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#### Notes



# Calcite precipitation driven by the common ion effect during groundwater–surface-water mixing: A potentially common process in streams with geologic settings containing gypsum

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## ABSTRACT

We report the results of a synoptic (“snapshot”) sampling of inorganic and isotopic geochemistry of surface water and groundwater during base flow in Red Canyon Creek watershed (Wyoming, USA) to evaluate how mixing of waters and geochemical processes modify stream-water chemistry. Our synoptic approach of studying the geochemistry of a stream mimics and has the same strengths of that widely used to characterize geochemical processes in groundwater systems. Gypsum dissolution, carbonate precipitation, and the influx of tributary and groundwater all affect Red Canyon Creek stream-water chemistry. Identical ranges of hydrogen and oxygen isotopes show good hydraulic connection between surface water and shallow groundwater. In contrast,  $\delta^{34}\text{S}_{\text{SO}_4}$  values of groundwater ( $15.2\text{‰} \pm 1.6\text{‰}$ ) and surface water ( $11.1\text{‰} \pm 1.6\text{‰}$ ) reflect sulfate mostly contributed by gypsum dissolution. Calcium contributed by gypsum dissolution causes calcite to rapidly precipitate in crusts observed in the streambed. This process occurs even though residence time of water in the stream is orders of magnitude less than that found in groundwater systems showing the same kind of common ion effect. Although microbes oxidize organic matter by sulfate reduction behind beaver dams and in the hyporheic zone, too little of this water reaches the stream to measurably affect the sulfur isotopic signature of its water. The results of this study suggest that calcareous accumulations in the fluvial sedimentary record, in association with gypsum, may pos-

sibly be paleohydrologic proxies for environments where mixtures of surface water with different chemical composition occurred.

## INTRODUCTION

The chemical composition of waters can be used to determine sources of elements, mineral weathering, water mixtures, and geochemical reactions (Bailey et al., 2004; Crandall et al., 1999; Rahman et al., 2006; Fitzhugh et al., 2001; Frey et al., 2007; Liu et al., 2004; McDonnell et al., 1991; Meixner et al., 2004; Winter et al., 1998). Except for a few long-term ecological study sites (e.g., Hubbard Brook, New Hampshire), research on small-order streams has generally focused on the variability of streamflow and water geochemistry at the base of watersheds to integrate processes within them (e.g., Rahman et al., 2006; Hooper and Shoemaker, 1986; Rose, 1996; Siegel and Pfannkuch, 1984). Although numerous small-scale studies have been done to understand nutrient cycling and trace metal geochemistry within watersheds (Fanelli and Lautz, 2008; Lautz and Siegel, 2007; Mulholland et al., 2004; Triska et al., 1989), synoptic (“snapshot”) studies of the ways in which major solutes in streams change along full reaches are rare. At a very large scale, a synoptic study of rivers in the Western Siberian lowlands of Russia was able to characterize sources of dissolved inorganic carbon, sulfur, and other solutes (Frey et al., 2007). However, because the rivers studied were so large, any products of chemical reactions within the rivers that affected major solute chemistry were hard to directly identify, and had to be inferred by theoretical considerations.

In this paper, we explore how stable isotope ratios and concentrations of major solutes can be used to characterize mixing of waters and

geochemical processes in Red Canyon Creek, Wyoming, USA, a small watershed in the Wind River Range of Wyoming transecting marine and terrestrial sedimentary rock formations characterized by minerals that react orders of magnitude faster than do silicate minerals (Bethke, 1996; Langmuir, 1997). Most similar-sized watersheds that have been historically studied, many to address the effects of atmospheric acid deposition on surface waters, are underlain by silicate rocks that weather too slowly to reach equilibrium with solid phases that control major solute concentrations (e.g., Bricker et al., 1983; Oliva et al., 2003; Siegel, 1981; Velbel and Price, 2007). Because of the faster reaction rates of minerals associated with marine sedimentary rocks, particularly calcite and gypsum, we can test the hypothesis that it is possible to identify multiple sources for major solutes and mixing dynamics in stream water as it moves from headwaters to mouth, and it is also possible to identify potential reaction products that affect major solute concentrations.

Major ion chemistry and stable isotope ratios are widely used to calculate source water mixing during stormflow. For example, chloride is widely used as a conservative tracer for hydrograph separation (Machavaram et al., 2006; Peters and Ratcliffe, 1998). Hydrogen (H) and oxygen (O) isotopes are particularly useful as source water tracers because H and O isotopic composition of stream water generally retains its distinctive isotopic signature unless it mixes with waters of different isotopic compositions (Kendall and McDonnell, 1998; Sidle, 1998). Stable isotopes of carbon ( $\delta^{13}\text{C}$ ) in dissolved inorganic carbon (DIC) and sulfur ( $\delta^{34}\text{S}$ ) in sulfate ( $\text{SO}_4^{2-}$ ) also can be used to identify different sources of the solutes, but the isotopic composition of these solutes can also be altered by both

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chemical (e.g., calcite precipitation) and biological (e.g., bacterial sulfate reduction) reactions.

Our research was designed to identify mixtures of tributary and groundwater discharge, and to investigate geochemical processes that affect major solute chemistry, specifically the effects of gypsum dissolution, carbonate precipitation, and sulfate reduction, from the variability of isotopic compositions and major ion concentrations along Red Canyon Creek watershed during low-flow conditions.

Much research has been done on the common ion effect in groundwater systems where residence time of water usually is factors to orders of magnitude longer than in streams (e.g., Langmuir, 1997). We explore how this effect may occur in a fast-moving stream where waters of different chemical composition mix. In particular, we investigate whether the introduction of calcium sulfate water to a normally carbonate-dominated stream at near-neutral pH can lead to rapid precipitation of calcite, much

as can happen with rapid degassing of carbon dioxide (e.g., Herman and Lorah, 1987; Pentecost, 2005; Siegel et al., 2004). If so, then this process may be expected elsewhere where sulfate-rich waters from dissolving evaporites enter similar carbonate-dominated streams, either along the Rocky Mountain front or elsewhere. Moreover, recognition of this process may lead to better recognition of paleohydrology conditions in the past where calcareous accumulations may be associated with evaporative minerals in the geologic record.

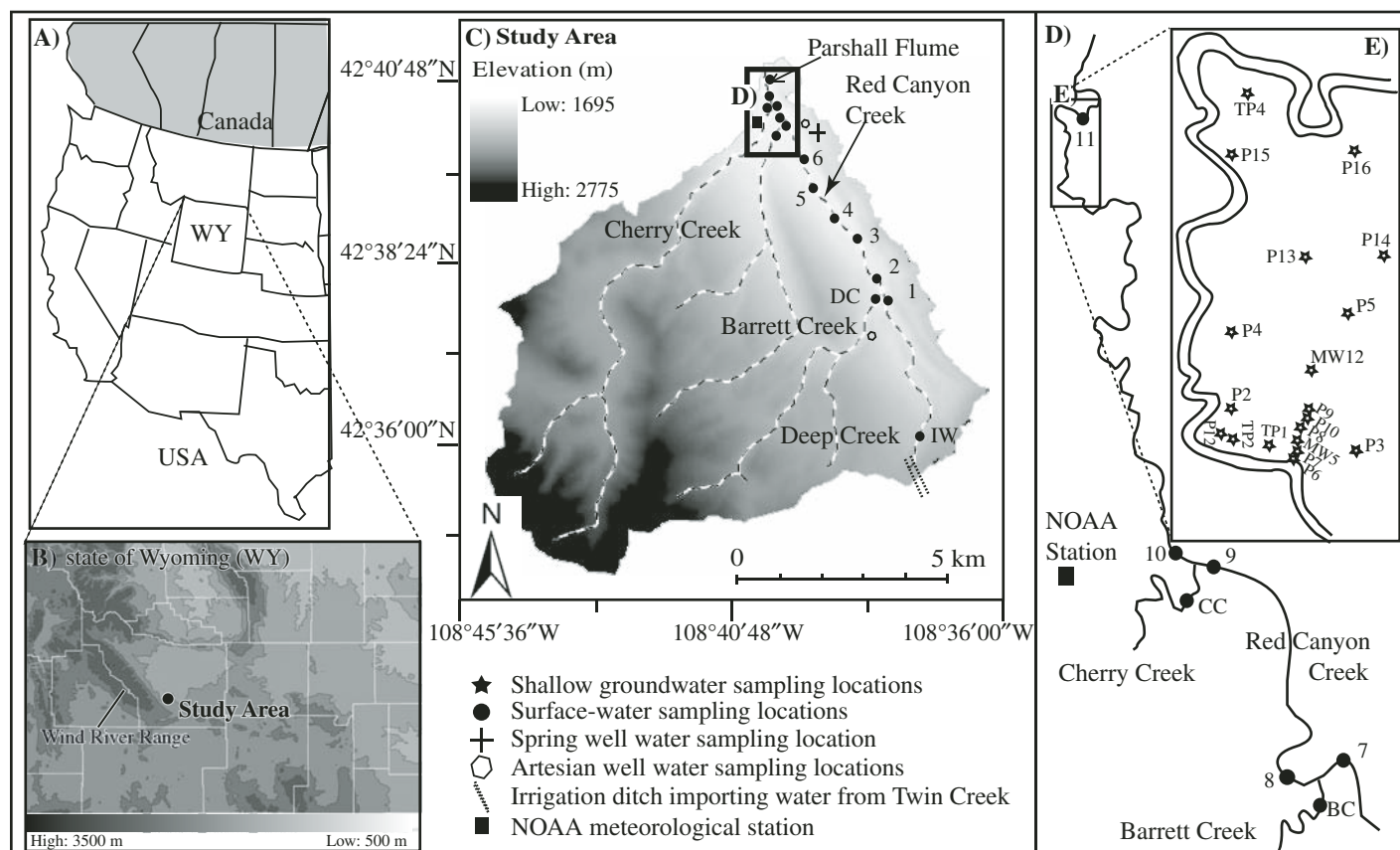
## GEOLOGIC AND HYDROLOGIC SETTINGS

### Current Geologic and Hydrologic Settings

Red Canyon Creek, a third-order stream located on the southeastern flank of the Wind River Range, lies in a transitional climate zone between the high altitude of the Wind River

Range and the adjacent desert in Wyoming, USA (Figs. 1A and 1B). The Nature Conservancy (TNC) of Wyoming owns the majority of the Red Canyon Creek watershed and manages the site for raising cattle and sustaining natural ecosystems (The Nature Conservancy, 2008).

The creek, ~10 km in length and flowing in north-northwest direction, discharges to the Little Popo Agie River. In general, between April and August, irrigation water from Twin Creek, located across the Red Canyon Creek watershed divide, is diverted into the Red Canyon Creek basin through a rectangular-shaped concrete irrigation channel at the top of the watershed (Fig. 1C). This water constitutes less than 10% of the water discharging in the entire creek. The ~80 km<sup>2</sup> watershed includes three major tributaries, Deep Creek (DC), Barrett Creek (BC), and Cherry Creek (CC), all of which are located on the western side of the creek valley (Fig. 1C). The elevation of the watershed ranges from 1700 to 2800 m above sea level (asl; Fig. 1C).



