SULFUR ISOTOPE DYNAMICS IN A HIGH-ELEVATION CATCHMENT, WEST GLACIER LAKE, WYOMING

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(Received July 13, 1994; accepted July 27, 1994)

Abstract. Stable isotopes of S are used in conjunction with dissolved SO_4^{2-} concentrations to evaluate the utility of $\delta^{34}S$ ratios in tracing contributions of bedrock-derived S to SO_4^{2-} in runoff. Water samples were collected over the annual hydrograph from two tributaries in the West Glacier Lake, Wyoming, catchment. Concentrations of SO_4^{2-} ranged from 12.6 to 43.0 μeq L^{-1}; $\delta^{34}S$ ratios ranged from –1.8‰ to +4.9‰. The $\delta^{34}S$ value of atmospherically derived SO_4^{2-} is about +5.6‰; four samples of pyrite from the bedrock had $\delta^{34}S$ ratios that ranged from +0.7 to +4.1‰. Concentrations of SO_4^{2-} were inversely related to $\delta^{34}S$ and discharge. The data for the tributary with the higher SO_4^{2-} concentrations were reasonably consistent with mixing between atmospheric S and S from a bedrock source with a $\delta^{34}S$ ratio of about –4.5‰. The difference from the measured bedrock values presumably indicates that S isotopes in the bedrock pyrite are heterogeneously distributed. The data from the tributary with lower SO_4^{2-} concentrations did not follow a two-component mixing line. Deviation from a two-component mixing line is most likely caused by preferential elution of SO_4^{2-} from the snowpack during the early stages of snowmelt, although microbially mediated fractionation of S isotopes in the soil zone also may cause the deviation from the mixing line. Sulfur isotopes are useful in identifying whether or not there is a substantial contribution of bedrock S to runoff, but quantifying that contribution is problematic.

1. Introduction

Cycling of atmospherically derived S through catchments is affected primarily by two processes (1) adsorption/desorption in the soil (e.g., Johnson and Cole, 1977; Johnson and Henderson, 1979; Fuller *et al.*, 1986; Harrison *et al.*, 1989), and (2) incorporation into vegetation, microbiota, or both (e.g., David *et al.*, 1982; Swank *et al.*, 1984). Acidification of catchments, associated with emission of gases during burning of fossil fuels, often is accompanied by increased loading of SO_4^{2-}, followed by leaching of base cations from the soil (Cole and Johnson, 1977; Christophersen and Wright, 1981; Reuss *et al.*, 1987). Thus, understanding the biogeochemistry of S in catchments is fundamental to assessing and modeling the effects of acid deposition.

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Water, Air and Soil Pollution **79:** 227–241, 1995.

Stable S isotopes represent a useful tool in tracing S through the myriad of chemical transformations occurring in a catchment (Krouse, 1980). The utility of the isotope method is demonstrated in the variety of studies ranging from input-output budgets in a Canadian Shield catchment (Hesslein *et al.*, 1988), tracing S uptake by soils and vegetation as affected by emissions from a sour-gas plant in Alberta, Canada (Krouse and Case, 1981), elucidating organic pathways of S in the soil zone (Fuller *et al.*, 1986), and investigating the relative influence of atmospherically derived S (as SO_4^{2-}) in a small, steep catchment in Maine, U.S.A. (Stam *et al.*, 1992). Turk *et al.* (1993) used stable S isotopes to estimate the contribution of bedrock S to a group of lakes in Colorado, U.S.A.

In an earlier phase of this study, we analyzed a small data set from the West Glacier Lake catchment, an area with well-defined bedrock containing small amounts of pyrite (Finley and Drever, 1993). The S isotopes of dissolved SO_4^{2-} were consistent with mixing between an atmospheric end member with a $\delta^{34}S$ ratio of +5.4% and a bedrock component with a $\delta^{34}S$ ratio of –6%. Finley and Drever attributed the difference between the calculated bedrock end member composition (–6%) and measured values for pyrite from the bedrock (4 samples, +0.7 to +4.1%) to either heterogeneity in the bedrock pyrite, or microbially mediated transformation of S in the soil on a seasonal basis.

In order to evaluate increases in atmospherically-derived SO_4^{2-}, the contribution from intra-basin sources of SO_4^{2-} must first be quantified. The data presented in this paper were collected in a catchment containing bedrock sources which clearly contribute SO_4^{2-} to surface water. Our objective was to expand the initial work of Finley and Drever (1993) to test whether or not stable S isotopes can be used to trace bedrock-derived SO_4^{2-} in stream water over a complete hydrologic cycle.

