

Nitrogen production from geochemical weathering of rocks in southwest Montana, USA

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[1] A 30 day time course laboratory weathering experiment was conducted using rock samples collected from the West Fork of the Gallatin River watershed (WFW) in southwestern Montana, USA. The goal of these experiments was to quantify the amount of labile nitrogen in rock samples collected from the watershed and determine if chemical weathering is a source of dissolved nitrogen in stream water. Several rock samples investigated produced nitrate in significantly higher concentrations than the silica bead control ($p < 0.05$), and the data were consistent with elevated NO_3^- concentrations measured in associated WFW streams. Isotopic analyses of $^{15}\text{N}\text{-NO}_3^-$ in 22 stream water samples from the WFW and four rock:water extracts from the laboratory experiments indicated that the isotopic composition of NO_3^- was comparable with rocks and stream water samples in the same watershed and differed strongly from waters downstream of development. We suggest that the NO_3^- measured in WFW streams includes nitrogen derived from mineral dissolution products from soils and rock. The results presented herein further indicate that rock weathering is a source of stream water N in the West Fork watershed and inform water quality assessment, total maximum daily load development, and the relative influences of natural and anthropocentrically derived N sources across this developing mountain watershed.

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1. Introduction

[2] Chemical reactions between soil minerals and water constitute a major source of solutes in streams and provide essential elements to biota. Contributions to the global biogeochemical cycling of elements such as carbon, iron, and phosphorous include geologic sources; however, there is little consensus or documentation on the importance of chemical weathering for the flux of nitrogen (N) through the biosphere and hydrosphere [Schlesinger, 1997; Kendall, 1998; Holloway et al., 1999]. The lithosphere contains 98% of global N, and an increasing number of studies have shown that geologic N could be a considerable nitrate (NO_3^-) source to both aquifers and surface waters [Morford et al., 2011; Holloway et al., 1999, 2001; Strathouse et al., 1980]. The ubiquity

of 1998 N weathered from geological sources is poorly understood. Sedimentary rocks, for example, are a long-term reservoir for ~20% of global N, but weathering rates and N content among sedimentary rocks span orders of magnitude [Freeze and Cherry, 1979; Holloway and Dahlgren, 2002]. Consequently, the linkages between geologic N sources and more dynamic watershed-scale processes such as fixation, export, or biomass production have not been evaluated in more than a handful of studies [Goodale et al., 2009; Morford et al., 2011; Gardner et al., 2011].

[3] Major sources of N to the biosphere include wet and dry atmospheric deposition, biological fixation, and mineralization from the breakdown of organic matter in soils [Schlesinger, 1997; Stevenson and Cole, 1999]. Atmospheric N deposition is typically derived from volatilized ammonia (NH_3) with 60–80% of N in precipitation falling as the protonated NH_4^+ ion (National Atmospheric Deposition Program Data Report (NADP) 2001-01) [Nanus et al., 2008]. The majority of N in surface waters is $\text{NO}_3\text{-N}$ as the oxidation of reduced N is rapid in aerobic surface waters [Mueller and Spahr, 2006]. Ammonium (NH_4^+) is the predominant form of nitrogen stored with soil minerals because it readily sorbs to negatively charged oxide compounds in solids such as $\text{AlSi}_3\text{O}_8^-$ and particulate organic matter [Drever, 1997]. Ammonium sorption is ubiquitous in soils, especially layered silicates [Holloway and Dahlgren, 2002]. The accumulation of NH_4^+ in soils is also closely linked to the amount and form of organic matter, which serve as ligands to retain nutrients [Stevenson and Cole, 1999]. The partial breakdown of litterfall/detritus

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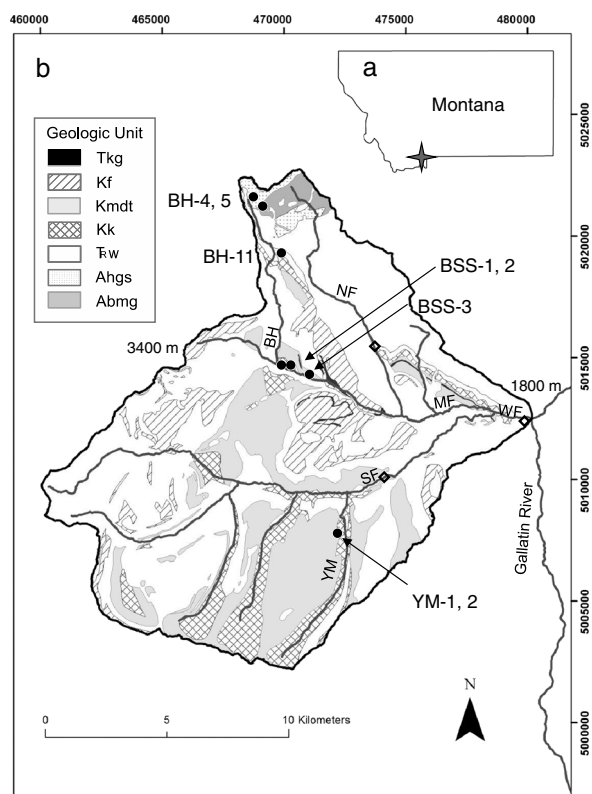


Figure 1. Watershed map of the West Fork of the Gallatin River. The elevation range is 1800–3400 m. Geologic formations from Kellogg and Williams [2005] are shown. TKg = gabbro sills; Kf = Frontier Formation (Fm); Kmdt = Thermopolis and Muddy Sandstone Fms; Kk = Kootenai Fm; TRw = Woodside Formation Fm; Ahgs = Hornblende plagioclase gneiss and amphibolite; Abmg = biotite-muscovite gneiss. Streams near rock sampling locations are labeled: BH = Beehive stream, MF = Middle Fork, SF = South Fork, WF = West Fork, YM = first tributary of Yellow Mule Stream. Black dots represent sampling locations for the eight rocks in this study: YM = outcrops above the first tributary of Yellow Mule Stream, BSS = rocks exposed along Big Sky Spur Road, BH = outcrops in Beehive Basin. Stream sampling locations for aqueous chemistry are represented by hollow diamonds.

is the most common pathway for N accumulation in soils. The organic N pool in soils varies from very low ($< 30 \text{ mg kg}^{-1}$) in mineral soils of igneous origin to $> 2000 \text{ mg kg}^{-1}$ in coal spoils [Holloway and Dahlgren, 2002]. Nitrogen in modern organic-rich marine sediments has been measured above 1000 mg kg^{-1} [Li, 1991].

[4] Nitrogen is buried by biogenic sedimentary rocks as organic matter (as reduced N in biomolecules), and the degree of diagenesis determines the amount of N left in rock [Wlotzka, 1972; Faure, 1986]. Commonly, N in rock is present as kerogen, which has been released from dolomites using 30% HCl [Beaumont and Robert, 1999]. The main source of N in silicate rocks is believed to originate from sedimentary rocks that react during metamorphism and are incorporated as fluid inclusions [Bottrell and Miller, 1990]. Ammonium levels in metamorphic micas in France were reported by Duit *et al.* [1986] and ranged from 120 to 500 mg kg^{-1} in

muscovite and 300 to 1500 mg kg^{-1} in biotite. Reservoirs containing the highest concentrations of N per mass are petroleum ($100\text{--}20,000 \text{ mg kg}^{-1}$), coals ($2000\text{--}30,000 \text{ mg kg}^{-1}$), modern marine sediment (1772 mg kg^{-1}), shales (600 mg kg^{-1}), and limestone (73 mg kg^{-1}) [Wlotzka, 1972]. Nitrate preservation in rocks is not common, but some nitrate minerals exist from evaporate deposits including niter, NaNO_3 [Böhlke *et al.*, 1997; Klein and Hurlbut, 1993].

