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Use of stable sulfur isotopes to identify sources of sulfate in Rocky Mountain snowpacks

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Abstract

Stable sulfur isotope ratios and major ions in bulk snowpack samples were monitored at a network of 52 high-elevation sites along and near the Continental Divide from 1993 to 1999. This information was collected to better define atmospheric deposition to remote areas of the Rocky Mountains and to help identify the major source regions of sulfate in winter deposition. Average annual $\delta^{34}\text{S}$ values at individual sites ranged from +4.0 to +8.2‰ and standard deviations ranged from 0.4 to 1.6‰. The chemical composition of all samples was extremely dilute and slightly acidic; average sulfate concentrations ranged from 2.4 to 12.2 $\mu\text{eq l}^{-1}$ and pH ranged from 4.82 to 5.70. The range of $\delta^{34}\text{S}$ values measured in this study indicated that snowpack sulfur in the Rocky Mountains is primarily derived from anthropogenic sources. A nearly linear relation between $\delta^{34}\text{S}$ and latitude was observed for sites in New Mexico, Colorado, and southern Wyoming, which indicates that snowpack sulfate in the southern part of the network was derived from two isotopically distinct source regions. Because the major point sources of SO_2 in the region are coal-fired powerplants, this pattern may reflect variations in the isotopic composition of coals burned by the plants. The geographic pattern in $\delta^{34}\text{S}$ for sites farther to the north in Wyoming and Montana was much less distinct, perhaps reflecting the paucity of major point sources of SO_2 in the northern part of the network. Published by Elsevier Science Ltd.

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1. Introduction

The rapid growth of urban areas in the Rocky Mountain region has increased concern about the environmental effects of atmospheric pollutants on high-elevation ecosystems, particularly in protected areas such as National Parks and Class I Wilderness Areas. Currently, nearly all SO_2 emissions and more than 70% of NO_x emissions in the Rocky Mountain region are produced by fossil-fuel combustion in urban areas and by electric utilities (Peterson et al., 1998; Alewell et al., 2000). SO_2 is of environmental concern because it can be

oxidized in the atmosphere to sulfate, which not only causes visibility impairment but is a major component of acidic deposition (Peterson et al., 1998). Many high-elevation lakes and streams in the Rocky Mountain region are particularly sensitive to acidic deposition because they are underlain by bedrock types that have little capacity to buffer acidic inputs (Mast et al., 1990; Turk and Spahr, 1991). In addition, most precipitation at high elevations accumulates in a seasonal snowpack, which serves as a reservoir for sulfate and other atmospheric pollutants that are released to surface waters over a relatively short period during spring snowmelt (Campbell et al., 1995; Williams et al., 1996; Turk and Campbell, 1997).

Although the major point sources of SO_2 in the Rocky Mountain region have been inventoried (Dickson et al., 1994), little is known about the dispersion and transport of SO_2 in the atmosphere and the influence of point

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sources on sulfate concentrations in precipitation. Increased understanding of the relation between emission sources and atmospheric deposition will improve the ability of land managers to protect sensitive ecosystems from atmospheric pollution (Peterson et al., 1998). Several recent studies have investigated sources of sulfur in atmospheric deposition in mountainous areas of Colorado. Heuer et al. (2000) compared precipitation chemistry at several high-elevation sites near Rocky Mountain National Park and determined that pollution sources on both sides of the Continental Divide influenced sulfate concentrations in precipitation. Annual snowpack surveys conducted along the Continental Divide revealed high sulfate concentrations in the Mount Zirkel Wilderness Area in northwestern Colorado (Ingersoll, 1995). The elevated concentrations were attributed to emissions from coal-fired powerplants located upwind from the wilderness area (Turk and Campbell, 1997). Baron and Denning (1993) compared wet-deposition chemistry at two sites in Rocky Mountain National Park to wind direction. They concluded that strong acid anions (nitrate and sulfate) primarily originate from agricultural and urban areas to the east of the park and are transported by upslope winds.