2. Materials and Methods

2.1. Site Description

West Glacier Lake is located in a small (91 ha), high-elevation catchment in the Snowy Range, Wyoming (Figure 1). Bedrock is comprised of Medicine Peak Quartzite which is crosscut by amphibolite dikes. Quartzite consists of 60–100% quartz and is chemically inert, whereas the amphibolite dike contains actinolite (44%), epidote (30%), albite (7–15%), and small quantities of pyrite (Rochette *et al.*, 1988). The amphibolite dikes are heterogeneously distributed in the catchment, as is the pyrite. Four tributaries feed West Glacier Lake, and each has varying amounts of pyrite-bearing amphibolite within the sub-catchment (Figure 1). Topographic relief is steep, reflecting the interaction between resistant quartzite and glacial erosion. Soils are thin ($<$ 1 m) and immature, and they cover talus formed during deglaciation. Subalpine and alpine ecotones are represented with sparsely forested (subalpine fir, *Abies lasiocarpa*) areas at lower elevation, which grade to

tundra and bare rock higher in the catchment. Grassy meadows form adjacent to tributary streams where the thickest soils also occur. Snow is the dominant form of precipitation, and supplies 80–90% of the annual precipitation (in water equivalence) (Sommerfeld *et al.*, 1990). Discharge is measured by Parshall flumes in Meadow Creek and at the outlet of West Glacier Lake. Spring snowmelt constitutes the main hydrologic event, generally beginning in mid- to late-March and contributing more than 66% of the total discharge by the end of July.

2.2. SAMPLE COLLECTION

Samples of stream water were collected monthly (Oct. 1991 – Sept. 1992) from Long and Meadow Creeks (Figure 1). Long Creek discharges year-round which allows collection of samples throughout the annual hydrograph, whereas discharge in Meadow Creek ends by September or October. Snowmelt water was collected twice weekly from snow lysimeters in the spring of 1989 and 1990. Snow lysimeters consist of 2× 2 m plastic sheets, bermed by 15-cm diameter PVC pipes which are placed on the ground to intercept snowmelt water prior to contact with bedrock or soil. Samples were collected in acid-washed 250 mL polyethylene bottles and were transported to the laboratory on ice (4 °C) and in the dark. All samples were passed through 0.45 μ m filters prior to analysis; analyses took place within 24 hr of collection. Cations (Ca, Mg, Na, K) were measured in acidified (1 N HNO_3 Ultrex^{TM}) solutions using flame atomic absorption spectrophotometry, and anions (Cl^-, SO_4^{2-}, NO_3^-) were measured in unacidified samples by ion chromatography. Charge balance errors were less than 10%.

Stable S isotope ratios were measured for SO_4^{2-} in the water samples. Large volumes of sample were required because of the low total concentration of SO_4^{2-} (< 20 μmol L^{-1}). Approximately 20 L of sample were collected in a large plastic container, and the pH was adjusted to roughly 4.5 to minimize HCO_3^- anion selectivity competition with SO_4^{2-}. The water was first prefiltered through glass wool, then passed through a plastic column packed with Amberlite IRA–400 anion exchange resin to concentrate SO_4^{2-} on the exchange column. Adsorbed SO_4^{2-} then was eluted with a slightly acidified, saturated KCl solution and precipitated as $BaSO_4$. The final precipitate then was transformed into gaseous form for mass spectrometric analysis.

Stable S isotope ratios in precipitation were measured in snowpack samples collected in large (50 L) polypropylene containers prior to initiation of snowmelt. The snow was allowed to melt at room temperature after which the sample was treated as described for stream water samples.

Pyrite-bearing amphibolite rocks were sampled from four locations in the catchment (Figure 1). Pyrite was extracted from the amphibolite material by crushing the rock and hand-picking the sulfide minerals. Most pyrite crystals were weathered on the surface, and the oxidized rind was removed by boiling in 6 M HCl. Cleaned pyrite was crushed and analyzed for stable S isotope ratios by mass spectrome-