**Figure 1.** Site maps showing (A) the location of Wyoming State; (B) the study area on the southeastern side of the Wind River Range on the elevation map of Wyoming State (modified from <http://geology.com/state-map/wyoming.shtml>); and (C) Red Canyon Creek watershed and synoptic sampling locations within the watershed. Three tributaries, Cherry, Barrett, and Deep Creeks, are located on the western side of the valley. (D) The base of the Red Canyon Creek watershed with surface-water sampling locations. (E) Detailed array of groundwater sampling locations in the meadow close to the mouth of the creek (modified from fig. 1 in Lautz and Siegel, 2006). NOAA—National Oceanic and Atmospheric Administration.

Deep Creek joins Red Canyon Creek close to its head of origin, whereas Barrett and Cherry Creek join Red Canyon Creek near the base of the watershed. Red Canyon Creek water is mostly supported by the tributary discharges.

Red Canyon Creek watershed has typical geomorphic features of low-order streams draining hogback regions in the Rocky Mountain Range, e.g., steep headwaters (~7.5%) through a narrow channel leading to shallower gradients (<2.0%) in broad meanders. A detailed description of the watershed can be found in Lautz and Siegel (2006). The stream channel width ranges from ~1.5 to 3.0 m and depth ranges from 0.15 to 0.35 m during base-flow condition.

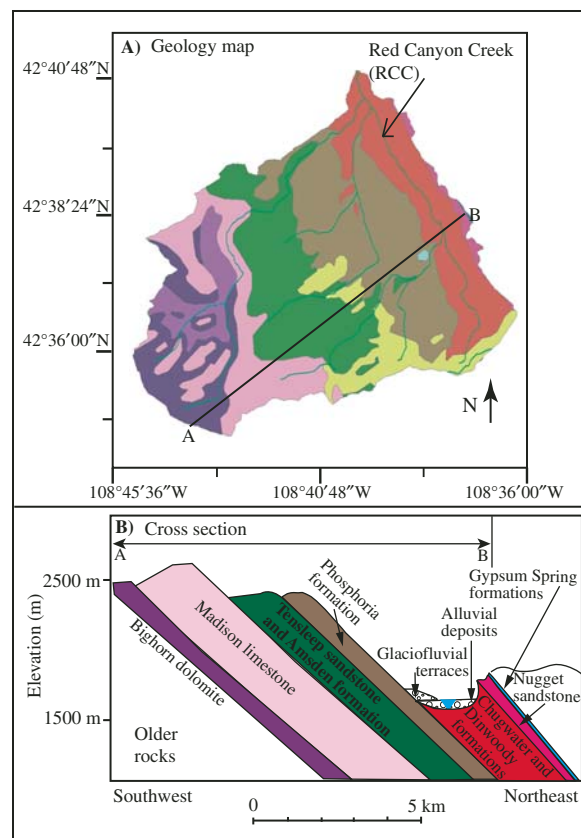
The watershed receives on average ~42.5 cm of precipitation per year (NOAA, 2008), with most falling as snow. About 40% precipitation falls during spring months (between March and May), coincident the timing of the snowmelt. Streamflow has been recorded hourly since August of 2005 at a Parshall flume equipped with two pressure transducers at the mouth of the watershed (Fig. 1C).

### Geologic History

The present configuration of Red Canyon Creek watershed formed from processes that involved pre-Pleistocene nonglacial and Pleistocene proglacial erosion into rocks of the Triassic-age Chugwater and Dinwoody Formations, which consist of red gypsiferous siliciclastic rocks (Love, 1948) overlain in the southeastern part by the Nugget Sandstone and the Gypsum Springs Formation. These rocks form the eastern crest of the watershed (Fig. 2). The most notable geomorphic feature of Red Canyon is the imposing dip slope of the Permian-age carbonate, the Phosphoria Formation along its west wall, and the glaciofluvial terraces that dominate the canyon floor. Further upslope from the Phosphoria Formation, sandstones of the Pennsylvanian-age Amsden and Tensleep Formations are topped by the Mississippian Madison Limestone and the Ordovician Bighorn Dolomite, which form the crest of the watershed divide on the western side of the watershed (Fig. 2).

The morphology of Red Canyon has probably remained essentially the same since its initial excavation by the proto-Red Canyon and Cherry Creek as they flowed into the Little Popo Agie River (the Little Popo Agie is the trunk stream that controls the local base level for the entire Red Canyon watershed). As these streams cut deep canyons into the more resistant Tensleep and Phosphoria Formations, and Madison Formation, they encountered the less resistant sandy shale of the Chugwater Group, which allowed the streams to continually erode at the base of

**Figure 2. (A) Geology map of the Red Canyon Creek watershed and (B) a geologic cross section A-B showing the watershed, which extends west of Bighorn Dolomite and Madison Limestone to east of Gypsum Spring Formation.**



the Chugwater while maintaining the structural surface of the Phosphoria Formation. The Madison, Tensleep, and Phosphoria Formations form nearly vertical cliffs in the headwater segments of the larger tributaries. This erosional process has caused the dip slope formed by the upper Phosphoria Formation to dominate the topography along the western slope of the canyon. East of the Phosphoria dip slope, a sequence of glaciofluvial terraces dominates the floor of Red Canyon. Each of the glaciofluvial units contains a two-stage depositional sequence. At depth, a cobble-rich deposit is incised into either the sandy-silty Chugwater material or into a previously existing alluvial unit predominantly composed of Chugwater materials.

### METHODS

#### Field Sampling

Fifty water samples were collected in June and July of 2005 and 2006 when the streamflow was low. This low-flow condition provides a perfect flow regime, where the geochemical signatures will be most strongly expressed, and slower flow rate allows additional time for water-rock interaction to proceed and enhance end-member geochemical fingerprints. Surface-water samples

were collected from 15 locations along the Red Canyon Creek main stream and its tributaries between 30 June and 1 July 2006 for both solutes and isotopic compositions of hydrogen and oxygen, carbon in dissolved inorganic carbon, and sulfur in sulfate (Figs. 1D and 1E). Thirty-two groundwater samples were collected from monitoring wells ( $n = 6$ ) and shallow piezometers ( $n = 13$  and two piezometers clusters: P12-1 to P12-6 and P15-1 to P15-7) in the summers of 2005 and 2006 in the meadow at the base of the watershed (Fig. 1E). The 2005 groundwater samples were collected for major chemical analysis only, and in 2006, groundwater samples were subsequently collected for stable isotopes to characterize major geochemical processes. Wells and piezometers were installed by standard methods, including sand packing and grout (Fetter, 1993), during the past 8 yr as part of the University of Missouri's Branson Geology Field Camp. They were constructed using 2-cm-diameter PVC pipe casing to depths of between 2.1 and 6.1 m, with the bottom screen at an interval of 0.6–3.0 m (Lautz and Siegel, 2006). Groundwater discharging from the lowermost terrace mostly consists of sediments derived from the Chugwater, Dinwoody, and Phosphoria Formations. Due to site accessibility for well installation, shallow groundwater samples

were mostly collected at the base of Red Canyon Creek watershed. Three samples from two artesian wells penetrating 500–1000 m below land surface, which obtain water probably from the Amsden Formation, and one spring from Chugwater Formation within the watershed were also collected (Fig. 1C).

### Hydrologic Measurements

Stream discharge measurements were taken at each sampling site using either velocity-area technique or dilution gauging. At the top of Red Canyon Creek watershed, where minor irrigation water from the Twin Creek is diverted into the basin, we used the velocity and cross-sectional area method to estimate stream discharge because the regular irrigation channel was ideal for this type of measurement. At other surface-water sampling locations, we used a salt-slug tracer test to calculate stream discharge. We injected a known amount of salt (NaCl) into the stream and monitored specific conductance changes downstream of the injection site. We then calculated the  $\text{Cl}^-$  concentration from observed specific conductance data using established linear relationships between  $\text{Cl}^-$  concentration and specific conductance at each sampling site. The  $\text{Cl}^-$  breakthrough curve was used to calculate the stream discharge based on mass conservation (Eq. 1). Using the equation for conservation of mass, we calculated the stream discharge rate from the total mass of the salt injected ( $M_i$ ) and integration under the breakthrough curve ( $A_c$ ) (Kilpatrick and Cobb, 1985).

$$Q_{\text{stream}} = \frac{M_i}{A_c} = \frac{C_i \cdot V_i}{A_c} \quad (1)$$

The total mass injected is a function of the concentration of the salt injection solution ( $C_i$ ) and the total volume of the slug injected ( $V_i$ ). We calculated the area under the breakthrough curve ( $A_c$ ) by multiplying each recorded concentration by the sampling interval.

### Chemical Analysis

Water temperature, pH, and specific conductance in the waters were measured in situ. The pH meter and conductance meter (WTW 340i multiparameter meter) were calibrated before use each day. All the samples were collected and analyzed for major ions and H and O isotope ratios. Selected samples were analyzed for stable isotope ratios of carbon (DIC) and sulfur (sulfate). Carbonate, bicarbonate concentrations, and DIC of surface-water samples in 2006 were determined immediately after sampling by standard titration. In 2005, we determined DIC

in groundwater by electrochemical difference (Drever, 1997; Mark et al., 2005) because sample volumes were small. Charge balances of surface waters were mostly within  $\pm 5\%$ , with a few exceptions up to 13%, so we are confident that our charge balance to estimate DIC for groundwater samples produced reasonable values.

Samples collected for cations were passed through 0.45  $\mu\text{m}$  hydrophilic polyvinylidene fluoride (PVDF) membrane filters and preserved by addition of 65%  $\text{HNO}_3$  to a level of 1% v/v. Samples were analyzed for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Sr}^{2+}$ , and Si using a Perkin-Elmer OPTIMA 3300DV ICP-OES (inductively coupled plasma–optical emission spectrometry) at State University of New York College of Environmental Sciences and Forestry (SUNY-ESF). Samples analyzed for  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  analysis were also passed through 0.45  $\mu\text{m}$  PVDF membrane filters and kept frozen before running them on the Dionex ICS-2000 Ion Chromatography (IC) system at SUNY-ESF.

Hydrogen, oxygen, and carbon isotope ratios were measured at the Environmental Isotope Laboratory at the University of Waterloo. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values were measured using the standard method with a Micromass IsoPrime-EA mass spectrometer (Drimmie and Heemskerk, 1993; Epstein and Mayeda, 1953). The isotopic ratios for oxygen and hydrogen are reported in standard delta notation ( $\delta$ ) relative to standard mean ocean water (SMOW). Analytical precision is estimated at 0.2‰ and 0.8‰ for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , respectively. Carbon-13 in total dissolved inorganic carbon (DIC) and carbon-13 in carbonate were measured on a Finnigan Delta-EA mass spectrometer. The carbon isotope ratio is reported in standard relative to the Peedee belemnite (PDB) with 0.2‰ analytical precision.

Sulfur isotope ratios of sulfate in stream waters and mineral gypsum were analyzed at the University of Calgary. Details of sulfur isotopic analysis can be found in Mayer and Krouse (2004) and Giesemann et al. (1994). Sulfur isotope ratios are reported relative to standard V-CDT (troilite from the Canyon Diablo meteorite) and with reproducibility better than  $\pm 0.3\%$ .

