0.006km$^2$). My research found that solute concentrations spatially distributed are not very constant, even when upslope accumulated area is calculated to be $\sim$25 ha (0.25km$^2$). The dissimilarities between REA values in the literature and the stream chemistry seen across Saddle and Martinelli suggest that sampling density and the mixing of waters with hotspots, such as seeps, play a large role in the determination of an appropriate REA value. Thus, the REA value may be dependent on the type of watershed. For example, by looking at ephemeral and intermittent streams in a headwater catchment, we found an REA value within those reported in the literature that did not predict the average hydro-chemical response for the catchments, like the REA concept argues. The evidence gathered from Saddle and Martinelli and compared to the data gathered by Temnerud and Bishop (2005) and Asano et al. (2009), suggest that an REA value calculated at the hill-slope or headwater scale may describe different physical and chemical controls on stream chemistry than an REA calculated across a river basin. For this study, REA represented the amount of snowmelt and water-contact time with the subsurface. However, a watershed is controlled by processes more complex than snowmelt and subsurface-contact time, and instead could be controlled by distinct but interweaving processes within the Critical Zone. Thus, we believe that the REA as a representative elementary area is questionable.

**CONCLUSION**

Hydrologic inputs and biogeochemical reactions occurring within a watershed influence spatial variations of stream solute concentrations. The fine-scale sampling of low-order stream water in a small alpine headwater catchment has shown that stream water chemistry is more variable across space and time than previously thought. The lack of evidence showing stabilizing solute concentrations at Saddle and Martinelli, a watershed with an REA value of $\sim$25 ha (0.25km$^2$), has shown that the REA concept is not as robust as the literature suggests as the concept depends on the scale of sampling and the type of watershed.
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