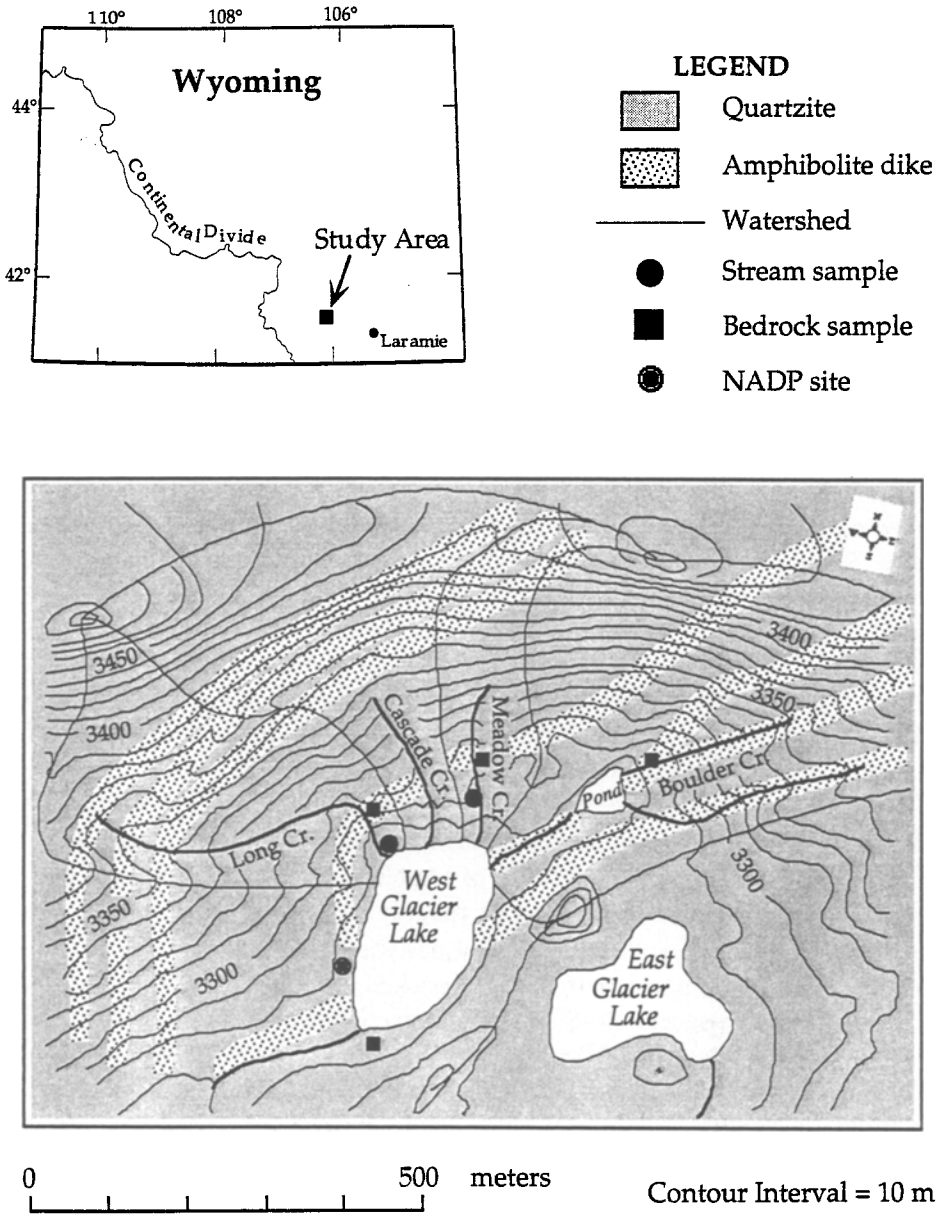

Fig. 1. Location and topographic map of the West Glacier Lake catchment showing the distribution of major rock types and sampling locations.

try. Precision for mass spectrometric analyses is ±0.2‰. All stable S isotope ratio measurements are made relative to Canyon Diablo Troilite, and results are reported in the standard δ notation

$$\delta^{34}S‰ = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000 \quad (1)$$

where R_{sample} and R_{standard} are the ratio of ^{34}S to ^{32}S in the sample and standard, respectively.

3. Results

3.1. Major element chemistry

Box plots for Ca^{2+}, Na^{+}, Cl^{-}, and SO_4^{2-} are shown in Figure 2. The box plot allows comparison of volume weighted mean concentrations for the major elements in stream water with those in precipitation. Concentrations of major elements in precipitation are based on five years of data (1986–1991) from the Snowy Range NADP site (Figure 1). Chloride is expected to be a reasonably conservative solute with no other sources in the basin except precipitation. Thus, differences in the concentration of Cl^{-} are due only to evapotranspiration. As shown in Figure 2a, the concentration of Cl^{-} is conservative between that input from precipitation and the Cl^{-} discharged in stream water. Volume-weighted mean concentrations of SO_4^{2-} are quite different in Meadow and Long Creeks. The volume-weighted mean concentration of SO_4^{2-} in Meadow Creek is not significantly different from the concentration of SO_4^{2-} in precipitation indicating that the sum of the biogeochemical processes active in the soil and bedrock apparently have only a minor effect on the overall balance of SO_4^{2-} on an annual basis. In contrast, the excess of SO_4^{2-} in Long Creek over the amount input by precipitation indicates that additional contributions of SO_4^{2-} must occur on an annual basis (Figure 2b).

Volume-weighted mean concentrations of Na^{+} and Ca^{2+} in Meadow and Long Creeks are indicative of biogeochemical reactions occurring in the soil and bedrock aquifer (Figure 2c, d). Sodium in stream water is produced by chemical weathering of albite either in the soil or in the bedrock aquifer. The concentration of Na^{+} in Meadow Creek is not significantly different from the input of Na^{+} by precipitation, indicating that the dominant flow path of solution is through soil or bedrock that is depleted in Na. Concentrations of Ca^{2+} in Meadow Creek indicate sources other than precipitation, which are likely a combination of cation exchange reactions in the soil and mineral weathering in the soil and bedrock. Calcium bearing minerals are more abundant in the bedrock than is albite, thus Ca-bearing minerals may exist in the soil without albite being present. In the case of Meadow Creek, mineral weathering in the soil over the last 10 kyr has removed almost all of the easily