The objective of this study was to identify major sources of dissolved sulfate in Rocky Mountain snowpacks through the use of stable sulfur isotope ratios. Sulfur isotopes have been widely used as a tool for separating sources of sulfur in atmospheric gases and in precipitation (Krouse and Grinenko, 1991; Alewell et al., 2000). The snowpack was sampled at the end of the accumulation period at 52 high-elevation sites along the Continental Divide from New Mexico to Montana. Because the snowpack represents most of the annual deposition to high-elevation areas, this data set should provide a regional picture of sulfur sources in atmospheric deposition to remote areas throughout the Rocky Mountain region.

2. Sampling network and methods

Snowpack samples were collected from a network of 52 sites situated along the Continental Divide in mountainous areas of New Mexico, Colorado, Wyoming, and Montana. Sampling sites in the snowpack network are shown in Fig. 1, and site names and locations are listed in Table 1. All sampling sites in the network were located in high-elevation areas (elevation 1865–3597 m) on National Forest or National Park lands with limited anthropogenic activity. Sites were established at distances ranging from about 50 m to several kilometers from plowed roadways to minimize contamination from vehicular traffic. Snowfall at the study sites accumulates from October through late March or early April and typically represents 50–70% of the annual precipitation (USDA Natural Resources Conservation Service, 2000). Snow-water

equivalent of the annual snowpacks ranged from about 0.2 m in the drier Southern Rocky Mountains to about 1.7 m in the Central and Northern Rocky Mountains. Most Colorado and New Mexico snow-sampling sites are at elevations between 2700 and 3600 m; Wyoming and Montana sites are lower at elevations between 1850 and 3100 m.

Snowpack samples were collected in early spring of 1993–99 just prior to the start of snowmelt in order to capture most of the winter deposition in a single sample. Depth-integrated samples were collected from the vertical face of a snowpit by using pre-cleaned plastic shovels (Ingersoll, 1999). Samples for sulfur isotope analysis were collected in pre-cleaned 60-l polyethylene carboys that were transported to the laboratory and stored at room temperature. Samples for major-ion analyses were collected in pre-cleaned Teflon bags and were kept frozen until processed. Samples for major-ion analyses were collected at all 52 sites during each of the 7 years of the study whereas slightly fewer samples (5–7) were collected at each site for sulfur isotope analysis.

Samples for sulfur isotope analysis were processed within 4 weeks of collection. Samples were acidified to pH 4 with HCl then pumped through a column containing KCl-saturated anion-exchange resin to extract the sulfate from the melt water. Sulfate was eluted from the resin using 200 ml of 0.4 M KCl and then 1–2 ml of saturated BaCl₂ were added to the eluant to precipitate BaSO₄. The precipitate was collected on a 0.45- μ m membrane filter, air dried, and scraped off the filter paper with a razor blade. Isotopic analyses were performed at the USGS stable isotope laboratory in Denver, Colorado. For the 1993–95 samples, analysis of BaSO₄ precipitates was performed by converting them to SO₂ gas in a vacuum line following Yanagisawa and Sakai (1983), and analyzing the isotopic composition of the gases using a Nuclide 6-60 mass spectrometer¹ equipped with a dual viscous inlet system. The 1996–99 samples were converted to SO₂ using a Carlo Erba elemental analyzer (Gieseemann et al., 1994). Isotopic analysis was by the continuous flow method using a Micromass Optima mass spectrometer (see fn 1). Standards were routinely analyzed along with unknowns to ensure that the laboratory calibration was unchanged over the 7 year duration of the project, and through the change from one mass spectrometer to another. Isotopic compositions are reported in δ -notation relative to the Cañon Diablo troilite standard. Replicate analyses typically agreed to within $\pm 0.2\text{‰}$. Average values obtained for internationally distributed isotope standards during the

¹ Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the US Government.