[5] Nitrogen-bearing mineral sources have previously been linked to water chemistry. Holloway *et al.* [1999, 2001] attributed 90% of stream water NO_3^- concentrations in certain low-order catchments in north central California to geologic sources. Saprolites and metasedimentary rocks present in this study area, including phyllite, slate, and biotite schist, released N under simulated field conditions. These findings were supported by total N measurements of up to 1460 mg kg^{-1} (104 mmol kg^{-1}) in saprolites [Holloway *et al.*, 2001]. Ammonium (NH_4^+) concentrations greater than 3.5 mM have been measured in geothermal outflows across Yellowstone National Park and are attributed to the dissolution (distillation) of marine rocks with hydrothermal waters near or above 100°C [Fournier, 1989; Holloway *et al.*, 2011]. Williams *et al.* [2006] showed that stream water from a high alpine rock glacier in the Green Lakes Valley in the Colorado Front Range contained concentrations of NO_3^- greater than local precipitation that could not be explained by biological fixation. Goodale *et al.* [2009] hypothesized that seasonal microbial activity in forested catchments in the Susquehanna watershed in New York caused a complex pattern of NO_3^- export but that baseflow N concentrations could be attributed to shales and limestone from the Genesee Formation. All of these studies suggest and partially document the significant role of mineral N sources across diverse systems. Streams flowing from alpine and subalpine areas can play a critical role in N export to larger rivers [Goolsby *et al.*, 1999; Stottlemeyer *et al.*, 1997; Campbell *et al.*, 2000]. Accordingly, modeling efforts have been made to evaluate and predict N export in alpine watersheds [e.g., Baron and Campbell, 1997; Sickman *et al.*, 2003; Gardner *et al.*, 2011]; however, in many models, the proportion of dissolved N from mineral weathering is typically assumed to be negligible and not quantified. Here we performed mineral weathering experiments to evaluate potential geologic sources of N and other nutrients and elements to stream water across the West Fork Watershed (WFW) in Big Sky, Montana.

[6] We investigated the mineral weathering environment in the West Fork Watershed as part of an ongoing study on NO_3^- export into the Gallatin River. Since the 1970s, a ten-fold increase in mean annual nitrate concentration has been observed at the watershed outlet. Concentration increases from < 0.04 to $0.3 \text{ mg L}^{-1} \text{NO}_3\text{-N}$ (2.8 to $21.4 \text{ } \mu\text{MNO}_3^-$) are correlated to the number of residential dwellings [Gardner and McGlynn, 2009]. Quarterly synoptic sampling campaigns across the WFW since 2005 revealed seasonal trends in the concentration of NO_3^- at 60 sites sampled in the area. Peak NO_3^- concentrations in most streams occurred in late winter; however, NO_3^- remained elevated year-round in numerous undisturbed headwater streams [Gardner and McGlynn, 2009]. We sought to identify potential sources of geologic N in the WFW in order to improve our stream-based assessment of N production and cycling across the watershed and

Table 1. Physical Geologic Characteristics of Samples

Sample Name	Description	Geologic Formation ^a	Bulk Mineralogy ^b	Surface Area of Rock Flour (m ² g ⁻¹)
<i>Outcrops Located Above Yellow Mule Streams</i>				
YM-1	Pale yellow Dolomitic limestone	Kootenai (Kk)	Ankerite-Ca, MgFe, Mn(CO ₃) ₂ SiO _x Ca-Fe silicate	1.1
YM-2	Dark gray shale interbedded with YM-1	Kootenai (Kk)	CaCO ₃ SiO _x CaSiO _x	2.1
<i>Exposed Rock Along Big Sky Spur Rd</i>				
BSS-1	Reddish-brown mudstone	Kootenai (Kk)	Alpha quartz-SiO ₂ CaMgFe(CO ₃) ₃ AlSi(OH) _x	5.96
BSS-2	Fossiliferous tan sandstone	Kootenai (Kk)	Alpha quartz-SiO ₂ AlSi(OH) _x KMgAlHSiO _x	1.09
BSS-3	Dark gray laminated shale	Thermopolis (Kmdt)	Alpha quartz-SiO ₂ NaCaAlSiO _x CaAlOH · H ₂ O	4.78
<i>Outcrops Located in Beehive Cirque and Drainage</i>				
BH-4	Pink granodiorite	Archean metaigneous (Ags)	FeSiO _x AlFeSiO _x CaMgFeSiO _x	0.687
BH-5	Schist	Archean metamorphic (Abm)	AlKSiO _x CaFeMgSiO _x	0.876
BH-11	Orange evaporite	Woodside (TR w)	NaAlSiO ₃ · H ₂ O CaSO ₄ · 2H ₂ O CaAlSiO _x OH FeAlSiOH	1.75
<i>Experiment Control</i>				
Control	1 mm silica/zircon beads	n/a	SiO ₂ /zircon (Biospec products, USA)	5.0

^aGeologic formations determined by analysis of the Ennis quadrangle geologic map and rock unit descriptions [Kellogg and Williams, 2005].

^bBulk mineralogy determined by X-ray diffraction on powder mounts.

ascertain the potential for geologic weathering to support elevated stream water N concentrations measured in relatively pristine headwater systems.

2. Materials and Methods

2.1. Site Description and Characteristics

[7] The 212 km² West Fork of the Gallatin River Watershed (WFW) is located in southwest Montana, USA (Figure 1). The West Fork is a fourth-order stream that flows into the Gallatin River, one of three headwater watersheds of the Upper Missouri River. A portion of the watershed has been developed in the last three decades and now contains three ski resorts and three golf courses. Land within the WFW is a mix of public (i.e., United States Forest Service, 2004, <http://www.fs.fed.us/r1/gallatin/?page=resources/fisheries/streams>, hereinafter referred to as USDA FS, 2004) and private land (businesses, resorts, and ~2000 structures). The South Fork and Middle Fork streams are the two major tributaries to the West Fork River (Figure 1). Beehive Basin (BH) is a pristine 8.3 km² subcatchment of the Middle Fork located in the northwestern part of the WFW. North Fork (NF) is a pristine, largely undeveloped watershed with an area of 24.3 km². The 14 km² area draining First Yellow Mule (YM) stream contains only road development to date. Elevations in the WFW range from 1800 to 3400 m above sea level at the watershed divide.