### Mineral Analysis

In the field, “coatings” were discovered on the surface of the streambed sediments. We tested to see if the precipitates were carbonate in the field with dilute acid (HCl) at several sampling locations. Encrustations sampled along the stream reaches were analyzed by X-ray diffraction using a PW 1729 X-ray diffractometer at Syracuse University for mineral compositions.

### PHREEQC Modeling

PHREEQC does a wide variety of low-temperature aqueous geochemical calculations (Parkhurst, 1995). We used PHREEQC to determine equilibrium states between waters and minerals and to evaluate on the ways in which mixing of waters change the chemical composition of the resulting mixed water sample.

First, the relative discharge of each tributary and groundwater was determined from our discharge measurements. We then used PHREEQC to calculate amounts of solutes in the mixed water samples according to the discharge percentage and solute concentrations of each water source, assuming no chemical reaction after mixing. We used the mean values for solute concentrations in the groundwaters collected in the detailed array in the meadow at the base of the creek (Fig. 1E). Modeled water chemistry was then compared to the measured values of the outlet water. Geochemical reactions were explored to account for the difference of solutes and isotopes between the modeled and measured values.

In addition, we used PHREEQC to calculate the saturation indices of each water sample between carbonate, gypsum, and other minerals to determine the extent to which waters were in equilibrium and whether waters could remain oversaturated with respect to minerals. The inputs to PHREEQC included pH, temperature, and chemical composition of each water sample. The inferred DIC concentrations calculated from the charge balance may have introduced uncertainties into the saturation index calculation, so we performed a sensitivity analysis on calculated saturation indices by increasing and decreasing DIC concentrations by 10%.

## RESULTS

### Hydrology

Streamflow of Red Canyon Creek varies throughout the year due to the spring snow-melt. The highest flow, on the order of a few hundred liters per second, occurs during late spring between April and May. During the summer (June to August), the headwater of Red Canyon Creek is supported by irrigation flow imported from Twin Creek, whereas water stored in terraces and wetlands supports tributary flow to the creek. At sampling, the discharge import from Twin Creek measured at the irrigation channel was only 8 L/s, or  $\sim 7.5\%$  of that measured at the mouth.

In June of 2006, downstream of the Red Canyon Creek headwaters, stream discharge increased from 8 L/s to 40 L/s at the confluence

of Deep Creek. Further downstream, Barrett Creek and Cherry Creek increased Red Canyon Creek flow by 8.3 L/s (16.2%) and 45.7 L/s (48.4%), respectively (Fig. 3A). These three tributary contributions to Red Canyon Creek primarily sustain streamflow to Red Canyon Creek and maintain perennial flow for the stream's ecosystems. In addition to the increase from tributary influx, 3–4 km upstream of the creek outlet and between Deep Creek and Barrett Creek confluences, there was an ~15% increase of streamflow, probably from groundwater discharge (Fig. 3A).

### Major Ion Chemistry of the Water

The first water entering Red Canyon Creek is minor irrigation water from Twin Creek. This water had a specific conductance of ~300  $\mu\text{S}/\text{cm}$  and was dominated by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  (Table 1). Approximately 2 km downstream and immediately before the confluence of Deep Creek, the total dissolved solids concentrations increased about three times, with an increase in DIC by less than a factor of 2, and increases were observed in calcium and sulfate by factors of 4 and 400, respectively (Fig. 3B; Table 1). These changes occurred without any measurable change in discharge, which remained the same at ~8 L/s (Fig. 3A).

Three major tributaries on the western side of creek valley had the dominant solutes of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$ , a pH of ~8.3, and specific con-

ductance of ~500  $\mu\text{S}/\text{cm}$  (Table 1). Major chemical changes in the creek occurred where three tributaries joined Red Canyon Creek (Fig. 3B). The most profound chemical change occurred at the Deep Creek (DC) confluence due to its significant contribution to downstream flow (~80%). Figure 3B also shows smaller changes in water chemistry at Barrett Cherry and Cherry Creek confluences.

Along the upper reach of Red Canyon Creek, where there was an ~15% increase in stream discharge from groundwater discharge, solute concentrations also changed (Fig. 3B; Table 1). For example, calcium and sulfate concentrations increased by 40% and 80%, respectively. Magnesium concentrations remained similar. In contrast, bicarbonate concentrations decreased by 12%.

Groundwater samples at the base of the watershed were dominated by  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ , and pH ranged between 7.1 and 7.8. The  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations varied from 1 to 9 mmol/L (Table 1).

### Isotope Compositions of Water and Dissolved Solutes

#### Oxygen and Hydrogen Isotope Ratio ( $\delta^{18}\text{O}$ and $\delta^2\text{H}$ )

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values for surface waters from the Red Canyon Creek watershed ranged from  $-19.1\text{‰}$  to  $-18.1\text{‰}$  and  $-144\text{‰}$  to  $-140\text{‰}$ , respectively, with mean  $\delta^{18}\text{O}$  values of

$-18.7\text{‰} \pm 0.3\text{‰}$  ( $n = 15$ ) and mean  $\delta^2\text{H}$  values of  $-142.3\text{‰} \pm 1.3\text{‰}$  ( $n = 15$ ), respectively (Table 2). The shallow groundwater samples from monitoring wells and piezometers had  $\delta^{18}\text{O}$  values ranging from  $-18.9\text{‰}$  to  $-18.1\text{‰}$ , with a mean value of  $-18.6\text{‰} \pm 0.2\text{‰}$  ( $n = 26$ ), and  $\delta^2\text{H}$  values from  $-144\text{‰}$  to  $-140\text{‰}$ , with a mean value of  $-141.7\text{‰} \pm 1.2\text{‰}$  ( $n = 26$ ) (Table 2). The oxygen and hydrogen isotopes in groundwater and surface water showed similar values with little variations (Fig. 4). Waters from two artesian well samples had the most negative isotopic values ( $\delta^{18}\text{O}$ :  $-19.5\text{‰}$  and  $19.6\text{‰}$ ;  $\delta^2\text{H}$ :  $-147\text{‰}$  and  $-148\text{‰}$ ), and the spring-water sample had the most positive value ( $\delta^{18}\text{O}$ :  $-17.2\text{‰}$ ;  $\delta^2\text{H}$ :  $-135\text{‰}$ ), which were different from surface waters and shallow groundwaters (Fig. 4).

Figure 4 also shows hydrogen and oxygen isotopic values of all water samples within the context of two local meteoric water lines (LMWL) developed for the Red Canyon Creek watershed (Jin and Siegel, 2008) and for southeastern Idaho, western Wyoming, and south-central Idaho (Benjamin et al., 2005). All water samples generally fell on both LMWLs. These two LMWLs have similar slopes but slight differences in deuterium-excess values, which might reflect localized precipitation conditions.

#### Sulfur Isotope Ratios of Sulfate ( $\delta^{34}\text{S}$ )

The  $\delta^{34}\text{S}$  values of sulfate in surface waters in Red Canyon Creek watershed ranged from  $6.3\text{‰}$  to  $12.4\text{‰}$ , with a mean value of  $11.1\text{‰} \pm 1.5\text{‰}$  ( $n = 14$ ) (Table 2). The  $\delta^{34}\text{S}$  values of groundwater sulfate ranged from  $14.1\text{‰}$  to  $21.2\text{‰}$ , with a mean value of  $15.2\text{‰} \pm 1.6\text{‰}$  ( $n = 17$ ) (Table 2). Groundwaters had higher  $\delta^{34}\text{S}$  values and sulfate concentrations than surface waters. The  $\delta^{34}\text{S}$  value of gypsum from the Gypsum Spring Formation was  $15.7\text{‰}$ .

Sulfur isotopic compositions of sulfate and sulfate concentrations appeared to be spatially correlated. The three tributaries have lower  $\delta^{34}\text{S}$  values and sulfate concentrations than those of Red Canyon Creek (Fig. 5). Changes between  $0.5\text{‰}$  and  $1.2\text{‰}$  in  $\delta^{34}\text{S}$  values and between 0.2 and 3.0 mmol/L in sulfate concentrations occurred at the confluences of tributaries. There was a 1‰ increase in  $\delta^{34}\text{S}$  along the upper reach of the Red Canyon Creek main stem between the Deep Creek and Barrett Creek confluences, which corresponds with a marked increase in the sulfate concentrations (Fig. 5).

#### Carbon Isotopes of Dissolved Inorganic Carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ )

The DIC of surface waters in the Red Canyon Creek watershed ranged from 3.51 to 6.14 mmol/L and from 1.77 to 10.14 mmol/L

**Figure 3.** (A) Variations of stream discharge at each sampling location with distance downstream on 30 June and 1 July 2006. (B) Spatial patterns in stream chemistry of Red Canyon Creek shown by total dissolved solids (TDS) and select ions. The gray bars in B indicate significant chemistry change occurred at the tributary confluences (DC, BC, and CC) and the place where groundwater discharges the creek.

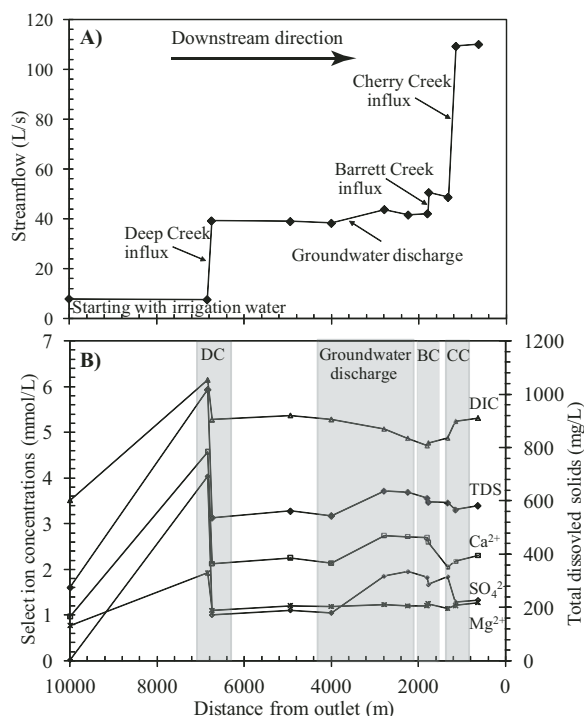


TABLE 1. SUMMARY OF CHEMICAL ANALYSIS AND PHREEQC MODEL RESULTS OF SURFACE WATERS (SW), SHALLOW GROUNDWATERS FROM MONITORING WELLS (MW) AND PIEZOMETERS (P), SPRING (S), AND DEEP WELLS (DW)