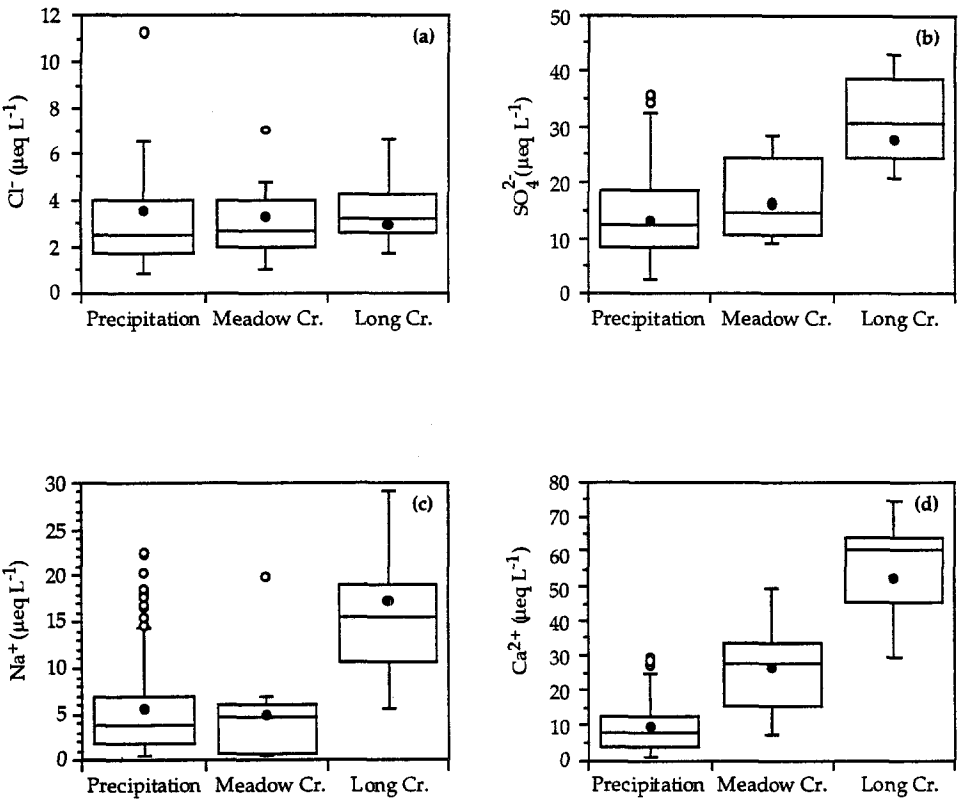

Fig. 2. Box plots of volume weighted mean concentrations of Cl^- (a), SO_4^{2-} (b), Na^+ (c), and Ca^{2+} (d) in precipitation, Meadow Creek, and Long Creek. The box encloses 50% of the data, the whiskers 90% of the data, the horizontal bar is the median, the solid circle is the volume-weighted mean, and open circles are outliers. See text for discussion.

weathered minerals, which implies a dominantly shallow hydrogeologic flow path of solutions in the Meadow Creek sub-catchment.

Concentrations of Na^+ and Ca^{2+} in Long Creek are greater than the concentrations in precipitation (Figures 2c, d). An excess of cations on an annual basis is consistent with a hydrologic flow path that results in a longer residence time of solution, allowing greater contact time and reaction between the circulating solution and bedrock minerals. The chemical evidence, when combined with field observations of year-round discharge support the interpretation that the main hydrologic flow path in the Long Creek sub-catchment is in the bedrock aquifer rather than a shallow flow path.

Interpretations of annual, volume-weighted mean concentrations are not good indicators of biogeochemical processes operating on seasonal time scales. As long as the chemical composition of precipitation has not changed dramatically, and disturbances of the vegetation in the catchment are minimal, solutes discharged in excess of the concentration in precipitation are attributed to chemical weathering of

minerals (Drever, 1988). Thus, interpreting the seasonal variation in concentrations and $\delta^{34}S$ values of SO_4^{2-} in stream water requires analysis of data collected on time scales over which seasonal biogeochemical processes occur.

3.2. Sulfate and stable S isotopes

Time-series plots for SO_4^{2-} concentrations and $\delta^{34}S$ ratios for Meadow and Long Creek samples, and the discharge hydrograph for Meadow Creek are shown in Figure 3. There are no data for Meadow Creek during November-May because discharge ceases at the end of October. The discharge hydrograph for Long Creek would presumably be similar to that of Meadow Creek, with the exception that discharge in Long Creek continues throughout the year. Discharge data collected early in the snowmelt season are unreliable because alternating freeze-thaw cycles interfere with the operation of the water-level recorder. During snowmelt the concentration of SO_4^{2-} in Meadow and Long Creeks is influenced strongly first by an initial, relatively concentrated 'pulse' of solution (Bales *et al.*, 1990), and then by dilution as the remainder of the snowpack melts (Figure 3a). Prior to snowmelt, concentrations of SO_4^{2-} are relatively high; they decrease reaching a minimum at peak discharge, and increase as base flow returns.

Concentrations of SO_4^{2-} are higher in Long Creek than in Meadow Creek, indicating differences in hydrology. Both field observation of discharge and the interpretation of major element chemistry indicate that the flow path of water through each sub-catchment has important consequences for the resultant chemical composition of stream water (see above). Discharge in Meadow Creek is primarily through shallow bedrock and soil, whereas Long Creek is more strongly influenced by deeper flow in the bedrock aquifer. In addition, Long Creek is crossed by more pyrite-bearing, amphibolite dikes than is Meadow Creek (Figure 1).