[8] The topography transitions from gently sloping alluvial valleys to steep, gravelly slopes of the Madison Range. The climate is typical of subalpine and alpine areas in the

western U.S., with a mean annual temperature of 2.6°C and a precipitation gradient of 50 cm yr⁻¹ to 127 cm yr⁻¹ from the WFW outlet to the Lone Mountain divide, where 60% of annual precipitation occurs during winter and spring months [USDA FS, 2004; Mueller and Spahr, 2006]. Peak discharge occurs as spring snowmelt runoff during late May to early June (USDA FS, 2004). Mixed conifer forest, mountain grasslands, and shrublands are present at low elevations, and alpine meadows are the predominant vegetation type at elevations above 2500 m (USDA NRCS, 1997, Montana Soils Map, <http://nris.mt.gov/nrcs/soils/datapage.asp>, hereinafter referred to as USDA NRCS, 1997). Soils in the WFW are composed of primarily colluvium and glacial till. They are classified by Natural Resources Conservation Service as predominantly typical or mollic Alfisols with loamy texture at low elevation and Cryoboralfs in alpine areas (USDA NRCS, 1997). Incepticols and Mollisols are present to a lesser extent throughout the study area. Higher-elevation soils have shallow depths (< 0.5 m). Headwater streams are boulder-dominated, and the lower Middle Fork and West Fork of the Gallatin streams contain a mixture of rocks and sandbars with fine-grained sediments.

2.2. Geologic Setting

[9] The entire WFW is underlain by Archean gneiss (> 2500 Ma) that outcrops in the Beehive Basin (Figure 1). Outcrops in the Beehive Basin and North Fork watersheds are generally composed of gneiss and other metasedimentary rocks (Figure 1) [Kellogg and Williams, 2005]. A nearly 500 m thick series of Cretaceous (45–65 Ma) sedimentary rocks of the

Kootenai, Thermopolis, and Muddy (Sandstone), Cody (Shale), and Frontier Formations are exposed on a major east-west trend across the WFW watershed. The Pinedale and Bull Lake glaciations (20–14 ka and 140–100 ka, respectively) left valley till deposits as deep as 50 m in some portions of the WFW [Kellogg and Williams, 2005]. The Yellow Mule tributaries to the South Fork incise the sedimentary rocks of the Kootenai and Thermopolis Formations. Lone Mountain, a dacite laccolithic intrusion into Cretaceous aged sedimentary rocks, is a prominent feature in the WFW and forms the headwaters of the Middle Fork tributary of the West Fork of the Gallatin River.

2.3. Stream Water and Snow Sample Collection

[10] Stream water from locations on the South Fork, North Fork, and West Fork were collected biweekly from 2005 through 2007. Grab samples were collected using clean 250 mL high-density polypropylene bottles and transported in coolers at 0–4°C to Montana State University in Bozeman, MT. The samples were filtered (0.45 µm Millipore Isopore polycarbonate membranes) within 6 h of collection into four clean 20 mL or 60 mL polypropylene bottles for anion, cation, dissolved organic carbon (DOC), and total dissolved nitrogen (TDN) analyses. Once filtered, samples were frozen (–20°C) until analysis. Additionally, 22 stream water samples were collected in February 2007 within 1–2 h (synoptic sampling) for analysis of stable isotopes of nitrate (NO_3^- , $\delta^{15}\text{N}-\text{NO}_3^-$, and $\delta^{18}\text{O}-\text{NO}_3^-$). These samples were filtered within 2 h of sampling and frozen until analysis at Woods Hole Oceanographic Institute (WHOI). Snow samples were collected from fresh surface snow in Beehive Basin in February 2007, thawed and filtered within 24 h of collection, and analyzed for major anions, cations, DOC, TDN, $^{15}\text{N}-\text{NO}_3^-$, and $^{18}\text{O}-\text{NO}_3^-$.

2.4. Rock Sample Collection

[11] Twenty-five (1–2 kg each) whole rock samples were collected from outcrops within the WFW in July 2007. Field samples were reacted with 6N HCl to determine the presence or absence of carbonate minerals. Eight rocks were selected for the time course experiment based on their features and locations in the watershed (see Table 1). The locations included Yellow Mule Basin, Big Sky Spur Road (representing areas draining into the Middle Fork Basin), and Beehive Basin. The locations of sample sites and geologic formations in the WFW are shown in Figure 1.

2.5. Rock Sample Preparation

[12] A diamond blade saw was used to remove the outer weathered surfaces of each rock sample collected except sample BSS-2, which is a fissile shale the outer surfaces of which could not be removed by rock sawing. The samples were crushed to fragments < 3 cm diameter in the Montana State University (MSU) Earth Sciences Department Rock Processing Facility. All machine parts were cleaned with ethanol and rinsed three times with 0.22 µm filtered ultrapure water between samples to avoid cross contamination between samples and reduce the introduction of microorganisms into the processed rock powders. The rock fragments were then crushed to a fine powder in zirconia cylinders using a Certiprep 8000 Mixer Mill in the Department of Land Resources and Environmental Sciences (LRES) Soil Analytical Facility (SpexCertiprep Inc., Metuchen, NJ), and finally passed through a 0.25 mm sieve. Zirconia vessels, crushing balls, and sieves were acid-washed

(2N HCl), rinsed with 0.2 µm filtered ultrapure water, and dried between samples.

2.6. Laboratory Weathering Experiment Setup

[13] Forty grams of rock powder and 75 mL of ultrapure ($18.2\text{M}\Omega\text{cm}^{-1}$) 0.2 µm filtered water (Barnstead Nanopure) were added to acid-washed and furnace (550°C) glass serum bottles. The solid:water mass ratio was 1:1.875 and is within the range for soil-water extracts (1:1 to 1:5 wt/wt soil:water) [Rhoades, 1996]. A total of 15 bottles for each of eight rock types were prepared to enable triplicate sampling at five time points. The bottles were crimped with butyl rubber septa and aluminum caps and incubated at room temperature for 1 h, 24 h, 70 h, 190 h, and 790 h (~30 days). Ultrapure water was reserved as a control (0 h time point), and clean 0.1 mm silica/zircon beads (Biospec Products, Carlsbad, CA) served as a weathering-resistant method control for all time points. Bottles were shaken on a shaker table for 10 min immediately following water addition and once every 7 days thereafter. For each time point, three bottles were selected, and rock-water slurries (60–75 mL) were decanted into 500 mL Nalgene filter towers and filtered through separate 0.45 µm polycarbonate membranes (Nalge-Nunc Inc., Rochester, NY). Filtrate from each bottle was divided into three clean 20 mL polypropylene scintillation vials designated for anions, cations, and DOC/TN analyses. The water samples were frozen at –20°C until all samples were collected following the 30 day experiment. All aqueous chemical analyses were performed immediately after the final time point.

2.7. Bulk Mineralogy

[14] The rock powders used in the experiments were characterized for bulk mineral composition and surface area. Bulk mineralogy was determined by X-ray diffraction (XRD) of powder samples at the Image and Chemical Analysis Laboratory at MSU using an XRD1 Scintag Inc. X-1 powder X-ray diffractometer (Cupertino, CA). Specific surface areas of all unweathered rock powders were analyzed using a Micromeritics Flow-Sorb 2300 surface area analyzer in the MSU LRES department (Micromeritics, Norcross, GA).