ID	Type	Sample date	pH	SC (mS/cm)	Temp (°C)	Ca <sup>2+</sup> (mmol/L)	K <sup>+</sup> (mmol/L)	Mg <sup>2+</sup> (mmol/L)	Na <sup>+</sup> (mmol/L)	Si (mmol/L)	Sr <sup>2+</sup> (mmol/L)	SO <sub>4</sub> <sup>2-</sup> (mmol/L)	Cl <sup>-</sup> (mmol/L)	TDS (Mg/L)	Measured		Charge balance	Model S <sub>labite</sub>	Model S <sub>grasam</sub>	Model pCO <sub>2</sub>
															DIC (mmol/L)	Calculated DIC (mmol/L)				
1	SW	6/30/2006	8.4	1142	15.5	4.58	0.12	1.95	0.47	0.37	0.025	4.04	0.12	1024	6.14	5.49	-2.3%	1.45	-0.84	-2.93
2	SW	6/30/2006	8.6	590	16.0	2.12	0.03	1.11	0.18	0.26	0.006	1.00	0.04	544	5.27	4.66	-4.4%	1.31	-1.59	-3.16
3	SW	6/30/2006	8.4	618	15.0	2.25	0.03	1.22	0.21	0.27	0.007	1.10	0.04	568	5.36	4.94	-2.9%	1.18	-1.53	-3.00
4	SW	6/30/2006	8.5	603	13.8	2.14	0.03	1.20	0.23	0.20	0.007	1.05	0.04	551	5.28	4.78	-3.5%	1.20	-1.56	-3.08
5	SW	6/30/2006	8.2	717	15.4	2.75	0.03	1.24	0.24	0.25	0.011	1.86	0.04	643	5.07	4.52	-3.2%	1.05	-1.25	-2.85
6	SW	6/30/2006	8.4	721	14.9	2.72	0.03	1.21	0.25	0.25	0.011	1.96	0.04	639	4.86	4.21	-3.8%	1.16	-1.24	-3.02
7	SW	6/30/2006	8.3	702	20.3	2.60	0.03	1.22	0.24	0.24	0.011	1.83	0.05	616	4.70	4.43	-1.6%	1.24	-1.28	-3.02
8	SW	6/30/2006	8.4	679	18.6	2.60	0.03	1.26	0.24	0.25	0.010	1.67	0.04	601	4.76	4.62	-0.9%	1.13	-1.32	-2.94
9	SW	6/30/2006	8.3	704	16.4	2.06	0.03	1.16	0.19	0.25	0.006	1.84	0.04	599	4.87	2.94	-12.6%	0.96	-1.36	-2.88
10	SW	6/30/2006	8.3	639	14.4	2.18	0.02	1.22	0.18	0.22	0.007	1.29	0.03	572	5.24	4.41	-5.6%	1.05	-1.47	-2.91
11	SW	6/30/2006	8.3	647	14.1	2.30	0.03	1.29	0.19	0.22	0.008	1.33	0.04	588	5.31	4.72	-3.8%	1.09	-1.44	-2.93
CC	SW	6/30/2006	8.3	556	12.0	1.84	0.02	1.21	0.12	0.20	0.004	0.69	0.03	526	5.68	4.83	-6.3%	0.97	-1.77	-2.86
BC	SW	6/30/2006	8.3	534	15.5	1.75	0.02	1.24	0.16	0.25	0.003	0.58	0.03	513	5.65	4.99	-5.1%	1.04	-1.88	-2.88
DC	SW	6/30/2006	8.7	478	17.8	1.69	0.02	0.97	0.13	0.25	0.003	0.44	0.02	444	4.90	4.57	-2.9%	1.32	-2.00	-3.26
IW	SW	6/30/2006	8.8	307	18.9	0.96	0.02	0.78	0.12	0.18	0.001	0.01	0.03	282	3.51	3.56	0.7%	1.22	-3.75	-3.51
Deep well 1	DW	7/1/2006	7.7	352	n.a.	0.97	0.07	0.79	0.23	0.21	0.003	0.27	0.06	345	4.10	3.22	-9.3%	n.a.	n.a.	n.a.
Deep well 2	DW	7/1/2006	7.6	514	n.a.	1.84	0.03	0.89	0.16	0.22	0.005	0.68	0.03	488	5.17	4.28	-7.3%	n.a.	n.a.	n.a.
Spring	S	7/1/2006	7.5	521	n.a.	1.16	0.05	1.23	1.12	0.28	0.009	0.13	0.07	547	n.a.	6.88	n.a.	n.a.	n.a.	
MW 5	MW	7/8/2005	7.2	n.a.	13.5	3.92	0.055	1.83	0.49	0.37	0.019	2.21	0.06	904	n.a.	7.60	n.a.	-0.02	-1.09	-1.67
MW 12	MW	7/8/2005	7.2	n.a.	12.7	4.12	0.041	1.67	0.74	0.22	0.024	3.77	0.09	891	n.a.	4.82	n.a.	-0.86	-0.86	-1.87
TP1	MW	7/8/2005	7.4	n.a.	11.8	3.11	0.119	1.67	0.42	0.45	0.013	0.52	0.12	799	n.a.	9.05	n.a.	0.48	-1.75	-1.83
TP2	MW	7/8/2005	7.3	n.a.	12.8	1.90	0.032	1.03	0.18	0.26	0.008	0.86	0.06	464	n.a.	4.35	n.a.	-0.08	-1.65	-2.05
TP3	MW	7/8/2005	7.2	n.a.	13.8	7.06	0.071	2.73	0.84	0.28	0.039	6.61	0.10	1464	n.a.	7.29	n.a.	0.32	-0.53	-1.69
TP4	MW	7/8/2005	7.2	n.a.	13.0	2.78	0.062	2.89	1.03	0.29	0.042	6.04	0.12	1578	n.a.	9.66	n.a.	-0.07	-1.23	-1.89
P2	P	7/8/2005	7.3	n.a.	12.5	7.43	0.039	2.62	0.31	0.24	0.012	1.85	0.14	632	n.a.	4.75	n.a.	0.62	-0.55	-1.70
P3	P	7/8/2005	7.3	n.a.	11.8	5.21	0.062	2.38	0.83	0.27	0.027	4.38	0.08	1164	n.a.	7.28	n.a.	0.38	-0.75	-1.82
P4	P	7/8/2005	7.2	n.a.	11.2	6.64	0.040	2.62	0.90	0.30	0.037	5.12	0.08	1420	n.a.	9.23	n.a.	0.38	-0.63	-1.60
P5	P	7/8/2005	7.1	n.a.	13.3	4.87	0.009	2.17	0.79	0.27	0.021	3.48	0.11	1095	n.a.	7.91	n.a.	0.18	-0.86	-1.58
P6	P	7/8/2005	7.4	n.a.	13.4	2.13	0.025	0.99	0.27	0.26	0.011	1.49	0.05	486	n.a.	3.56	n.a.	-0.09	-1.39	-2.17
P7	P	7/8/2005	7.2	n.a.	12.4	4.43	0.040	1.89	0.67	0.30	0.024	3.75	0.08	970	n.a.	5.85	n.a.	0.14	-0.84	-1.82
P8	P	7/8/2005	7.1	n.a.	14.5	5.56	0.053	2.50	0.77	0.31	0.029	4.51	0.08	1233	n.a.	7.93	n.a.	0.30	-0.74	-1.63
P9	P	7/8/2005	7.1	n.a.	13.4	3.55	0.022	1.72	0.38	0.38	0.016	2.22	0.06	816	n.a.	6.50	n.a.	0.00	-1.11	-1.65
P10	P	7/8/2005	7.2	n.a.	13.0	5.48	0.055	2.44	0.76	0.29	0.029	4.98	0.09	1198	n.a.	6.71	n.a.	0.29	-0.69	-1.79
P12-1	P	7/8/2005	7.2	n.a.	13.1	9.00	0.068	2.98	1.12	0.35	0.050	7.66	0.11	1815	n.a.	9.87	n.a.	0.54	-0.41	-1.58
P12-2	P	7/8/2005	7.2	n.a.	13.0	8.77	0.057	2.89	1.08	0.33	0.048	7.98	0.10	1750	n.a.	8.52	n.a.	0.46	-0.40	-1.65
P12-3	P	7/8/2005	7.2	n.a.	12.8	7.81	0.061	2.49	0.94	0.34	0.042	7.89	0.10	1529	n.a.	5.87	n.a.	0.24	-0.42	-1.79
P12-4	P	7/8/2005	7.2	n.a.	12.9	7.67	0.069	2.41	0.91	0.31	0.041	5.51	0.10	1553	n.a.	10.14	n.a.	0.51	-0.56	-1.56
P12-5	P	7/8/2005	7.2	n.a.	12.3	7.42	0.040	2.03	0.86	0.27	0.035	7.60	0.11	1237	n.a.	4.53	n.a.	-0.20	-0.42	-1.92
P12-6	P	7/8/2005	7.2	n.a.	11.9	6.45	0.047	2.03	0.86	0.27	0.035	7.60	0.11	1237	n.a.	2.70	n.a.	0.20	-0.47	-2.17
P13	P	7/8/2005	7.1	n.a.	12.2	6.64	0.030	2.77	0.89	0.29	0.034	5.41	0.08	1431	n.a.	8.93	n.a.	0.30	-0.61	-1.55
P14	P	7/8/2005	7.2	n.a.	12.9	3.37	0.039	1.92	0.52	0.22	0.020	3.06	0.09	892	n.a.	6.09	n.a.	0.10	-0.96	-1.78
P15-1	P	7/8/2005	7.4	n.a.	13.4	3.37	0.015	1.34	0.43	0.30	0.016	4.19	0.08	683	n.a.	1.49	n.a.	-0.32	-0.87	-2.62
P15-2	P	7/8/2005	7.4	n.a.	12.8	3.76	0.027	1.49	0.45	0.30	0.018	4.33	0.09	768	n.a.	2.33	n.a.	-0.10	-0.83	-2.41
P15-3	P	7/8/2005	7.4	n.a.	12.4	5.42	0.054	2.27	0.69	0.33	0.027	4.23	0.07	1177	n.a.	7.67	n.a.	0.52	-0.75	-1.88
P15-4	P	7/8/2005	7.4	n.a.	12.7	5.29	0.042	2.24	0.69	0.32	0.027	4.29	0.07	1149	n.a.	7.22	n.a.	0.52	-0.76	-1.92
P15-5	P	7/8/2005	7.3	n.a.	11.9	4.86	0.024	2.05	0.66	0.35	0.025	4.29	0.07	1048	n.a.	5.94	n.a.	0.31	-0.77	-1.94
P15-6	P	7/8/2005	7.4	n.a.	11.5	5.10	0.046	2.14	0.46	0.28	0.026	4.24	0.07	1100	n.a.	6.69	n.a.	-0.28	-0.85	-2.53
P15-7	P	7/8/2005	7.4	n.a.	12.0	3.45	0.035	1.44	0.46	0.28	0.017	4.26	0.07	713	n.a.	1.77	n.a.	0.13	-0.80	-1.71
P16	P	7/8/2005	7.4	n.a.	12.8	4.52	0.082	2.55	1.56	0.22	0.024	4.45	0.18	1142	n.a.	6.87	n.a.	0.03	-1.38	-1.78
P17	P	7/8/2005	7.2	n.a.	12.3	2.85	0.022	1.31	0.27	0.26	0.013	1.26	0.06	655	n.a.	6.09	n.a.	0.03	-1.38	-1.78

Note: SC—specific conductance; TDS—total dissolved solids; DIC—dissolved inorganic carbon; SI—saturation index.