Stable S isotope ratios in both creeks are inversely related to concentrations and discharge, but there is a lag between the maximum $\delta^{34}S$ ratios and the minima in concentration of SO_4^{2-} (Figure 3b). The maximum $\delta^{34}S$ ratios in Meadow and Long Creeks occur in April and May, a time when concentrations of SO_4^{2-} have begun to decrease. Concentration decreases and $\delta^{34}S$ ratio increases occur before flow is recorded at the flume in Meadow Creek. A better indicator of the behavior of SO_4^{2-} during early snowmelt is provided by the water collected at the snowmelt lysimeters (Figure 4). High concentrations of SO_4^{2-} ($>100\ \mu eq\ L^{-1}$) in early April are indicative of preferential elution of SO_4^{2-} during the early stages of snowmelt (Tranter *et al.*, 1986; Bales *et al.*, 1990). Thus, discharge associated with snowmelt actually begins in late March or early April. The maximum $\delta^{34}S$ ratios coincide with high concentrations of SO_4^{2-} in snowmelt water, early in the snowmelt season (cf. Figures 3, 4).

The $\delta^{34}S$ ratio of SO_4^{2-} in Meadow Creek is higher than that from Long Creek with a maximum in May of +4.9‰. In Long Creek, $\delta^{34}S$ ratios steadily decrease during the base-flow period when there is no direct precipitation input; the annual

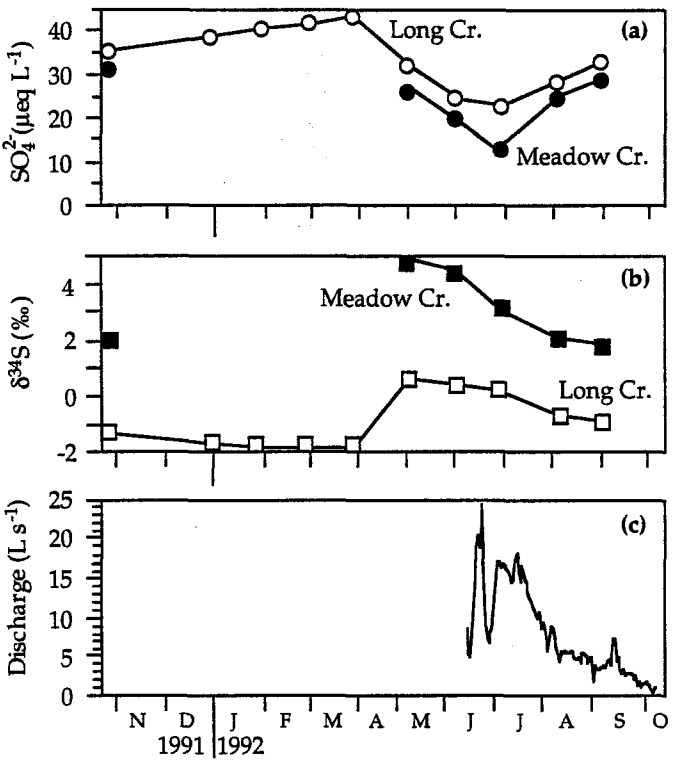

Fig. 3. Time series for concentrations of SO_4^{2-} (a), $\delta^{34}S$ ratios (b), and discharge (c) in Meadow Creek during 1991 and 1992. Meadow Creek does not flow from October to April, whereas Long Creek discharges throughout the year.

snowpack begins to accumulate in October of each year. Thus, the base-flow season (October – March) values of concentration and $\delta^{34}S$ in Long Creek are interpreted to represent the approach to steady-state reactions occurring within the bedrock aquifer.

Stable S isotopes vary with the concentration of SO_4^{2-} along a distinct hysteresis loop (Figure 5a). Values in Meadow Creek offset to higher $\delta^{34}S$ ratios and lower SO_4^{2-} concentrations than those in Long Creek. The hysteresis loop for Meadow Creek is much more pronounced than in Long Creek, and has a wider range in $\delta^{34}S$ ratios. During the peak of discharge and the approach to base flow, $\delta^{34}S$ ratios and concentrations of SO_4^{2-} change in Meadow Creek, whereas in waters of Long Creek, $\delta^{34}S$ ratios are nearly constant with changes only in the concentration of SO_4^{2-} (Figure 3). On a plot of $\delta^{34}S$ ratios against the inverse of SO_4^{2-} concentration a reasonable mixing trend exists for data from Long Creek, whereas there is no clear linear trend for data from Meadow Creek (Figure 6).