2.8. Aqueous Chemistry

[15] Electrical conductivity (EC) and pH of water samples collected at each time point were measured using Fisher Accumet EC and Orion 720A pH meters. Concentrations of anions including F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} were measured by ion chromatography using a Metrohm ion chromatograph equipped with a chemical suppressor and a 4×250 mm Metrosep 250A exchange column (Metrohm, Herisau, Switzerland). The calibration range was from 0.005 to 20 mg L^{-1} , and samples were diluted to values within the range of the standards. Analytical detection limits were 2 $\mu\text{g L}^{-1}$ for Cl^- and SO_4^{2-} , and 5 $\mu\text{g L}^{-1}$ for all other anions. Procedure blanks analyzed between every 10 samples contained less than 5 $\mu\text{g L}^{-1}$ of all anions. Concentrations of cations including Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} were measured by ion chromatography using a Metrohm IC equipped with a 4×250 mm cation exchange column. The calibration range was 0.010 to 20 mg L^{-1} , and detection limits were 5 $\mu\text{g L}^{-1}$ for Na^+ and 10 $\mu\text{g L}^{-1}$ for all other cations. Accuracy was determined as the percent error against a certified standard and was analyzed

Table 2. Mean Chemical Compositions in Rock-Water Slurries After 70 h Equilibration at 21 C^a

Sample Name	pH	Ionic Strength (mM)	Na ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Total Dissolved C	Total Dissolved N	¹⁸ O-NO ₃ (‰) ^d	¹⁵ N-NO ₃ (‰) ^c
YM-1	10.0	8.02	394 (3.7) ^b	179 (10.3)	2257 (85.3)	643 (30.6)	435 (7.5) ^c	15.8 (0.7)	2783 (237)	529 (55)	5.1 (0.04)	3.00 (0.06)
YM-2	8.4	5.70	270 (49.1)	512 (31.7)	114 (11.7)	433 (42.0)	51.4 (10.9)	35.2 (1.6)	1525 (131)	134 (11)	5.2 (0.13)	1.7 (0.14)
BSS-1	9.1	2.72	181 (2.7)	284 (38.3)	781 (25.3)	75.0 (7.7)	0.23 (0.0)	34.0 (0.4)	2008 (300)	47.6 (3.1)	-	-
BSS-2	7.6	1.15	52.4 (2.9)	64.2 (2.4)	21.8 (1.9)	17.5 (0.2)	8.81 (0.4)	21.5 (3.2)	658 (70)	51.5 (15)	5.3 (0.02)	2.1 (0.05)
BSS-3	7.7	3.08	911 (25.4)	279 (25.5)	113 (1.8)	23.1 (0.5)	5.4 (4.6)	< 0.5	2108 (66)	21.2 (0.5)	-	-
BH-4	8.7	1.98	158 (6.7)	136 (6.8)	102 (3.9)	6.14 (0.2)	0.93 (0.1)	11.8 (0.4)	781 (8.0)	53.9 (0.1)	-	-
BH-5	9.2	1.07	22.8 (8.1)	50.4 (2.1)	152 (7.4)	4.65 (0.8)	0.98 (0.3)	8.05 (0.2)	438 (50)	18.7 (0.7)	-	-
BH-11	4.7	6.41	65.1 (2.3)	741 (5.7)	197 (8.6)	151 (10.0)	0.32 (0.0)	31.3 (0.6)	249 (2.0)	49.3 (1.9)	-	-
Control	7.2	0.15	5.49 (1.19)	13.1 (1.1)	4.15 (1.2)	2.1 (0.12)	0.4 (0.03)	< 0.5	87.5 (9.2)	2.44 (0.8)	-	-

^aConcentrations in units of $\mu\text{mol L}^{-1}$ unless otherwise noted.

^bParentheses represent standard deviations from triplicate sample bottles.

^cBold values indicate concentration of N species significantly higher than the silica bead control using the Student's *t* test ($p=0.05$).

^d‰ versus VSMOW.

^e‰ versus air.

every tenth sample and was within 10% for all ions. Concentrations of total dissolved C (TC), dissolved organic C (DOC), and total dissolved N (TN) were measured by oxidative combustion at 720°C on a Shimadzu TOC-V_{CSN} Carbon Analyzer attached to a TNM-1 total nitrogen measuring unit (Shimadzu Corp., Kyoto, Japan). Detection of C compounds was by a nondispersive infrared CO₂ detector, and combustible N was detected as excited NO₂ by chemiluminescence. Dissolved inorganic C (DIC) was calculated as the difference between TC and DOC. The detection limits for DOC were 0.6 μM and 0.14 μM for TDN. Procedural blanks averaged 10.6 μM DOC and <0.14 μM TDN, and experimental controls (Si/zircon bead treatments) averaged 87.5 μM DOC and 2.44 μM TDN.

[16] Concentrations of total dissolved silicon (Si) and other major and trace elements were determined on the T2 (1 h time point) and T5 (30 day time point) samples by inductively coupled plasma optical emission spectroscopy using a Perkin Elmer 3700 DV (Perkin Elmer, New York, NY). Trace metals were calibrated from 0 to 1 mg L^{-1} , and major elements Na, K, Ca, Si, and Mg were calibrated 0–500 mg L^{-1} .

[17] Ionic strengths (*I*) of rock slurries at all time points were calculated from the mean dissolved concentrations of measured ions using the PhreeQ-C geochemical modeling program [Parkhurst, 1995]. *I* is defined as

$$I = 0.5 \sum (C_i z_i)^2, \quad (1)$$

where C_i equals the concentration (*M*) of the *i*th species and z_i equals its ionic charge. Charge balance errors for our data set were also calculated using PhreeQ-C.

[18] Stable isotopes of NO₃⁻, $\delta^{15}\text{N-NO}_3$, and $\delta^{18}\text{O-NO}_3$ were analyzed at Woods Hole Oceanographic Institute (WHOI) using the Sigman-Casciotti microbial denitrifier denitrification method [Sigman *et al.*, 2001; Casciotti *et al.*, 2001]. The stable isotope ratio was determined relative to the atmospheric standard and Vienna standard mean

ocean water (VSMOW) for N and O, respectively, in units of per mille (‰).

3. Results and Discussion

3.1. Stream Water Chemistry

[19] During the 2005–2007 study period, nitrate (NO₃⁻) concentrations generally were elevated in the West Fork just before its confluence with the Gallatin River during winter months (November to March). Maximum NO₃⁻ concentrations at the watershed outlet during winter (28–32 μM NO₃⁻) coincides with the timing and magnitude of peak NO₃⁻ concentrations observed at several other locations in the watershed, including the Middle Fork (42–45 μM), South Fork (22–36 μM), and the individual subcatchments of the South Fork [Gardner and McGlynn, 2009]. During the 2 year study period, the First Yellow Mule tributary and two other undisturbed streams feeding the South Fork repeatedly displayed an increase of 14–19 μM NO₃⁻ just prior to peak Gallatin discharge [Gardner and McGlynn, 2009]. The NO₃⁻ concentrations observed in winter months were also consistently higher for the South Fork than for the North Fork (NF). The maximum NO₃⁻ concentrations measured in the North Fork (~10.0 μM) occurred in July 2006, October 2006, and February 2007, indicating no seasonal trends. The consistently low concentration of NO₃⁻ observed for North Fork was similar to that for Beehive Basin: The mean annual NO₃⁻ concentrations in the North Fork and Beehive Basin over 2005–2007 were 7.1 μM and 0.71 μM , respectively [Gardner and McGlynn, 2009]. Mean annual NO₃⁻ for the South Fork was 18.6 μM . The concentrations of NO₂⁻ and NH₄⁺ at all locations were near or below method detection limits (0.11 μM NO₂⁻ and 0.55 μM NH₄⁺) on all dates sampled. Overall, these results indicate that a lithogenic source of N likely exist in some undisturbed headwater catchments [Gardner and McGlynn, 2009]. Fresh snow collected from Lone