TABLE 2. SUMMARY OF ISOTOPIC ANALYSIS OF SURFACE WATERS (SW), SHALLOW GROUNDWATERS FROM MONITORING WELLS (MW) AND PIEZOMETERS (P), SPRING (S) AND DEEP WELLS (DW), AS WELL AS CALCITE ENCRUSTATIONS AND MINERAL GYPSUM FROM GYPSUM SPRING FORMATION

ID	Type	Sample date	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{13}\text{C}$ (‰)
1	SW	6/30/2006	-18.1	-140	12.4	-9.5
2	SW	6/30/2006	-19.0	-141	11.3	-9.1
3	SW	6/30/2006	-19.0	-144	11.7	-8.6
4	SW	6/30/2006	-18.9	-143	11.8	-9.0
5	SW	6/30/2006	-18.7	-144	11.8	-8.6
6	SW	6/30/2006	-18.7	-143	11.9	-8.5
7	SW	6/30/2006	-18.7	-144	12.3	-8.3
8	SW	6/30/2006	-18.7	-143	11.8	-8.3
9	SW	6/30/2006	-18.6	-143	11.2	-8.8
10	SW	6/30/2006	-18.5	-141	12.1	-8.4
11	SW	6/30/2006	-18.7	-141	10.5	-7.4
CC	SW	6/30/2006	-18.5	-141	9.5	-7.7
BC	SW	6/30/2006	-18.7	-142	6.3	-9.2
DC	SW	6/30/2006	-19.1	-144	10.5	-8.4
IW	SW	6/30/2006	-18.3	-142	n.a.	-6.2
Deep well 1	DW	7/1/2006	-19.6	-147	n.a.	n.a.
Deep well 2	DW	7/1/2006	-19.5	-148	n.a.	n.a.
Spring	S	7/1/2006	-17.3	-135	n.a.	n.a.
MW 5	MW	7/5/2006	-18.8	-141	n.a.	n.a.
MW 12	MW	7/5/2006	-18.5	-142	n.a.	n.a.
TP1	MW	7/5/2006	-18.5	-141	n.a.	-12.28
TP2	MW	7/5/2006	n.a.	n.a.	n.a.	n.a.
TP3	MW	7/5/2006	-18.6	-140	n.a.	n.a.
TP4	MW	7/5/2006	-18.5	-141	n.a.	n.a.
P2	P	7/5/2006	-18.9	-144	14.1	n.a.
P3	P	7/5/2006	-18.6	-144	15.5	n.a.
P4	P	7/5/2006	n.a.	n.a.	n.a.	n.a.
P5	P	7/5/2006	-18.6	-143	n.a.	n.a.
P6	P	7/5/2006	-18.7	-142	21.2	n.a.
P7	P	7/5/2006	-18.6	-142	15.8	n.a.
P8	P	7/5/2006	-18.1	-140	15.2	n.a.
P9	P	7/5/2006	-18.5	-142	14.9	n.a.
P10	P	7/5/2006	-18.3	-143	14.6	n.a.
P12-1	P	7/5/2006	-18.4	-141	14.7	n.a.
P12-2	P	7/5/2006	n.a.	n.a.	n.a.	n.a.
P12-3	P	7/5/2006	-18.6	-140	14.5	n.a.
P12-4	P	7/5/2006	n.a.	n.a.	n.a.	n.a.
P12-5	P	7/5/2006	-18.7	-141	14.6	n.a.
P12-6	P	7/5/2006	-18.6	-140	14.4	n.a.
P13	P	7/5/2006	-18.6	-142	n.a.	n.a.
P14	P	7/5/2006	n.a.	n.a.	n.a.	n.a.
P15-1	P	7/5/2006	n.a.	n.a.	n.a.	n.a.
P15-2	P	7/5/2006	-18.6	-141	14.8	n.a.
P15-3	P	7/5/2006	-18.8	-141	14.8	n.a.
P15-4	P	7/5/2006	-18.6	-142	14.9	n.a.
P15-5	P	7/5/2006	-18.4	-143	14.9	n.a.
P15-6	P	7/5/2006	-18.4	-143	14.7	n.a.
P15-7	P	7/5/2006	-18.5	-143	14.7	n.a.
P16	P	7/5/2006	-18.9	-143	n.a.	-10.13
P17	P	7/5/2006	-18.6	-140	n.a.	n.a.
Calcite crust 1		6/30/2006	n.a.	n.a.	n.a.	-6.6
Calcite crust 2		6/30/2006	n.a.	n.a.	n.a.	-7.6
Mineral gypsum		6/30/2006	n.a.	n.a.	15.7	n.a.

for groundwater. The  $\delta^{13}\text{C}$  of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) of surface waters ranged from  $-9.2\text{‰}$  to  $-6.2\text{‰}$ , with a mean value of  $-8.4\text{‰} \pm 0.9\text{‰}$  ( $n = 15$ ) (Table 2). Two selected shallow groundwater samples at the base of the Red Canyon Creek watershed had  $\delta^{13}\text{C}_{\text{DIC}}$  values of  $-12.3\text{‰}$  and  $-10.1\text{‰}$ , respectively (Table 2). Groundwaters had higher DIC concentrations and lower  $\delta^{13}\text{C}$  values than surface waters. Two samples of encrustation on the streambed sediments had  $\delta^{13}\text{C}_{\text{carbonate}}$  values of  $-6.6\text{‰}$  and  $-7.6\text{‰}$ .

The  $\delta^{13}\text{C}_{\text{DIC}}$  values of surface-water samples were similar (within  $0.4\text{‰}$ ) at each tribu-

tary confluence (Fig. 6). The  $\delta^{13}\text{C}_{\text{DIC}}$  values of three tributaries slightly differed from each other ( $\sim 1.5\text{‰}$ ).

### PHREEQC Calculations

We used PHREEQC to heuristically evaluate changes in water chemistry resulting from mixing of Red Canyon Creek headwaters with each tributary and groundwater discharge (steps 1–4 in Table 3). When we compared the modeled chemistry with measured data, results showed the percent difference between modeled and measured solute concentrations, which were

less than 5%, except for potassium (9.6%), silica (7.1%), and sulfate (18.4%) (Table 3).

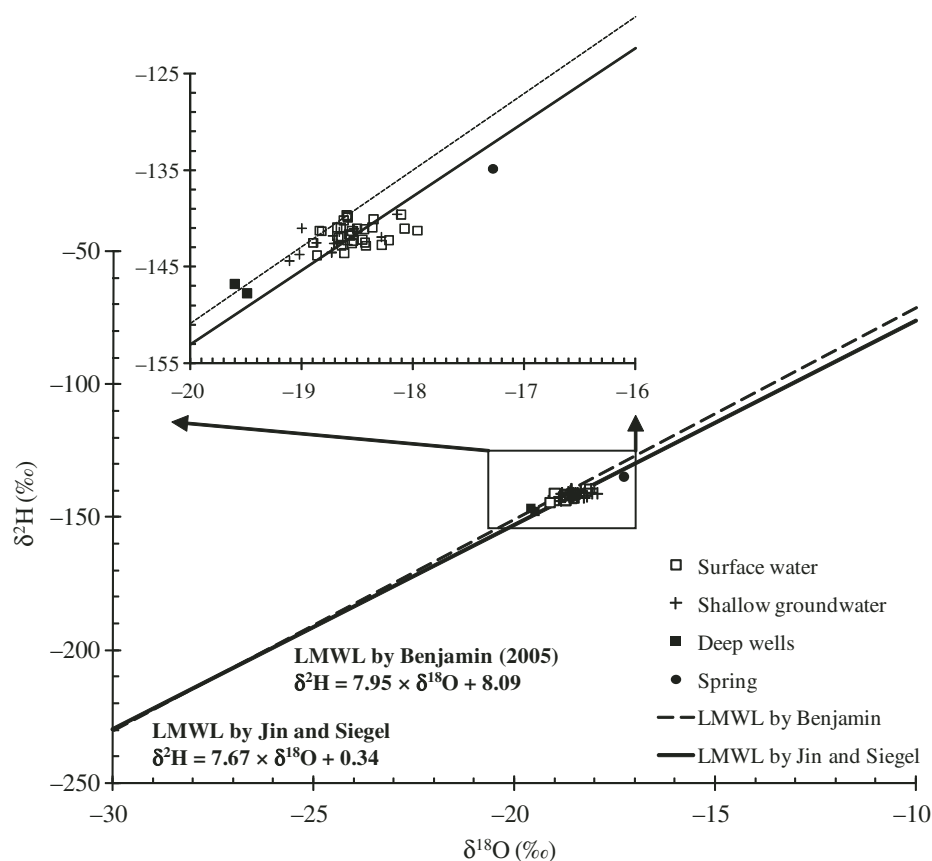
We also used PHREEQC to calculate the activities of major ions and equilibrium states with respect to calcite and gypsum from water analysis data (Table 1). The saturation of waters with respect to calcite or gypsum is expressed as a saturation index ( $\text{SI}_{\text{mineral}}$ ). Figure 7 shows that the  $\text{SI}_{\text{calcite}}$  value for most groundwater samples is close to zero, indicating near-equilibrium condition. Results of sensitivity analysis done on DIC concentrations showed that increasing or decreasing concentrations by 10% affected saturation index by less than 0.05 units, which assures reasonable calculation of saturation indices of groundwater using DIC concentrations calculated from the charge balance. In contrast, SI values of surface-water samples were generally greater than one, suggesting that these waters are supersaturated with respect to the mineral calcite. Saturation indices of surface and groundwater samples with respect to mineral gypsum ( $\text{SI}_{\text{gypsum}}$ ) were less than zero, indicating undersaturation.

## INTERPRETATION AND DISCUSSION

### Water and Solute Sources in the Watershed

At sampling, a small amount of groundwater discharge and a larger tributary flux supported streamflow along Red Canyon Creek. At smaller scale, detailed studies of hyporheic interactions at the base of the watershed show complex surface-water and groundwater exchange associated with beaver dams and other obstructions (Lautz and Siegel, 2006). Our work supports the conclusion that only 15% of water in Red Canyon Creek consists of groundwater discharge along the main stem, and 85% of water is from tributaries influx; however, the extent of groundwater involved in hyporheic interaction may be much larger.

The abrupt increase in concentrations of major solutes, particularly calcium and sulfate, in the Red Canyon Creek water from low concentrations provided in irrigation water within the first 2 km of channel indicates that groundwater that has dissolved gypsum enters the stream (Fig. 3B). From measurements of irrigation water at the entrance culvert and base flow along the creek, we can deduce that the amount of irrigation water imported from the adjacent watershed, Twin Creek, is substantially less than 10% of the total flow. We could not obtain details on the dispersal of this water in the upper headwater area. Therefore, the focus of this paper starts where Red Canyon Creek water first obtains its calcium sulfate signature (labeled as number 1 in Fig. 1C) and not in the



**Figure 4.**  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  of surface waters (SW), shallow groundwaters (GW), and water from two deep artesian wells and one shallow spring within the context of local meteoric water line (LMWL). One LMWL shown in solid straight line was developed for the Red Canyon Creek area, and another LMWL in dashed line was developed by Benjamin (2005) for southeastern Idaho, western Wyoming, and south-central Idaho.

uppermost reach of the watershed, where small amounts of irrigation water enter the system. Uncertainty introduced by lack of information on the dispersal of irrigation water in the watershed does not change any conclusion drawn from this paper.