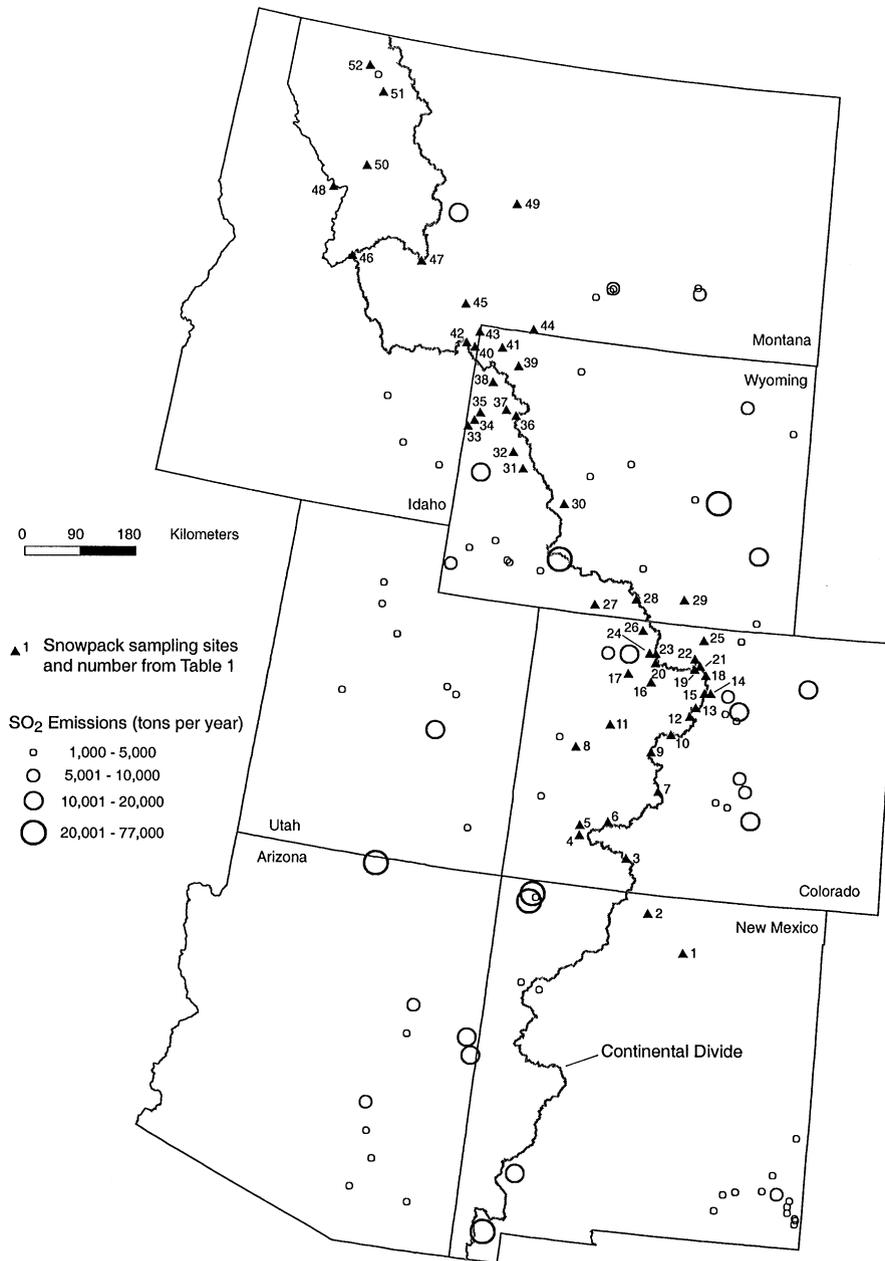


Fig. 1. Locations of 52 sites in Rocky Mountain snowpack network and SO₂ emissions from major point sources in the region.

period of sample analysis were NBS127 = 21.1‰, NBS123 = 17.3‰, and IAEA-S-1 = -0.5‰.

Samples for major-ion analyses were melted just prior to laboratory processing according to the method described by Ingersoll (1999). Samples for major cations were filtered through 0.45- μm polycarbonate filters into acid-washed bottles then acidified with double-distilled, concentrated nitric acid. Samples for major anions were filtered through 0.45- μm membrane filters into prerinse

bottles. An unfiltered sample was collected for alkalinity and pH determination. Major cations were analyzed by inductively coupled plasma atomic-emission spectroscopy, and major anions were analyzed by ion chromatography. Analytical detection limits were less than $1.0\mu\text{eq l}^{-1}$ for all major cation and anion analyses.