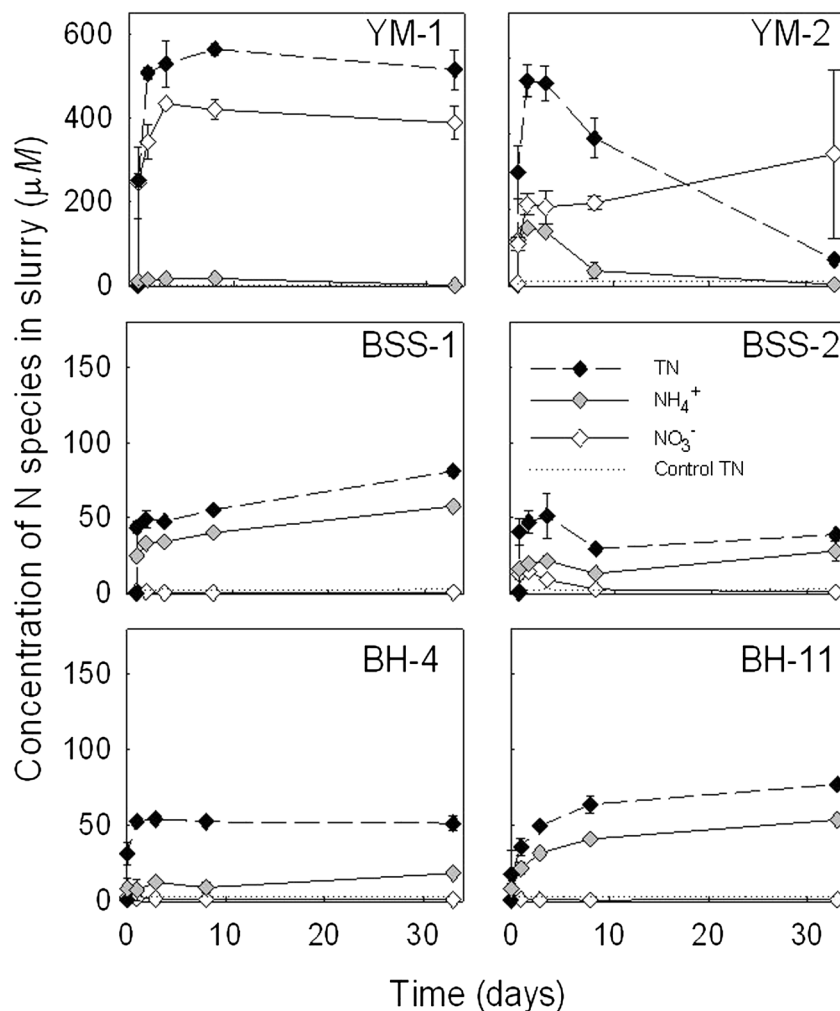


Figure 2. Concentrations (in μM) of total nitrogen (TN), nitrate (NO_3^-), and ammonium (NH_4^+) produced by six of the experimental rock-water mixtures plotted over the 30 day experiment period. Note the change in y axis scale for YM-1 data. All other plots show a 0–160 μM scale. The silica bead control mixture is shown for reference. The YM-1 mixture produced approximately 6 times more TN, measured predominantly as NO_3^- , than any other mixture. Results for BSS-3 and BH-5 slurries were not included in this figure because they contained near detection limit levels of NO_3^- or TN and did not show an increasing trend in N species.

Peak in February 2007 contained very low levels of all ions ($< 20 \mu\text{M}$). Chloride dominated the anionic charge and NO_3^- and ranged from 1.6 to 1.8 μM NO_3^- [Christner et al., 2008].

3.2. Mineralogy of Rock Flours

[20] Bulk mineralogical analysis of rocks based on XRD identified alpha quartz (SiO_2), most commonly present in samples BSS-1, BSS-2, and BSS-3 (Table 1). Aluminosilicates were detected in BSS-1, BSS-2, BSS-3, BH-4, BH-5, and BH-11 (Table 1). Carbonates were detected in three of the eight rock flours: in YM-1, a manganese-enriched form of ankerite (general formula $\text{CaFe}(\text{CO}_3)_2$) was detected; in YM-2, $\text{CaCO}_3\text{SiO}_x$ was detected; and $\text{CaMgFe}(\text{CO}_3)_3$ was detected in the BSS-1 mudstone. The XRD results are consistent with the description of the Kootenai limestone (YM-1) as an “impure” dolomitic limestone [Suttner, 1969]. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was detected in the BH-11 sample and was the only sulfate mineral type measured in this study. Samples YM-1 and YM-2 contained the greatest

percent weight of carbon (12.3 and 10.3%, respectively) which verify carbonate mineralogy. Samples YM-1, YM-2, and BH-11 were expected to be readily weathered based on the general order of dissolution rates: evaporates $>$ carbonates $>$ shale $>$ granite $>$ sandstone [Freeze and Cherry, 1979].

3.3. Aqueous Chemistry of Rock-Water Slurries

[21] Values of pH (4.6–10.0) and the concentrations of dissolved major ions and C and N species in the rock powder extracts increased by at least an order of magnitude during the first 3 days (Table 2). Triplicate bottle samples produced consistent chemical results across all time points, and statistically significant changes in most analytes from time zero (T0) to all subsequent time points were observed ($p < 0.05$). Concentrations of Cl^- and SO_4^{2-} , and cations including Na^+ , K^+ , Ca^{2+} , and Mg^{2+} increased from 0 to 3 days in all samples except the silica bead control and typically stabilized or showed slight increase between 3 and

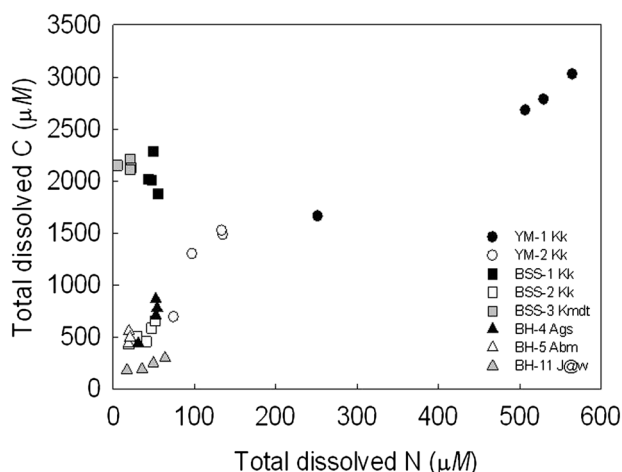


Figure 3. Total C concentrations versus total N (both in μM) over all time points. Note three typologies formed by rock-water interactions: waters low in both C and N (type 1), those that may be a source of C but low in N (type 2), and Yellow Mule slurries high in both C and N (type 3). Symbol labels correspond to sample location and surface geology.

30 days. These results indicate that chemical equilibrium for these major ion species dissolved in water was reached in our sample bottles within a 3 day time period. Charge balance errors were less than 2% for all samples when using CO_3^{2-} calculated from pH and DIC, indicating analyses reasonably balanced the sum of total anionic and cationic charge in each sample over the course of the experiment.