In any case, the similarity of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values in groundwaters and surface waters indicates that groundwater derived from local precipitation sustains Red Canyon Creek during low flow. This observation shows a strong hydrologic connection between surface and groundwater in Red Canyon Creek. The deep well waters with the most negative  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values are probably from the Amsden Formation, which is recharged ~1000 m higher than the valley below (Figs. 1 and 2). The shallow spring with the highest  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values is recharged only ~50 m above Red Canyon Creek on the eastern ridge adjacent to the Cherry Creek confluence (Fig. 1C). The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of surface and groundwaters fall between those of the deep wells and shallow spring

water, which suggests that surface and groundwaters may effectively be bracketed by these two end members (Fig. 4).

The  $\delta^{34}\text{S}$  values of sulfate from surface waters and groundwaters in the watershed fall within the range between an atmospheric source  $\delta^{34}\text{S}$  value (3.8‰–8.4‰) (Finley et al., 1995; Turk et al., 1993) and mineral gypsum  $\delta^{34}\text{S}$  value (15.7‰, Table 2). The  $\delta^{34}\text{S}$  value of the mineral source end member is consistent with that of Mesozoic marine evaporates such as those found in the Gypsum Spring Formation or in the Dinwoody Formation (Claypool et al., 1980). However, sulfate in atmospheric precipitation cannot be the end-member solution providing sulfate with lower  $\delta^{34}\text{S}$  values to the creek system because of its much lower sulfate concentration compared to creek values.

For example, the average sulfate concentration in the creek waters was 1.5 mmol/L, compared to 0.01 mmol/L in 2006 average precipitation (NADP, 2006). Therefore, another source of sulfate with  $\delta^{34}\text{S}$  values significantly

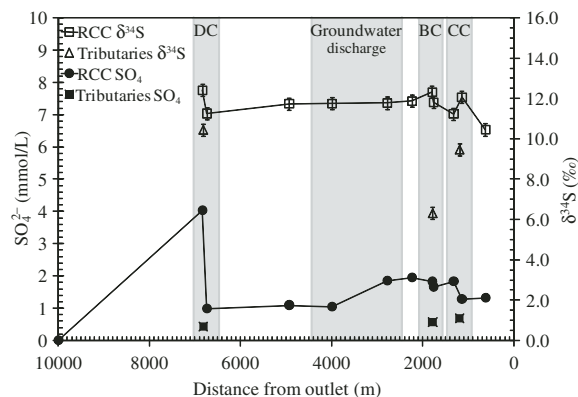
lower than those of the gypsum source must occur in the tributary watersheds. Oxidation of pyrite with biogenic origin in the Phosphoria Formation or in younger formations in the headwaters of the canyons (Whalen, 1991) could have strongly negative  $\delta^{34}\text{S}$  values. Therefore, a small amount of sulfate contributed by sulfide oxidation could cause a relatively large change in  $\delta^{34}\text{S}$  of sulfate values in stream waters.

The  $\delta^{34}\text{S}$  values of groundwaters with high sulfate concentrations are close to those of mineral gypsum (Table 2). Furthermore, a bivariate plot of calcium and sulfate shows that all the groundwater samples fall close to the gypsum stoichiometric dissolution line with a slope of unity (Fig. 8). The intercept on the x-axis shows the  $\text{Ca}^{2+}$  excess from carbonate dissolution. In total, the chemistry and isotopic values of sulfate are consistent with a gypsum contribution dominating the sulfate chemistry at Red Canyon Creek.

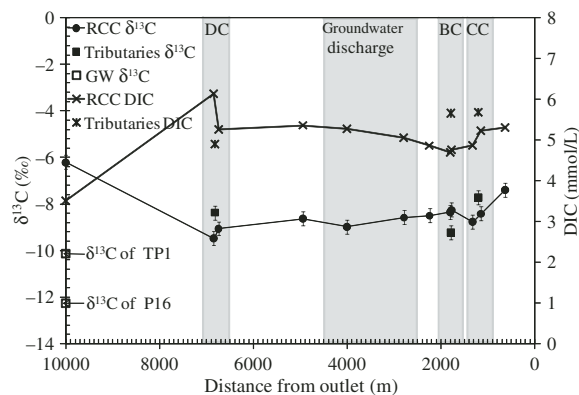
### Mixing Model

Table 3 shows that the percentage differences between PHREEQC modeled and measured solute concentrations were less than 5%, except for potassium, silica, and sulfate. This agreement falls within the error of most measurements and indicates that the majority of solutes are effectively nonreactive in the streams, and that concentration changes can be explained by simple mixing models. The higher predicted silica and potassium concentrations compared to the measured values could be due to biotic demand for these elements. However, the calculated sulfate concentration at the base of watershed was 18% less than measured, suggesting that additional sulfate may have been contributed by gypsum dissolution in the streambed. If more gypsum dissolves, excess calcium could have precipitated as calcite. Variations in sulfur and carbon isotope ratios agreed in our heuristic model within 7%, suggesting that the mixing model remains essentially sound (Table 3).

The wells within Red Canyon Creek watershed only were placed in the floodplain alluvium. We recognize this spatial limitation of groundwater collection imposes some uncertainty on our calculation. However, groundwater in the upper portion of the watershed mostly discharges from the lowermost fluvial terrace, which consists of sediments derived from the Chugwater, Dinwoody, and Phosphoria Formations, i.e., the same as the sediments hosting groundwater at the base of the watershed. Additional shallow groundwater wells need to be installed at different locations within the watershed as future work.



**Figure 5.** Longitudinal profiles of  $\delta^{34}\text{S}$  and sulfate concentrations in Red Canyon Creek (RCC) waters with distance downstream. The single point indicates  $\delta^{34}\text{S}$  value or sulfate concentration of each tributary.



**Figure 6.** Longitudinal profiles of  $\delta^{13}\text{C}_{\text{DIC}}$  and dissolved inorganic carbon (DIC) concentrations in Red Canyon Creek (RCC) with distance downstream. The single point indicates  $\delta^{13}\text{C}_{\text{DIC}}$  or DIC of each tributary and groundwater sample.

TABLE 3. TWO END-MEMBER MIXING MODELS PERFORMED BY PHREEQC

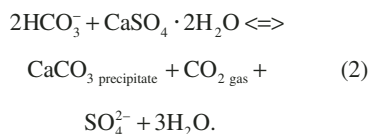
	Mixing percentage (%)	Ca <sup>2+</sup> (mmol/L)	K <sup>+</sup> (mmol/L)	Mg <sup>2+</sup> (mmol/L)	Na <sup>+</sup> (mmol/L)	Sr <sup>2+</sup> (mmol/L)	Si (mmol/L)	SO <sub>4</sub> <sup>2-</sup> (mmol/L)	DIC (mmol/L)	Cl <sup>-</sup> (mmol/L)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)
Starting headwater	17.7	4.57	0.12	1.92	0.47	0.025	0.37	4.04	6.14	0.118	-9.5	12.4
Mixing with DC (step 1)	82.3	1.69	0.02	0.96	0.13	0.003	0.25	0.44	4.97	0.025	-8.4	10.5
Resulting water 1 (M1)	85.4	2.20	0.04	1.13	0.19	0.007	0.27	1.08	5.18	0.041	-8.6	11.7
Mixing with groundwater (step 2)	14.6	5.17	0.05	2.05	0.70	0.027	0.30	4.52	6.19	0.093	-11.2	14.8
Resulting water 2 (M2)	83.8	2.64	0.04	1.26	0.27	0.010	0.28	1.58	5.33	0.049	-9.0	13.0
Mixing with BC (step 3)	16.2	1.75	0.02	1.23	0.16	0.003	0.25	0.58	5.65	0.029	-9.2	6.3
Resulting water 3 (M3)	51.6	2.49	0.03	1.26	0.25	0.009	0.27	1.42	5.38	0.045	-9.1	12.6
Mixing with CC (step 4)	48.4	1.84	0.02	1.20	0.12	0.004	0.20	0.69	5.68	0.026	-7.7	9.5
Resulting water 4 (M4)		2.18	0.03	1.23	0.19	0.007	0.24	1.07	5.53	0.036	-8.4	11.6
Mean outlet water chemistry (Ow)		2.23	0.02	1.24	0.18	0.007	0.22	1.31	5.27	0.035	-7.9	11.3
Difference b/w M4 and Ow		-0.06	0.00	-0.01	0.00	0.000	0.02	-0.24	0.26	0.001	-0.5	0.3
Difference in %		-2.5%	9.6%	-1.0%	1.2%	-4.4%	7.1%	-18.4%	4.8%	3.0%	6.2%	2.9%

Note: DIC—dissolved inorganic carbon; DC—Deep Creek; BC—Barrett Creek; CC—Cherry Creek.

### Geochemical Mass Balance Reactions

In order to account for the difference of PHREEQC modeled and measured sulfate, we evaluated some potential chemical reactions in the system.

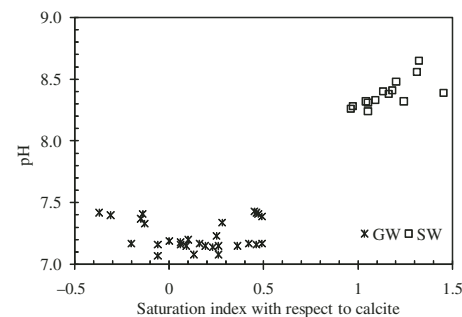
According to sulfur isotope data, sulfate in base flow is predominantly derived from gypsum dissolution. Dissolution of calcite and gypsum both contribute Ca<sup>2+</sup>. Both surface and groundwater samples are undersaturated with respect to gypsum ( $SI_{\text{gypsum}} < 0$ ). Since gypsum continually dissolves in water, it will cause stream waters to be supersaturated with respect to calcite, causing it to precipitate because of the common ion effect (Eq. 2):



PHREEQC results indicate that most groundwater samples have  $SI_{\text{calcite}}$  values close to zero with respect to calcite and high  $p\text{CO}_2$  values, indicating groundwaters near equi-

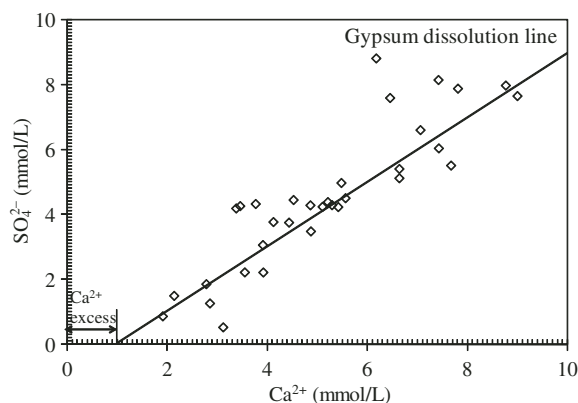
librium with respect to calcite. In contrast, SI values of surface-water samples exceed unity, indicating that they are oversaturated with respect to calcite. The degree of calcite saturation of water is primarily related to its calcium and bicarbonate activity, pH, and temperature (Neal et al., 1998). Surface waters had higher pH and temperature than groundwaters, which drive the water to supersaturation because of loss of carbon dioxide and shifting of carbonate speciation from bicarbonate toward the carbonate ion. We also occasionally saw white to green (algal component) crustal coatings on surfaces of streambed sediments through the creek system (Fig. 9). X-ray diffraction results confirmed that the crusts consisted of pure calcite (Jin et al., 2006).