Point-source SO₂ emissions in the study area are represented in Fig. 1 for point sources greater than

Table 1

Locations of sampling sites in the Rocky Mountain snowpack network with $\delta^{34}\text{S}$ values for 1993–99 (numbers refer to site locations in Fig. 1)

No.	Site name	Latitude	Longitude	1993	1994	1995	1996	1997	1998	1999	Avg.	SD. ^a
1	Gallegos Peak, NM	36°11'00"	105°33'00"	3.2	4.2	4.9	4.6	3.3	4.6	5.4	4.3	0.8
2	Hopewell, NM	36°43'00"	106°16'00"	3.6	3.6	3.8	4.8	3.9	3.8	4.3	4.0	0.4
3	Wolf Creek Pass, CO	37°29'00"	106°47'00"	3.6	4.0	4.5	6.0	3.9	3.5	4.3	4.3	0.8
4	Molas Lake, CO	37°45'00"	107°42'00"	2.8	4.1	4.6	3.8	4.6	4.2	3.2	3.9	0.7
5	Red Mountain Pass, CO	37°54'00"	107°43'00"	3.5	4.4	5.0	5.2	3.9	4.7	—	4.5	0.7
6	Slumgullion Pass, CO	37°59'30"	107°12'00"	5.8	—	4.4	3.5	4.1	3.7	—	4.3	0.9
7	Monarch Pass, CO	38°31'00"	106°19'30"	3.7	4.8	5.8	6.3	—	5.4	5.5	5.3	0.9
8	Grand Mesa, CO	39°01'58"	107°58'39"	4.6	4.7	5.0	5.4	4.4	3.5	—	4.6	0.6
9	Brumley, CO	39°05'00"	106°32'30"	—	5.4	4.9	6.6	4.9	4.8	—	5.3	0.8
10	Fremont Pass, CO	39°22'00"	106°12'00"	3.7	—	3.9	—	4.5	5.1	5.2	4.5	0.7
11	Sunlight Peak, CO	39°25'16"	107°22'30"	5.0	5.2	5.8	6.6	5.2	5.5	4.1	5.3	0.8
12	Loveland Pass, CO	39°40'00"	105°53'30"	4.3	5.0	4.9	7.1	—	5.5	6.0	5.5	1.0
13	Berthoud Pass, CO	39°48'00"	105°47'00"	4.8	5.9	6.0	6.3	5.7	6.0	6.1	5.8	0.5
14	Niwot Snotel, CO	40°02'00"	105°32'00"	—	5.8	6.0	—	5.3	6.1	6.7	6.0	0.5
15	University Camp, CO	40°02'00"	105°34'00"	5.2	5.5	5.7	7.5	6.0	6.3	—	6.0	0.8
16	Lynx Pass, CO	40°06'45"	106°42'00"	5.8	6.7	6.3	7.4	5.1	6.7	5.6	6.2	0.8
17	Dunckley Pass, CO	40°12'00"	107°09'00"	5.8	6.0	5.7	7.4	5.6	6.0	4.6	5.9	0.8
18	Loch Vale, CO	40°17'24"	105°40'00"	4.5	5.8	6.2	7.4	6.0	—	—	6.0	1.0
19	Phantom Valley, CO	40°23'50"	105°50'54"	5.0	6.2	5.7	7.2	5.5	7.2	6.5	6.2	0.8
20	Rabbit Ears Pass, CO	40°23'59"	106°39'25"	6.7	7.3	7.2	7.7	7.0	8.1	7.8	7.4	0.5
21	Lake Irene, CO	40°24'40"	105°48'47"	5.2	6.1	6.1	6.7	5.3	7.0	6.3	6.1	0.7
22	Cameron Pass, CO	40°31'00"	105°54'00"	4.6	6.1	6.5	7.3	6.8	6.2	6.3	6.3	0.8
23	Buffalo Pass, CO	40°32'00"	106°40'00"	6.2	7.2	7.2	7.6	6.6	7.8	7.3	7.1	0.6
24	Dry Lake, CO	40°32'00"	106°47'00"	6.6	7.7	7.2	8.5	7.0	8.6	8.4	7.7	0.8