[22] All extracts, except YM-2, were dominated by HCO_3^- as the major anion and predominant cations varied across the samples analyzed (Table 2). YM-1, BH-5, and BSS-1 mixtures generated a majority of cationic strength from Mg^{2+} , while samples BSS-2, BSS-3, and BH-4 generated a greater proportion of I from monovalent cations Na^+ and K^+ (Table 2). YM-1 and YM-2 slurries contained similar concentrations of SO_4^{2-} (643 and 433 μM , respectively), which were ~ 2 times greater than other slurries. Total soluble Si was highest in sample BH-5 (290 μM Si_{TS} at the final time point) and was lowest in samples BSS-1 and BH-4 (data not presented). The relative percentages of major ions in rock:water extracts differed from stream waters in that, generally, mineral extracts contained a greater percentage of Na^+ and K^+ , while stream waters at Big Sky contained 55% Ca^{2+} and 40% Mg^{2+} relative to total cation concentration.

[23] Nitrate (NO_3^-) concentrations in five of the eight rock-water slurries were significantly different from concentrations generated by the silica bead control at the 3 day time point based on paired Student's t tests (Table 2). The highest NO_3^- concentration was measured in the YM-1 slurry, which produced ~ 435 μM NO_3^- (Figure 2). Conversely, BSS-2, BSS-3, and BH-5 slurries contained near detection limit levels of NO_3^- that increased between 0 h and 3 days but declined after 3 days. The apparent decrease in NO_3^- for sample BSS-2 was accompanied by a slight increase in NH_4^+ at 30 days (Figure 2). Sample BSS-2 is a fissile shale, and its outer surfaces were not removed by rock sawing, so the decrease in NO_3^- concentration in YM-2 is likely the result of biotic contamination of this rock powder.

[24] Ammonium (NH_4^+) remained below detection limit (5 ppb) in the silica bead control over all five time points. The highest concentrations of NH_4^+ were detected in YM-2 (shale), BH-11 (gypsum-rich rock), and BSS-1 (mudstone) mixtures (35.2 μM , 31.3 μM , and 34 μM , respectively) (Table 2). Ammonium comprised the majority of TDN in BSS-1, BSS-2, BH-4, and BH-11 sample bottles at all time points (Figure 2), while TDN was dominated by NO_3^- in YM-1 and YM-2 treatments. The source of N as either organic (e.g., kerogen), NH_4^+ , or NO_3^- is not certain based on leachate results but is discussed further in section 3.4. The difference between TDN and inorganic N indicates a portion of TDN composed of organic forms of N, and/or some analytical error between two types of N measurement. The organic N fraction of the YM slurries was 14–35% of TDN, while the organic fraction was higher in all other samples (Table 2, Figure 2).

[25] Mean dissolved inorganic carbon (DIC) concentrations ranged from 20.5 to 2505 μM across all rock-water extracts and was 66 μM in the silica bead control after 30 days (Table 2). Generally, DIC concentrations were greatest at the final time point (30 days). DIC concentrations were greatest in slurry mixtures YM-1, YM-2, and BSS-1 (producing 2.17, 2.50, and 1.99 μM C, respectively), which are all rocks from the Kootenai Formation (Kk). Congruent dissolution was observed for the ankerite based on the approximate 1:1 relationship between $\text{Ca} + \text{Mg}$ versus DIC, while incongruent dissolution of silicate minerals was evidenced by the comparison between bulk mineralogy and base cation production (Table 2).

[26] Three types of slurries were identified based on the total dissolved C (TC) in relation to TDN (Figure 3). BH-11, BH-5, BH-4, and BSS-2 samples produced less than 1000 μM total dissolved C and less than 100 μM TDN across all time points. BSS-1 (mudstone) and BSS-3 (Thermopolis sandstone) samples produced similar concentrations of TC (~ 1900 to 2300 μM) and low (> 100 μM) TDN. The YM-1 (limestone) released the greatest TC and TDN with a positive linear correlation between the two constituents (Figure 3). This sample mixture represents a lithology that serves as a source of both DIC and NO_3^- .

[27] Organic C in all slurries except the Si bead control, BSS-3, and BH-5 was positively correlated to TDN similar to the total C trend in Figure 3. The ratio of DOC:N ranged from 2.4 in the YM-1 slurry to 51.7 in the BSS-3 slurry (Table 2), and DOC:TDN ratios in samples YM-1, BSS-1, and BH-11 were lower than the Redfield ratio (106:16, or

Table 3. Mean Surface Area-Normalized Concentrations Nitrogen Species Produced by Rock Powder Slurries

Sample	Surface Area ($\text{m}^2 \text{g}^{-1}$)	NO_3^- ($\mu\text{mol L}^{-1} \text{m}^{-2}$)	NH_4^+ ($\mu\text{mol L}^{-1} \text{m}^{-2}$)	TDN ($\mu\text{mol L}^{-1} \text{m}^{-2}$)
Si Control	5.00	0.003	0.002	0.011
YM-1	1.10	8.309	0.260	10.7
YM-2	2.10	0.510	0.266	1.09
BSS-1	5.96	0.003	0.163	0.24
BSS-2	1.09	0.183	0.459	0.97
BSS-3	4.78	0.023	0.003	0.08
BH-4	0.69	0.034	0.382	1.75
BH-5	0.88	0.024	0.200	0.56
BH-11	1.75	0.004	0.439	0.69

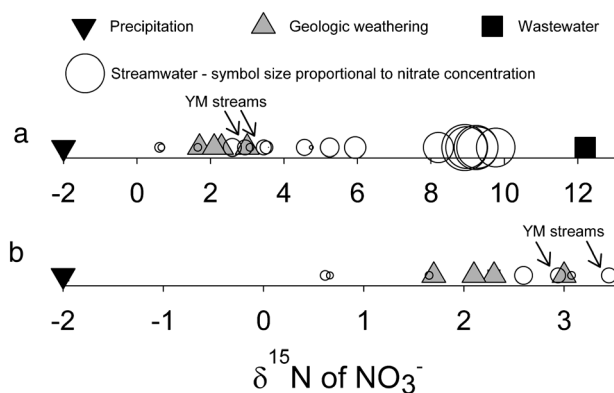


Figure 4. Results of $^{15}\text{N}\text{-NO}_3$ analyses of snow, stream waters, and mineral weathering experiment slurries. The $^{15}\text{N}\text{-NO}_3$ values for three different slurry samples had a small range of $\delta^{15}\text{N}\text{-NO}_3$, from 1.9 to 3.0, which fell within the normal range for soils. The concentration of NO_3^- in stream waters, represented by circle size, ranged from 0.05 to 75 μM , where headwaters generally contained the lowest NO_3^- and waters near sewage effluent contained the greatest NO_3^- concentration. Several stream water isotopic signatures overlapped with $^{15}\text{N}\text{-NO}_3$ from mineral weathering, including Yellow Mule stream waters ($\delta^{15}\text{N}\text{-NO}_3 = 2.9$).

6.6), a common ecological indicator for nutrient limitation [Schlesinger, 1997]. Median DOC:TDN for all synoptic sampling sites across the West Fork Watershed during the 2005–2007 study period was 2.26 in winter (dormant) season, increased to 9.89 during snowmelt, and was 24.55 during summer (K. G. Gardner and B. L. McGlynn, in preparation, 2013). The mean DOC:TDN from rock slurries is 9.4; however, the slurries that generated NO_3^- above 30 μM have lower DOC:TDN ratios that are close to the winter baseflow stream water ratio.