Calcite crusts occurred on pebbles at the ends of pool-riffle sequences, downstream of debris and beaver dams, where groundwater upwells (Fanelli and Lautz, 2008; Harvey and Bencala, 1993), and 4 km upstream from the mouth of Red Canyon Creek, where groundwater discharge occurs (Fig. 3A). When groundwater with high concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> from gypsum dissolution mixes with stream water already nearly saturated with calcite, the



**Figure 7.** Saturation index (SI) with respect to calcite versus pH of surface waters (SW) and groundwaters (GW). The values of groundwaters are close to equilibrium, while surface waters have values greater than 1, which are 10 times greater than saturation.

common ion effect quickly causes calcite precipitation, similar to that found in groundwater systems that require much greater residence times for reaction to occur (Bischoff et al., 1994; Busby et al., 1991; Dobrzynski, 2007; Plummer and Back, 1980; Plummer et al., 1990; Sacks and Tihansky, 1996).



**Figure 8.** Bivariate plot of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  of groundwater samples. Groundwaters fall close to the gypsum stoichiometric dissolution line with a slope of unity. The intercept on x-axis shows the  $\text{Ca}^{2+}$  excess from carbonate dissolution.



**Figure 9.** An example of calcite encrustation on the surface of streambed pebbles.

In the equation for the common ion effect (Eq. 2), one mole of  $\text{H}^+$  and  $\text{SO}_4^{2-}$  is produced when gypsum dissolves, and one mole of  $\text{HCO}_3^-$  is lost as one mole of  $\text{CaCO}_3$  forms. After theoretically mixing Red Canyon Creek headwaters with groundwater and tributaries, we found that there remained a small surplus of 0.26 mmol/L DIC and almost an equal deficit of sulfate (Table 3). The common ion effect can consume this surplus of 0.26 mmol/L of DIC while producing 0.26 mmol/L of calcite precipitate and 0.26 mmol/L of sulfate in the water, which balance the sulfate deficit.

Carbon isotope values of the calcite precipitates in the streambed at two different locations had slightly higher  $\delta^{13}\text{C}$  values ( $-6.6\%$  and  $-7.6\%$ ) than DIC in all surface-water samples, as would be expected due to preferential precipitation of the heavier carbon isotope  $^{13}\text{C}$ . The loss of DIC by calcite precipitation only accounts for 5% of total DIC, and the change of  $\delta^{13}\text{C}_{\text{DIC}}$  in the stream waters on a mass basis is too small to see a clear trend.

Bacterial dissimilatory sulfate reduction (Eq. 3) occurs in organic-rich areas behind beaver dams and in overbank stream deposits (Fanelli and Lautz, 2008).



This reaction generates sulfide with significantly lower  $\delta^{34}\text{S}$  values than those of the reactant, and consequently  $^{34}\text{S}$ -enriched sulfate in the remaining reactant (Brown, 1985; Clark and Fritz, 1997; Knoller et al., 2004). Water from some shallow in-stream piezometers showed high  $\delta^{34}\text{S}$  values, which clearly indicated bacterial sulfate reduction taking place at certain locations in the streambed (Fanelli and Lautz, 2008).

The extent of stream and groundwater exchange depends on the degree of connectivity between the stream and streambed sediments. We found that the depletion of sulfur isotopes in the stream water falls within the uncertainty of our analytical method, and so, despite sulfate reduction occurring in storage behind beaver dams, simple gypsum dissolution best explains the sulfur isotope composition of the stream water. It appears that because of the poor hydraulic connection between stream and streambed at locations where sulfate reduction takes place, minimal sulfate from hyporheic interaction affects the stream-water quality.

## CONCLUSIONS

The effects of hydrologic and geochemical processes on the water chemistry of Red Canyon Creek can be clearly determined from the chemical and isotopic composition of base-flow water samples coupled with geochemical mixing and mass balance models. Red Canyon Creek water initially begins as dilute irrigation water from Twin Creek, located across the Red Canyon Creek watershed divide. As water moves downstream, its chemistry quickly changes because of influx from tributaries and diffuse groundwater discharge. The nonreactive influx of solutes from three tributaries, along with

small amounts of groundwater discharge, explains most of the spatial variation of the major solutes in Red Canyon Creek, except for sulfate and, to a small extent, DIC.

The difference in DIC and sulfate concentrations between measured and modeled values can be explained by the common ion effect driven by gypsum dissolution that precipitates calcite. A factor that we found striking is how, despite short residence times of surface water moving from headwaters to mouth of Red Canyon Creek, the introduction of calcium sulfate-bearing groundwater to carbonate-rich stream water sufficiently drives calcite precipitation onto the streambed. Calcite also can precipitate when carbon dioxide degasses in streams (Herman and Lorah, 1987; Pentecost, 2005), from groundwater in caves, and where carbon dioxide-charged saline groundwater discharges to the land surface (Siegel et al., 2004). However, here, at Red Canyon Creek, we identified similar rapid precipitation of carbonate driven by the common ion effect by mineral dissolution.

Common ion-driven precipitation of carbonate (and associate trace elements) may be far more prevalent wherever gypsiferous rocks dissolve in groundwater to discharge to surface water bodies. Knowing this, the occurrence of calcite nodules in fluvial sedimentary records associated with evaporites may provide clues on former paleohydrologic conditions. Apparently, the kinetics of carbonate precipitation caused by either carbon dioxide degassing or the common ion effect occur at the same order of magnitude, even in rapidly moving streams.

We also found that the hyporheic waters affected by sulfate reduction, common in organic-rich sediments in the Red Canyon streambed and overbank deposits (Fanelli and Lautz, 2008), minimally affected the concentrations of DIC and sulfate in the creek or the isotopic composition of carbon and sulfur, respectively, in these solutes. This conclusion suggests that, although hyporheic interactions may locally control nutrient and other fluxes at the groundwater-surface-water interface, care must be taken when extrapolating the magnitude of the control over larger stream reaches.