25	Deadman Pass	40°48'00"	105°46'00"	4.4	—	6.0	6.7	6.9	6.8	—	6.2	1.0
26	Elk River, CO	40°51'00"	106°58'00"	5.4	6.8	6.4	8.4	6.1	5.3	7.0	6.5	1.1
27	Old Battle, CO	41°09'00"	107°58'00"	6.0	7.2	6.3	8.1	6.6	7.1	6.9	6.9	0.7
28	Divide Peak, CO	41°18'00"	107°10'00"	6.2	6.6	6.6	7.8	6.2	7.4	—	6.8	0.7
29	Brooklyn Lake, WY	41°22'00"	106°14'00"	6.4	6.7	6.0	7.5	4.9	7.3	7.0	6.5	0.9
30	South Pass, WY	42°34'00"	108°50'00"	7.2	7.5	7.3	9.6	7.4	10.2	—	8.2	1.3
31	Elkhart Park, WY	43°00'00"	109°45'00"	3.9	6.6	7.3	6.9	7.3	7.3	8.2	6.8	1.4
32	Gypsum Creek, WY	43°13'22"	109°59'27"	5.8	—	6.3	5.5	6.2	—	—	6.0	0.4
33	Teton Pass, WY	43°30'00"	110°59'00"	4.9	7.2	6.8	6.6	5.2	5.9	—	6.1	0.9
34	Rendevous Mtn., WY	43°36'06"	110°52'22"	6.4	5.2	5.9	5.8	5.7	7.2	—	6.0	0.7
35	Garnet Canyon, WY	43°43'26"	110°46'59"	5.4	—	5.2	—	5.1	6.3	7.4	5.9	1.0
36	Togwotee Pass, WY	43°45'00"	110°03'00"	6.3	7.1	5.4	7.0	5.7	6.9	—	6.4	0.7
37	Four Mile Meadow, WY	43°49'00"	110°16'00"	5.7	8.0	5.7	8.7	—	7.9	—	7.2	1.4
38	Lewis Lake Divide, WY	44°13'00"	110°40'00"	4.5	5.2	4.3	5.9	6.6	7.1	7.0	5.8	1.2
39	Sylvan Lake, WY	44°29'00"	110°09'00"	3.2	5.3	5.0	4.9	3.8	5.5	—	4.6	0.9
40	West Yellowstone, MT	44°40'00"	111°06'00"	4.6	6.4	4.4	6.0	5.0	5.8	—	5.4	0.8
41	Canyon, WY	44°43'00"	110°32'00"	4.4	6.4	4.1	—	2.0	4.7	—	4.3	1.6
42	Lionshead, MT	44°43'00"	111°17'00"	4.6	6.4	4.5	5.8	6.0	5.5	6.3	5.6	0.8
43	Twenty-one Mile, MT	44°54'00"	111°03'00"	4.3	6.0	4.4	6.2	4.6	4.8	—	5.1	0.8
44	Daisy Pass, MT	45°03'00"	109°57'00"	4.1	5.3	4.2	4.0	2.9	4.4	—	4.2	0.8
45	Big Sky, MT	45°16'30"	111°26'00"	4.1	7.3	5.0	6.3	5.9	6.1	5.8	5.8	1.0
46	Chief Joseph Pass, MT	45°41'13"	113°55'56"	4.8	6.0	4.1	—	4.8	6.8	5.1	5.3	1.0
47	Red Mountain, MT	45°47'30"	112°29'30"	6.1	8.2	5.3	5.8	6.2	7.0	—	6.4	1.0
48	Granite Pass, MT	46°38'23"	114°36'41"	5.2	5.4	4.0	—	5.9	7.1	7.7	5.9	1.3
49	Kings Hill, MT	46°51'00"	110°42'00"	7.5	9.7	6.4	7.4	6.2	6.5	7.2	7.3	1.2
50	Snow Bowl, MT	47°02'11"	113°59'43"	4.5	5.4	4.6	5.2	7.4	6.1	—	5.5	1.1
51	Noisy Basin, MT	48°09'19"	113°56'36"	4.9	5.3	5.5	6.3	6.8	6.3	—	5.9	0.7
52	Big Mountain, MT	48°30'29"	114°20'42"	5.3	5.0	5.2	6.0	6.7	7.5	5.7	5.9	0.9

^aSD = standard deviation.