[28] Nitrate concentration normalized to surface area in the YM-1 slurry was $9.8 \mu\text{mol L}^{-1} \text{m}^{-2}$ at the 3 day time point, with a mean production (over all time points) of $8.3 \mu\text{mol L}^{-1} \text{m}^{-2}$ (Table 3). The lowest values for normalized NO_3^- production were measured in the BSS-1 (mudstone) slurry, which generated $0.006 \mu\text{mol L}^{-1} \text{m}^{-2}$ at 3 days with a mean production of $0.003 \mu\text{mol L}^{-1} \text{m}^{-2}$. Surface area correction generally did not alter the order of slurries for N production magnitude (Tables 2 and 3). Assuming that differences in concentration between time points indicate changes in 0.1pt?>solute production over time, the amount of NO_3^- production in YM-1 bottles was highest between 0 h and 1 h ($609 \mu\text{mol NO}_3^- \text{m}^{-2} \text{h}^{-1}$) and was $12.1 \mu\text{mol NO}_3^- \text{m}^{-2} \text{h}^{-1}$ between 1 h and 24 h time points.

[29] Comparisons of aqueous chemical composition between rock:water extracts and stream waters from the same areas provided some insights toward a potential mineral source of stream water NO_3^- in the watershed. Yellow Mule tributaries to the South Fork exhibited elevated NO_3^- (~3 times higher than undisturbed headwaters at Beehive Basin) in stream water as compared to other pristine headwater streams across the greater WFW [Gardner and McGlynn, 2009; Gardner et al., 2011]. Concentrations of NO_3^- measured during base flow and snowmelt in the Yellow Mule catchments indicate that the difference between Yellow Mule stream water NO_3^- and other pristine streams could

be a product of mineral dissolution. While solute production as a result of geochemical weathering might not reach equilibrium in mountain stream systems such as the West Fork Watershed (WFW), there was good evidence for equilibrium in closed-headspace laboratory experiments within 3–7 days (e.g., Figure 2). These results indicate that the concentrations generated from our experiments represent a likely upper limit to the solutes generated by these rocks in Big Sky. Rock weathering can be used to constrain estimations of chemical flux for the WFW system, including the maximum rate of N production by mineral weathering of mechanically weathered rocks [Gardner et al., 2011]. The maximum rate of NO_3^- production from each rock type has been utilized, based on their areal extents within each subwatershed, in an N export model to determine sources of NO_3^- to streams [Gardner et al., 2011]. The mixing model results show that soil/geology contributes the vast majority of NO_3^- to the South Fork compared to atmospheric inputs and anthropogenic waste year-round. All streams studied showed the largest percentage of N was from a soil/geology source during snowmelt [Gardner et al., 2011].

3.4. Stable Isotope Ratios of N and O⁻

[30] The natural abundances of $^{15}\text{N}\text{-NO}_3^-$ in snow cores and 22 stream waters samples collected in February 2007 were compared to four isotope signatures selected from rock-water experiment: samples YM-1 at the 1 h and 30 day time points (Kootenai ankerite), YM-2 (Kootenai shale), and BSS-2 (Kootenai sandstone) (Figure 4). Snow collected from Beehive Basin contained $\delta^{18}\text{O}\text{-NO}_3$ of +76.5‰ and $\delta^{15}\text{N}\text{-NO}_3$ of -2.0‰. The values for snow and stream waters are within the range of ^{15}N abundance reported for lake sites in Grand Teton, Rocky Mountain, and Glacier National Parks: -4 to +4‰ $\delta^{15}\text{N}\text{-NO}_3$ [Nanus et al., 2008]. Values of $\delta^{15}\text{N}\text{-NO}_3$ in stream samples ranged from +0.6 to 3.5‰ in undeveloped headwaters and one developed headwater site (at the base of Big Sky ski area) and were +4.5 to 9.8‰ in stream waters draining more developed watersheds (septic systems) or wastewater-influenced stream sites (Middle Fork) [Gardner and McGlynn, 2009]. An increase in the ^{15}N isotope along a development gradient was observed at our study site: higher concentrations of NO_3^- generally coincided with a more positive isotopic signature for NO_3^- (Figure 4). The elevated $\delta^{15}\text{N}\text{-NO}_3$ values in stream waters on the lower Middle Fork were likely influenced by the 12.2‰ $\delta^{15}\text{N}\text{-NO}_3$ source from Big Sky Water and Sewer District wastewater which is used as irrigation water on the adjacent golf course ~1 km upstream from the confluence of the Middle Fork and South Fork. Big Sky, Beehive, and North Fork stream $\delta^{15}\text{N}\text{-NO}_3$ signatures were 2.59, 3.58, and 0.66‰, respectively. Water collected at the West Fork Watershed outlet near the confluence with the Gallatin River contained $\delta^{15}\text{N}\text{-NO}_3$ of 8.2‰, indicating that the NO_3^- in the West Fork was enriched in ^{15}N relative to upland headwater sites through the process of denitrification [Kendall, 1998; Groffman et al., 2006].

[31] The range of $\delta^{15}\text{N}\text{-NO}_3$ values in all rock-water extracts analyzed were between 1.9 and 3.1‰, which is within the large observed range for natural soil extracts [Kendall, 1998; Clark and Fritz, 1997]. Standard deviations of $\delta^{15}\text{N}\text{-NO}_3$ were less than 0.18‰ for all samples (Table 2). YM-1 showed a slight increase in $\delta^{15}\text{N}\text{-NO}_3$, from 2.3 to 3.0, at the 1 h time

point versus the 30 day time point. The $\delta^{18}\text{O}\text{-H}_2\text{O}$ among the three slurries analyzed ranged from +5.1 to 5.3‰. The source of O-NO_3^- in rock slurries is unclear, but two scenarios are likely: either NO_3^- (or NO_x) is present in rock and the $\delta^{18}\text{O}\text{-NO}_3^-$ from rock-water slurries represents water and atmospheric isotopic conditions during the Cretaceous period; or NO_3^- is formed by oxidation of lithified organic matter or NH_4 [Holloway *et al.*, 2011]. The mechanism for nitrogen oxidation results in two O atoms in the NO_3 molecule with the $\delta^{18}\text{O}$ of H_2O and one atom with isotopic signature of atmospheric O_2 (+23.5‰) [Casciotti *et al.*, 2010]. Assuming fractionation from N oxidation is negligible, the $\delta^{18}\text{O}\text{-NO}_3^-$ resulting from reaction of local ultrapure water and atmospheric O_2 can be calculated as reported by Granger *et al.* [2008]. The calculated $\delta^{18}\text{O}\text{-NO}_3$ resulting from N oxidation using the mean ultrapure water signature used in the experiments (-18.8‰ $\delta^{18}\text{O}\text{-H}_2\text{O}$) is -4.6‰ . These values are considerably lower than measured values from the slurries, suggesting that either a different process occurs or that the $^{18}\text{O}\text{-H}_2\text{O}$ may be fractionated prior to reaction with N. Nitrification and/or denitrification within the rock:water slurries may therefore be an unlikely process. This allows us to suggest that a NO_3 may be an impurity in ankerite matrix in the Kootenai limestone and the other Cretaceous rocks analyzed [Kellogg and Williams, 2005].