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## REFERENCES CITED

- Bailey, S.W., Mayer, B., and Mitchell, M.J., 2004, Evidence for influence of mineral weathering on stream water sulphate in Vermont and New Hampshire (USA): *Hydrological Processes*, v. 18, no. 9, p. 1639–1653, doi: 10.1002/hyp.1410.
- Benjamin, L., Knobel, L.L., Hall, L.F., Cecil, L.D., and Green, J.R., 2005, Development of a Local Meteoric Water Line for Southeastern Idaho, Western Wyoming, and South-Central Montana: U.S. Geological Survey Scientific Investigations Report 2004-5126, 23 p.
- Bethke, C.M., 1996, *Geochemical Reaction Modeling, Concepts and Applications*: New York, Oxford University Press, 397 p.
- Bischoff, J.L., Julia, R., Shanks, W.C., and Rosenbauer, R.J., 1994, Karstification without carbonic-acid-bedrock dissolution by gypsum-driven dedolomitization: *Geology*, v. 22, no. 11, p. 995–998, doi: 10.1130/0091-7613(1994)022<0995:KWCABD>2.3.CO;2.
- Bricker, O., Katz, B., Afifi, A., Puckett, L., Olson, C., and Kennedy, M., 1983, Geochemistry of small Appalachian watersheds developed on silicate bedrock, in Nahon D., and Noack, Y., eds., *Petrologie des Alterations et des Sols: Sciences Geologiques Memoire* 73, p. 41–52.
- Brown, K.A., 1985, Sulfur distribution and metabolism in waterlogged peat: *Soil Biology & Biochemistry*, v. 17, no. 1, p. 39–45, doi: 10.1016/0038-0717(85)90088-4.
- Busby, J.F., Plummer, L.N., Lee, R.W., and Hanshaw, B.B., 1991, *Geochemical Evolution of Water in the Madison Aquifer in Parts of Montana, South Dakota, and Wyoming*: U.S. Geological Survey Professional Paper 1273-F, 89 p.
- Clark, I.D., and Fritz, P., 1997, *Environmental Isotopes in Hydrogeology*: Boca Raton, Florida, USA, CRC Press, Lewis Publishers, 328 p.
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: *Chemical Geology*, v. 28, no. 3–4, p. 199–260, doi: 10.1016/0009-2541(80)90047-9.
- Crandall, C.A., Katz, B.G., and Hirten, J.J., 1999, Hydrochemical evidence for mixing of river water and groundwater during high-flow conditions, lower Suwannee River basin, Florida, USA: *Hydrogeology Journal*, v. 7, no. 5, p. 454–467, doi: 10.1007/s100400050218.
- Dobrzynski, D., 2007, Chemical diversity of groundwater in the Carboniferous-Permian aquifer in the Unislaw Slaski-Sokolowosko area (the Sudetes, Poland); a geochemical modelling approach: *Acta Geologica Polonica*, v. 57, no. 1, p. 97–112.
- Drever, J.I., 1997, *The Geochemistry of Natural Waters: Surface and Groundwater Environments* (3rd ed.): New Jersey, Prentice Hall, 436 p.
- Drimmie, R.J., and Heemscker, R.A., 1993, Water <sup>18</sup>O by CO<sub>2</sub> equilibration. Technical Procedure 13.0, Rev. 02: Waterloo, Ontario, Environmental Isotope Laboratory, Department of Earth Sciences, University of Waterloo, 11 p.
- Epstein, S., and Mayeda, T.K., 1953, Variation of O<sup>18</sup> content of waters from natural sources: *Geochimica et Cosmochimica Acta*, v. 4, p. 213–224, doi: 10.1016/0016-7037(53)90051-9.
- Fanelli, R.M., and Lautz, L.K., 2008, Patterns of water, heat, and solute flux through streambeds around small dams: *Ground Water*, v. 46, no. 5, p. 671–687, doi: 10.1111/j.1745-6584.2008.00461.x.
- Fetter, C.W., 1993, *Contaminant Hydrogeology*: New York, Macmillan Publishing Co., 458 p.
- Finley, J.B., Drever, J.I., and Turk, J.T., 1995, Sulfur isotope dynamics in a high-elevation catchment, West Glacier Lake, Wyoming: *Water, Air, and Soil Pollution*, v. 79, no. 1–4, p. 227–241, doi: 10.1007/BF01100439.
- Fitzhugh, R.D., Furman, T., and Korsak, A.K., 2001, Sources of stream sulphate in headwater catchments in Otter Creek Wilderness, West Virginia, USA: *Hydrological Processes*, v. 15, no. 4, p. 541–556, doi: 10.1002/hyp.169.
- Frey, K.E., Siegel, D.I., and Smith, L.C., 2007, Geochemistry of west Siberian streams and their potential response to permafrost degradation: *Water Resources Research*, v. 43, no. 3, p. W03406, doi: 10.1029/2006WR004902.
- Giesemann, A., Jager, H.J., Norman, A.L., Krouse, H.P., and Brand, W.A., 1994, Online sulfur-isotope determination using an elemental analyzer coupled to a mass spectrometer: *Analytical Chemistry*, v. 66, no. 18, p. 2816–2819, doi: 10.1021/ac00090a005.
- Harvey, J.W., and Benecala, K.E., 1993, The effect of streambed topography on surface-subsurface water exchange in mountain catchments: *Water Resources Research*, v. 29, no. 1, p. 89–98, doi: 10.1029/92WR01960.
- Herman, J.S., and Lorah, M.M., 1987, CO<sub>2</sub> outgassing and calcite precipitation in Falling Spring Creek, Virginia, U.S.: *Chemical Geology*, v. 62, p. 251–262, doi: 10.1016/0009-2541(87)90090-8.
- Hooper, R.P., and Shoemaker, C.A., 1986, A comparison of chemical and isotopic hydrograph separation: *Water Resources Research*, v. 22, no. 10, p. 1444–1454, doi: 10.1029/WR022i10p01444.
- Jin, L., and Siegel, D.I., 2008, Temporal geochemical variations in a mountain stream: Expectations to anomalies: *Eos (Transactions, American Geophysical Union)*, v. 89, no. 53, Fall meeting supplement, abstract H11B-0745.
- Jin, L., Siegel, D.I., Lautz, L.K., and Kranes, N.T., 2006, The relationship between source waters and geochemical processes on the chemistry of Red Canyon Creek, a 2nd order stream in Wind River Range, Wyoming: *Geological Society of America Abstracts with Programs*, v. 28, no. 7, p. 105.
- Kendall, C., and McDonnell, J., 1998, *Isotope Tracers in Catchment Hydrology*: Amsterdam, Elsevier Science B.V., 839 p.
- Kilpatrick, F.A., and Cobb, E.D., 1985, Measurement of Discharge Using Tracers: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 3, Chapter A16, 52 p.
- Knoller, K., Fauville, A., Mayer, B., Strauch, G., Friese, K., and Veizer, J., 2004, Sulfur cycling in an acid mining lake and its vicinity in Lusatia, Germany: *Chemical Geology*, v. 204, no. 3–4, p. 303–323, doi: 10.1016/j.chemgeo.2003.11.009.
- Langmuir, D., 1997, *Aqueous Environmental Geochemistry*: New Jersey, Prentice Hall, 600 p.
- Lautz, L.K., and Siegel, D.I., 2006, Modeling surface and ground water mixing in the hyporheic zone using MODFLOW and MT3D: *Advances in Water Resources*, v. 29, no. 11, p. 1618–1633, doi: 10.1016/j.advwatres.2005.12.003.
- Lautz, L.K., and Siegel, D.I., 2007, The effect of transient storage on nitrate uptake lengths in streams: An inter-site comparison: *Hydrological Processes*, v. 21, no. 26, p. 3533–3548, doi: 10.1002/hyp.6569.
- Liu, F.J., Williams, M.W., and Caine, N., 2004, Source waters and flow paths in an alpine catchment, Colorado Front Range, United States: *Water Resources Research*, v. 40, no. 9, W09401, doi: 10.1029/2004WR003076.
- Love, J.D., 1948, Mesozoic stratigraphy of the Wind River Basin, central Wyoming, in *Guidebook for the 3rd Annual Field Conference*: Casper, Wyoming, Wyoming Geological Society, p. 96–111.
- Machavaram, M.V., Whittemore, D.O., Conrad, M.E., and Miller, N.L., 2006, Precipitation-induced stream flow: An event-based chemical and isotopic study of a small stream in the Great Plains region of the USA: *Journal of Hydrology (Amsterdam)*, v. 330, no. 3–4, p. 470–480, doi: 10.1016/j.jhydrol.2006.04.004.
- Mark, B.G., McKenzie, J.M., and Gomez, J., 2005, Hydrochemical evaluation of changing glacier meltwater contribution to stream discharge: Callejon de Huaylas, Peru: *Hydrological Sciences Journal—Journal Des Sciences Hydrologiques*, v. 50, no. 6, p. 975–987, doi: 10.1623/hysj.2005.50.6.975.
- Mayer, B., and Krouse, H.R., 2004, Procedures for sulfur isotope abundance studies, in De Groot, P., ed., *Handbook of Stable Isotope Analytical Techniques*: Amsterdam, Elsevier, p. 538–596.
- McDonnell, J.J., Stewart, M.K., and Owens, I.F., 1991, Effect of catchment-scale subsurface mixing on stream isotopic response: *Water Resources Research*, v. 27, no. 12, p. 3065–3073, doi: 10.1029/91WR02025.
- Meixner, T., Shaw, J.R., and Bales, R.C., 2004, Temporal and spatial variability of cation and silica export in an alpine watershed, Emerald Lake, California: *Hydrological Processes*, v. 18, no. 10, p. 1759–1776, doi: 10.1002/hyp.1416.
- Mulholland, P.J., Valett, H.M., Webster, J.R., Thomas, S.A., Cooper, L.W., Hamilton, S.K., and Peterson, B.J., 2004, Stream denitrification and total nitrate uptake rates measured using a field N-15 tracer addition approach: *Limnology and Oceanography*, v. 49, no. 3, p. 809–820.
- NADP, 2006, National Atmospheric Deposition Program (NADP), NADP/NTN Monitoring Program—WY97, 2006 Annual Data Summary: <http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=WY97>.
- Neal, C., House, W.A., and Down, K., 1998, An assessment of excess carbon dioxide partial pressures in natural waters based on pH and alkalinity measurements: *Science of the Total Environment*, v. 210, no. 1–6, p. 173–185.
- NOAA, 2008, Monthly Summary of Climatic Data for WY Lander 11 SSE Station (Nature Conservancy—Red Canyon Ranch, Lander, Wyoming), April 2008: National Oceanic and Atmospheric Administration (NOAA), National Climatic Data Center, [http://www.ncdc.noaa.gov/crn/hourly?station\\_id=1144](http://www.ncdc.noaa.gov/crn/hourly?station_id=1144).
- Oliva, P., Viers, J., and Dupre, B., 2003, Chemical weathering in granitic environments: *Chemical Geology*, v. 202, no. 3–4, p. 225–256, doi: 10.1016/j.chemgeo.2002.08.001.
- Parkhurst, D.L., 1995, *User's Guide to PHREEQC: A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations*, General Geochemistry: U.S. Geological Survey Water-Resources Investigations 95-4227, 143 p.
- Pentecost, A., 2005, *Travertine*: New York, Springer-Verlag, 445 p.
- Peters, N.E., and Ratcliffe, E.B., 1998, Tracing hydrologic pathways using chloride at the Panola Mountain Research Watershed, Georgia, USA: *Water, Air, and Soil Pollution*, v. 105, no. 1–2, p. 263–275, doi: 10.1023/A:1005082332332.
- Plummer, L.N., and Back, W., 1980, Mass balance approach—Application to interpreting the chemical evolution of hydrologic systems: *American Journal of Science*, v. 280, no. 2, p. 130–142.
- Plummer, L.N., Busby, J.F., Lee, R.W., and Hanshaw, B.B., 1990, Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota: *Water Resources Research*, v. 26, no. 9, p. 1981–2014.
- Rahman, A.F.A., Hiura, H., and Shino, K., 2006, Trends of bulk precipitation and streamwater chemistry in a small mountainous watershed on the Shikoku Island of Japan: *Water, Air, and Soil Pollution*, v. 175, no. 1–4, p. 257–273, doi: 10.1007/s11270-006-9137-7.
- Rose, S., 1996, Temporal environmental isotopic variation within the Falling Creek (Georgia) watershed: Implications for contributions to streamflow: *Journal of Hydrology (Amsterdam)*, v. 174, no. 3–4, p. 243–261, doi: 10.1016/0022-1694(95)02767-X.
- Sacks, L.A., and Tihansky, A.B., 1996, Geochemical and Isotopic Composition of Ground Water, with Emphasis on Sources of Sulfate, in the Upper Floridan Aquifer and Intermediate Aquifer System in Southwest Florida: U.S. Geological Survey Water-Resources Investigations Report 96-4146, 54 p.
- Sidle, W.C., 1998, Environmental isotopes for resolution of hydrology problems: *Environmental Monitoring and Assessment*, v. 52, no. 3, p. 389–410, doi: 10.1023/A:1005922029958.
- Siegel, D.I., 1981, *Hydrogeochemistry and Kinetics of Silicate Weathering in a Gabbroic Watershed; Filson Creek, Northeastern Minnesota* [Ph.D. dissertation]: Minneapolis, University of Minnesota at Minneapolis, 275 p.
- Siegel, D.I., and Pfannkuch, H.O., 1984, Silicate dissolution influence on Filson-Creek chemistry, northeastern Minnesota: *Geological Society of America Bulletin*, v. 95, no. 12, p. 1446–1453, doi: 10.1130/0016-7606(1984)95<1446:SDIOFC>2.0.CO;2.
- Siegel, D.I., Lesniak, K.A., Stute, M., and Frappe, S., 2004, Isotopic geochemistry of the Saratoga springs:

- Implications for the origin of solutes and source of carbon dioxide: *Geology*, v. 32, no. 3, p. 257–260, doi: 10.1130/G20094.1.
- The Nature Conservancy, 2008, The Nature Conservancy: <http://www.nature.org/wherework/northamerica/states/wyoming/preserves/art13451.html> (August 2009).
- Triska, F.J., Kennedy, V.C., Avanzino, R.J., Zellweger, G.W., and Bencala, K.E., 1989, Retention and transport of nutrients in a 3rd-order stream in northwestern California—Hyporheic processes: *Ecology*, v. 70, no. 6, p. 1893–1905, doi: 10.2307/1938120.
- Turk, J.T., Campbell, D.H., and Spahr, N.E., 1993, Use of chemistry and stable sulfur isotopes to determine sources of trends in sulfate of Colorado lakes: *Water, Air, and Soil Pollution*, v. 67, no. 3–4, p. 415–431, doi: 10.1007/BF00478156.
- Velbel, M.A., and Price, J.R., 2007, Solute geochemical mass-balances and mineral weathering rates in small watersheds: Methodology, recent advances, and future directions: *Applied Geochemistry*, v. 22, no. 8, p. 1682–1700, doi: 10.1016/j.apgeochem.2007.03.029.
- Whalen, M.T., 1991, Oceanographic restriction and deposition of the Permian–Park City and Phosphoria Formations: Northeastern Utah and western Wyoming: *The American Association of Petroleum Geologists Bulletin*, v. 75, no. 3, p. 692–692.
- Winter, T.C., Harvey, J.W., Franke, O.L., and Alley, W.M., 1998, Ground Water and Surface Water—A Single Resource: U.S. Geological Survey Circular 1139, 79 p.

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