The $\delta^{34}S$ ratios measured in precipitation (snow) and pyrite in the bedrock are shown as histograms in Figure 5b. The sample size for precipitation and pyrite is

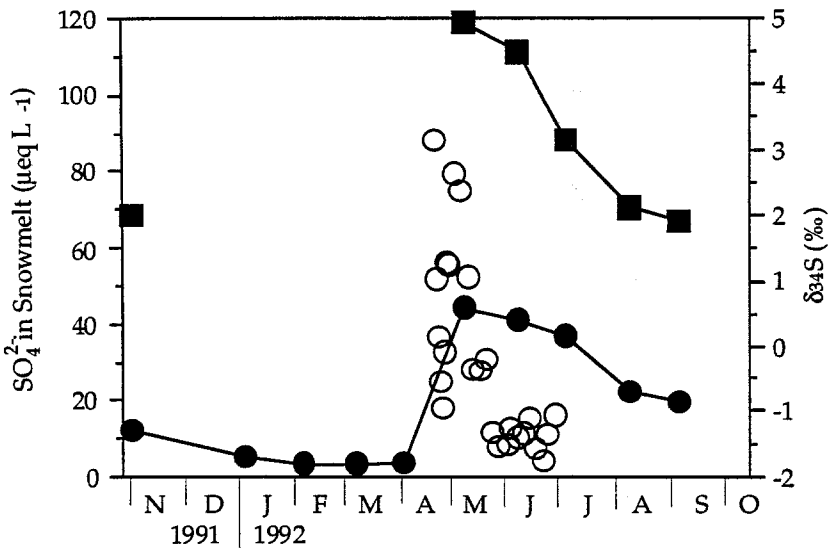

Fig. 4. Plot showing the relation between the concentration of SO_4^{2-} in snowmelt (o) and $\delta^{34}S$ ratios in Meadow (■) and Long (•) Creeks. The maximum $\delta^{34}S$ ratios coincide with peak SO_4^{2-} concentrations in snowmelt, showing the effect of preferential elution of SO_4^{2-} from the snowpack.

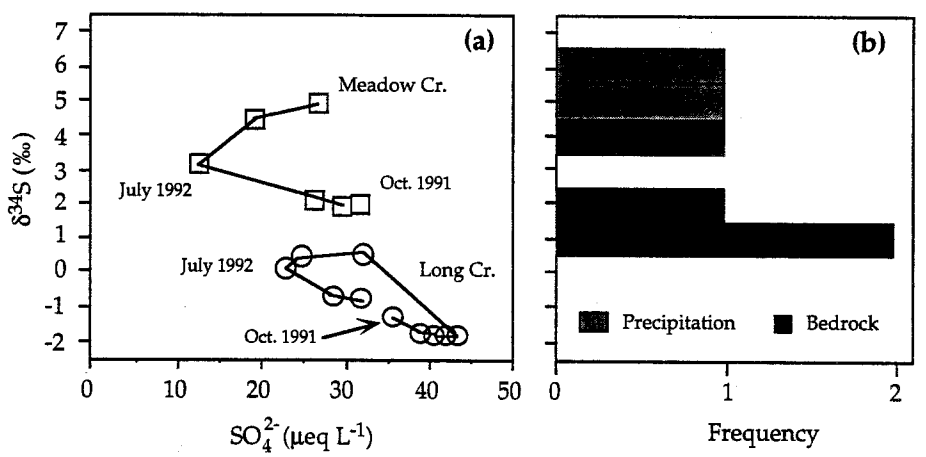

Fig. 5. $\delta^{34}S$ ratios against SO_4^{2-} (a) showing the hysteresis loop and differences between Meadow and Long Creeks. Right plot (b) is a histogram of $\delta^{34}S$ ratios from SO_4^{2-} in precipitation and in pyrite from bedrock samples.

small. Although $\delta^{34}S$ ratios in precipitation have been shown to vary seasonally (Cortecci and Longinelli, 1970; Hesslein *et al.*, 1988; Stam *et al.*, 1992), the majority of the annual precipitation input (~ 90%) is in the form of snowfall, and the $\delta^{34}S$ ratio of the snowpack (mean of +5.6‰) is considered the best measure of the atmospheric input of SO_4^{2-}. Snowpack in the region generally has values

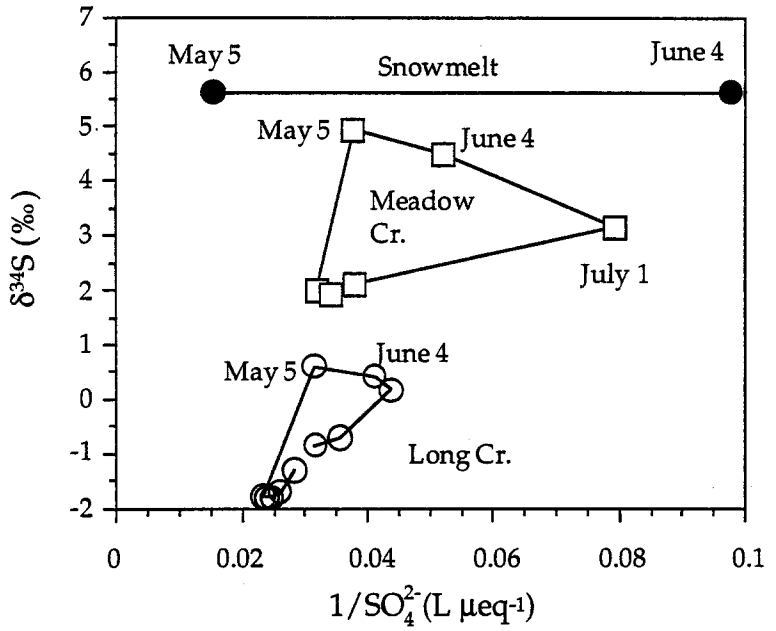

Fig. 6. $\delta^{34}S$ against $1/SO_4^{2-}$ ($L\mu eq^{-1}$). Snow points represent concentration for the dates shown plotted at the average $\delta^{34}S$ ratio of snow. Values in Long Creek are reasonably consistent with mixing between mid-season snowmelt and a bedrock component with a $\delta^{34}S$ ratio of about –4.5‰. Values in Meadow Creek are strongly influenced by the changing $\delta^{34}S$ ratios in snowmelt.