[32] The abiotic chemical weathering experiments conducted in the laboratory resulted in ^{15}N isotopic signatures within the range of pristine stream waters from Big Sky (Figure 4) and reported values for soil organic matter [Clark and Fritz, 1997] or soil N reported by Kendall [1998]. A small range in rock-water extract $^{15}\text{N}\text{-NO}_3$ signatures was observed despite the different rock slurries analyzed (limestone, shale, and sandstone). The $\delta^{15}\text{N}\text{-NO}_3$ signatures of the two Yellow Mule tributary stream waters where naturally elevated concentrations of NO_3^- have been measured during base flow were 2.9 and 3.4‰ $\delta^{15}\text{N}\text{-NO}_3$ (Figure 4). These values are within 1.0‰ of the YM-1 slurry $\delta^{15}\text{N}\text{-NO}_3$ signature. Values of $\delta^{18}\text{O}\text{-NO}_3$ were negative for all stream samples, and a slight fractionation could be observed for the wastewater sample from the 2:1 relative increase in $\delta^{15}\text{N}$ versus $\delta^{18}\text{O}$ [Bottcher *et al.*, 1990; Kendall, 1998].

[33] The $\delta^{15}\text{N}\text{-NO}_3$ values (1.9 to 3.1‰) generated from the rock-weathering experiment separate headwater streams from those downstream of development (wastewater influences) and establish a background $^{15}\text{N}\text{-NO}_3$ signature consistent with watershed geology (Figure 4). These results are not conclusive for a geologic N weathering source of N at Yellow Mule streams but support the concept that chemical weathering of minerals in this location provides a distinct isotopic signature of $\text{NO}_3\text{-N}$. One can also postulate that biological fractionation in the WFW system can be explained by $^{15}\text{N}\text{-NO}_3$ values above the rock-weathering signal ($\sim 3.0\text{‰}$). The enrichment of the heavier isotope is typically due to fractionation during denitrification (dissimilatory nitrate reduction) [Clark and Fritz, 1997; Böhlke *et al.*, 2006]. Consistent with our results, Goodale *et al.* [2009] found $^{15}\text{N}\text{-NO}_3$ from shale weathering in the Susquehanna River system in New York ranged from -2.5 to 0.5‰ which averaged several per mille below the surface water signatures.

[34] Other reported values for $\delta^{15}\text{N}$ content in rock fall in the $\delta^{15}\text{N}$ range of -4 to $+5\text{‰}$ [Faure, 1986]. Marine sediment $\delta^{15}\text{N}\text{-NO}_3$ values range $+6.8 \pm 4.1\text{‰}$, but lacustrine sediments occupy a smaller window, from 2.7 to 5.5‰

[Wada *et al.*, 1975; Faure, 1986]. Our Kootenai nitrogen source signatures were consistent with both lacustrine and marine sediments. Rau *et al.* [1987] found a potential link between $\delta^{15}\text{N}$ and the origin of organic matter: Cretaceous sequences with low organic concentrations and $\delta^{15}\text{N}$ values in $+1.45\text{--}5.5\text{‰}$ range were interpreted to reflect a marine origin or are a product of diagenesis. A recent study on rocks, clays, and hot springs deposits in nearby Yellowstone National Park showed a wide range in $\delta^{15}\text{N}$ values ($+0.2$ to $>24\delta^{15}\text{N}$), while marine-origin rocks ranged from $\delta^{15}\text{N}$ 1.6 to 6.6‰ [Holloway *et al.*, 2011]. Our study shows that leachate isotopic signatures are directly comparable to those of whole rock digestions.

[35] Comparison of isotope data from the mineral weathering study with local stream isotope signatures and chemistry data has been the basis for attributing sources of N and quantifying nutrient retention and export processes across the West Fork watershed (WFW). In a related WFW study, $\delta^{15}\text{N}\text{-NO}_3$ for sampled precipitation, mineral weathering, and mean stream waters were compared during the winter (dormant season), snowmelt, and summer (growing season) (K. G. Gardner and B. L. McGlynn, in preparation, 2013). WFW stream water $\delta^{15}\text{N}\text{-NO}_3$ signatures in largely undisturbed watersheds where rock-weathering samples collected were within the range of rock-weathering $\delta^{15}\text{N}\text{-NO}_3$ during both winter and summer months. However, strongly wastewater-impacted watersheds exhibited stream water $\delta^{15}\text{N}\text{-NO}_3$ signatures indicative of wastewater loading, especially during winter months. Streams across the WFW exhibited a decrease in $\delta^{18}\text{O}\text{-NO}_3$ from snowmelt to summer consistent with nitrification (K. G. Gardner and B. L. McGlynn, in preparation, 2013). Our observed experimental mineral weathering isotopic composition is strongly consistent with observed stream water N composition, especially during winter months when stream water N predominantly reflects processes occurring from reaction of stored water with mineral soils of low biological activity [Campbell *et al.*, 2000, 2002].

4. Conclusions

[36] The stream water chemistry of the West Fork watershed suggests that a lithologic source of N exists within the catchment. Elevated NO_3^- concentrations at South Fork headwater sites, relative to other undisturbed stream sites, do not appear to be a result of human activity or residential and commercial development. Our stream water chemistry monitoring data and stable isotope data from water samples and laboratory experiments indicate that inorganic fixed N is generated from mineral weathering reactions with sedimentary and metasedimentary rocks in the WFW. Our controlled rock-weathering experiments indicate that sedimentary rocks, including sandstones and impure limestones (e.g., ankerite) from the Kootenai Formation, are a likely source of dissolved N to stream and ground water in the West Fork of the Gallatin watershed.

[37] Our results reinforce the value of coupled laboratory and field-based investigations to quantify the sources, processes, and pathways associated with nutrient movement through ecological systems. For example, our laboratory rock-weathering experiment based rates of N production on each rock type. These comparative analyses allowed for

quantification of surface area-normalized nitrate production across rock types to constrain maximum mineral weathering nitrate release across the WFW [e.g., *Holloway et al.*, 2011; *Gardner et al.*, 2011].

[38] While other studies have investigated N production from geologic sources, few studies have examined the role of weathering on the production of N across alpine and headwater catchments. Alpine headwater streams can be particularly sensitive to nutrient loading, given that they are often strongly nutrient-limited ecosystems.

[39] Headwater watersheds also set the initial nutrient status for downstream river networks that can comprise more than 90% of the streams within a given river network and nearly half of all rivers miles in the U.S. [*Leopold et al.*, 1964]. The WFW is a distant headwater of the Mississippi River supplying water to downstream communities and millions of people for drinking water and recreational use. Studies of N and/or C production are therefore vital for water resource management and water quality attribution. In the West Fork watershed, bedrock geology was an explanatory variable in seasonal spatial linear models of synoptically sampled stream water nitrate concentrations from WFW for winter, summer, and fall. It was further found to be a significant component in subsequent N export modeling of the watershed [*Gardner and McGlynn*, 2009; *Gardner et al.*, 2011]. The results presented herein further indicate that rock weathering is a source of stream water N in the West Fork watershed and inform water quality assessment, total maximum daily load development, and the relative influences of natural and anthropocentrically derived N sources across this developing mountain watershed.

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