that range from +4 to +6‰ (Turk *et al.*, 1993) (Table I). Stable S isotopes are not fractionated during oxidation of pyrite to form aqueous SO_4^{2-}, thus the $\delta^{34}S$ ratio of SO_4^{2-} produced by oxidation of pyrite should provide an isotopic tracer of bedrock sources (Nakai and Jensen, 1964; Field, 1966; Taylor *et al.*, 1984). The isotopic composition of pyrite ranges from +0.7‰ to +4.1‰ (Figure 5b). Variation of $\delta^{34}S$ ratios in Meadow Creek is within the range of $\delta^{34}S$ ratios of atmospheric and bedrock sources, whereas most of the $\delta^{34}S$ ratios in Long Creek are less than the minimum $\delta^{34}S$ ratios measured in either pyrite or snowpack.

4. Discussion

Our initial hypothesis stated that concentrations of SO_4^{2-} in stream water could be described by a two end-member mixing model with SO_4^{2-} sources from precipitation and oxidation of pyrite in the local bedrock. According to our definition of two end-member mixing, the concentration and $\delta^{34}S$ ratio of SO_4^{2-} from each end member should remain relatively constant. If mixing between two sources were controlling the concentration of SO_4^{2-} in Meadow and Long Creek, temporal variations in discharge at a given sampling location would cause data points to plot along the mixing line toward the end member that occurs in the greatest

TABLE I

Stable S isotope ratios in precipitation for locations within 200 km of the West Glacier Lake catchment (from Turk *et al.*, 1993; Turk unpubl. data)

Site	Date	$\delta^{34}S$ (‰)
Rocky Mountain National Park, snow	05/11/88	+6.6
Glacier Lakes, Wyoming, snow	05/01/89	+5.4
	05/01/90	+5.9
Mt. Evans, Colorado, snow (wetfall)	05/31/89	+4.4, +4.3
	07/27/89	+3.5
	10/19/89	+3.7
	03/16/90	+4.0
	06/01/90	+3.8
	07/13/90	+3.8
	08/23/90	+5.5
	10/03/90	+3.4
	12/04/90	+6.6
Rabbit Ears Pass, Colorado, snow[a]	03/13/89	+8.4
	03/30/90	+7.3
Flat Tops Wilderness, Colorado, snow	04/13/89	+5.3

[a] Rabbit Ears Pass is located immediately downwind of a coal-fired electrical power plant.

proportion. For example, if the time series of $\delta^{34}S$ ratio vs. the inverse of the SO_4^{2-} concentration in either Long or Meadow Creek were the result of two end-member mixing, the points should plot along a line, be closest to the atmospheric composition during snowmelt, and approach the composition of the $\delta^{34}S$ ratios in pyrite during base flow. The hysteresis loops for Meadow and Long Creeks in Figure 5a are inconsistent with the pattern expected from mixing of two end members.

Decreasing $\delta^{34}S$ ratios with increasing concentrations of SO_4^{2-} was also observed by Hesslein *et al.* (1988) in a study of a catchment in the Canadian Shield. They interpreted the inverse relation between $\delta^{34}S$ ratios and SO_4^{2-} concentration as the result of isotopic fractionation in the soil zone either by adsorption or SO_4^{2-} reduction. However, Van Stempvoort *et al.* (1990) concluded that adsorption of SO_4^{2-} onto Al or Fe-oxyhydroxides does not fractionate stable S isotopes. In addition, Hesslein *et al.* (1988) observed that $\delta^{34}S$ ratios increased after peak discharge when residence time of water in the soils increases. Greater residence time of solution in the soil zone should favor microbially mediated fractionation of stable S isotopes. Thin soils and steep terrain in Meadow and Long Creeks will minimize the residence time of water in soils during snowmelt when microbial processes in the soil should be most active. Thus, in contrast with the observations of Hesslein *et al.*, the time period of shortest residence time corresponds with the

highest $\delta^{34}S$ ratios and lowest concentrations of SO_4^{2-}, whereas later in the season when residence time in the soil is greatest, concentrations of SO_4^{2-} increase while $\delta^{34}S$ ratios decrease (Figure 5a).

Assimilatory reduction of SO_4^{2-} generally results in only slight fractionation of stable S isotopes (Kaplan and Rittenberg, 1964; Thode, 1991). Fuller *et al.* (1986), in looking at different fractions of organic S extracted from soils at the Hubbard Brook Experimental Forest in New Hampshire, determined that $\delta^{34}S$ ratios can vary as much as 10‰ with depth in different soil zones. They attributed the observed variations to rapid immobilization/mineralization of S in the soil zone. Finley and Drever (1993) proposed that seasonal redox cycling within the soil could produce the observed trends in $\delta^{34}S$ ratios and SO_4^{2-} concentrations, a conclusion similar to that of Hesslein *et al.* (1988). The inverse relation in Figure 5a could be explained by (1) microbial processes in the soil zone affecting the isotopic composition and concentration of SO_4^{2-} as soils are alternately saturated (sulfate reduction) and drained (sulfide oxidation) during the late season or (2) rapid immobilization/mineralization of S in the soil zone under aerobic conditions. Distinguishing between the two possibilities, both of which are microbially mediated reactions, would require additional isotopic data for soil solutions during the hydrologically dynamic time period of snowmelt.

The shifts in $\delta^{34}S$ ratios and SO_4^{2-} concentrations between Meadow and Long Creeks, plus the hysteresis loops, argue against microbially mediated reduction as the process that produces the observed trends. In addition, soil samples taken from Meadow Creek were treated by standard microbiological procedures in an attempt to establish the presence of sulfate reducing bacteria in the soil; no evidence of sulfate reducing bacteria was observed (P. Colberg, Univ. Wyoming, pers. comm.).

Deviations from a two-component mixing line on the plot of $\delta^{34}S$ ratios against SO_4^{2-} concentration are interpreted to result from preferential elution of SO_4^{2-} from the snowpack. The concentrations of SO_4^{2-} in snowmelt for May 5 and June 4 are plotted with the mean snowmelt $\delta^{34}S$ ratios in Figure 6. The value for June 4, corresponding to the main snowmelt period when SO_4^{2-} concentrations are low, lines up well with the Long Creek points. The Long Creek data thus are interpreted as mixing between mid-season snowmelt and bedrock-derived S. The value for May 5, however, plots far from the line defined by the Long Creek data. It is apparent that variations in the input of atmospheric S between the two points will cause deviations from a two component mixing line.

The differences in $\delta^{34}S$ ratios and SO_4^{2-} concentrations between Meadow and Long Creeks are most likely a consequence of local hydrology. Meadow Creek is dominated by direct snowmelt runoff and ephemeral, shallow bedrock/soil circulation, whereas Long Creek is influenced more by bedrock discharge, which indicates a longer residence time and greater mixing of water in the subsurface. The stable S isotopic composition of SO_4^{2-} in Meadow Creek is more susceptible to microbially mediated transformations in the soil. An alternative explanation is

that preferential elution of snowpack and heterogeneity of $\delta^{34}S$ ratios in bedrock pyrite generate the observed trends. Strong hydrological controls in Meadow and Long Creeks are consistent with the observations of Stam *et al.* (1992) in which the slight fractionation of S isotopes was attributed to either time variations in micropore versus macropore flow in the soil, or to the influence of an additional source of S in the catchment.

Ultimately, the SO_4^{2-} in stream waters in the West Glacier Lake catchment is controlled by mixing of atmospherically derived SO_4^{2-} and SO_4^{2-} produced by oxidation of pyrite in the amphibolite dikes. Additional processes, primarily hydrological in nature but possibly microbially mediated fractionation, affect the chemical and isotopic signal, limiting strict interpretation in terms of a two-component mixing model.

5. Conclusion

Overall, S isotopes seem to be a good indicator of whether or not there is a bedrock source of S, but quantifying the relative contributions of bedrock and atmospheric sources is problematic. In the case of the West Glacier Lake catchment, deviation of $\delta^{34}S$ ratios of SO_4^{2-} in surface waters is indicative of a bedrock source of SO_4^{2-}. Although microbially mediated fractionation of stable S isotopes could produce hysteresis loops similar to those observed in the present set of data, the seasonal variation in $\delta^{34}S$ ratios and in SO_4^{2-} concentrations is most likely related to the major hydrological flow paths. Steep slopes and shallow soils produce a residence time of water in the soil zone that is probably insufficient to permit microbially mediated fractionation of stable S isotopes. The transient influence of preferential elution of SO_4^{2-} from the melting snowpack results in deviation from a two-component mixing line on a plot of $\delta^{34}S$ ratios against the concentration of SO_4^{2-}. More negative $\delta^{34}S$ ratios in SO_4^{2-} from Long Creek than observed in pyrite indicate heterogeneity in $\delta^{34}S$ ratios of the bedrock source. It can be argued that runoff provides a more integrated measure of $\delta^{34}S$ ratios in bedrock than direct sampling, but this argument assumes that all processes affecting the distribution of S isotopes are fully understood.

Differentiating the stable S isotopic signal from a bedrock source versus from microbially mediated fractionation of $\delta^{34}S$ ratios in the soil zone requires careful description of bedrock mineralogy and a clear understanding of the dominant hydrological processes. Additional research is necessary to fully understand and quantify the effect of microbial processes on stable S isotopes.

Acknowledgements

We thank the Rocky Mountain Forest and Range Experiment Station, USDA Forest Service for supplying the discharge measurements for Meadow Creek. The

comments of two anonymous reviewers helped clarify the manuscript. Funding for this research was provided by a series of grants from the Wyoming Water Research Center (JID), and in part by the U.S. Geological Survey (JTT).

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