1000 t yr⁻¹ year. Data were obtained from the US Environmental Protection Agency AIRSData program (<http://www.epa.gov/airsdata>, accessed 02 July 1999) for Arizona (1995), Colorado (1998), Montana (1998), New Mexico (1999), and Wyoming (1998). Point-source emission data for Utah (1996) were obtained from the Utah Department of Natural Resources Division of Air Quality (http://www.eq.state.ut.us/eqair/aq_home.htm) and data for Idaho (1996) were obtained from Peterson et al. (1998).

3. Results and discussion

3.1. Range of $\delta^{34}\text{S}$ values and major-ion concentrations

$\delta^{34}\text{S}$ values for the 52 sites in the snowpack network over the period 1993–99 are presented in Table 1. The average $\delta^{34}\text{S}$ values measured in the network ranged from a minimum of +4.0‰ at Hopewell, in northern New Mexico and Molas Lake in southwestern Colorado, to as much as +8.3‰ at South Pass in southwestern Wyoming. The range of $\delta^{34}\text{S}$ values measured during this study was similar to the range of values reported for precipitation at remote sites in the Eastern United States. For example, $\delta^{34}\text{S}$ values ranged from +1.6 to +7.6‰ at Bear Mountain in Maine (Mitchell et al., 1998); +1.1 to +12.7‰ in the White Mountains of New Hampshire (Zhang et al., 1998); +3.3 to +5.8‰ in the Catskill Mountains of New York (J.T. Turk, U.S. Geological Survey, unpublished data); and +1.7 to +5.1‰ in the Blue Ridge Mountains of North Carolina (J.T. Turk, U.S. Geological Survey, unpublished data). Fewer data exist for precipitation in remote areas of the Western United States. $\delta^{34}\text{S}$ values for precipitation samples collected on Mount Evans in the Colorado Front Range ranged from +1.8 to +6.6‰ (J.T. Turk, unpublished data), and Popp et al. (1986) reported values of +2.7 to +4.1‰ for precipitation in central New Mexico.

Reproducibility of $\delta^{34}\text{S}$ values was assessed by collecting samples at paired snowpits (located less than 50 m apart) at the Rabbit Ears Pass site in Colorado from 1993 to 1999. Values at the paired sites ranged from +6.4 to +8.1‰ at the main snowpit and +6.2 to +7.9‰ at the replicate snowpit and averaged +7.4‰ and +7.3‰, respectively, over the period 1993–99. The difference in values between the paired snowpits for individual years ranged from 0.1 to 0.4‰, indicating that spatial variation in $\delta^{34}\text{S}$ at individual sites was small compared to variability from year to year. Inter-annual variability in $\delta^{34}\text{S}$ values is reflected in the range of standard deviations calculated for each site (Table 1). The variability, although fairly large, is similar among sites in the network. The standard deviation of the annual $\delta^{34}\text{S}$ values at individual sites ranged from 0.4 to 1.6‰, and more than half of the sites fell in the 0.7–1.0‰ range. The relative

Table 2

Mean $\delta^{34}\text{S}$ and major-ion concentrations in lower and upper snow strata at 7 sites in Colorado sampled during 1993–95. The *p*-values are from results of paired *t*-tests between the lower and upper snow strata. Difference in concentrations between layers is shown in bold for constituents with *p* ≤ 0.010

	Mean conc. lower	Mean conc. upper	Mean conc. difference	<i>p</i> -Value (<i>n</i> = 18)
$\delta^{34}\text{S}$	6.5	6.6	– 0.1	0.694
H ⁺ (μeq l ⁻¹)	10.0	12.6	– 2.7	0.001
Ca (μeq l ⁻¹)	6.4	7.5	– 1.1	0.284
Mg (μeq l ⁻¹)	1.2	1.6	– 0.3	0.075
Na (μeq l ⁻¹)	0.9	1.5	– 0.6	0.021
K (μeq l ⁻¹)	1.2	0.6	0.6	0.014
NH ₄ (μeq l ⁻¹)	5.4	6.0	– 0.6	0.408
Cl (μeq l ⁻¹)	1.2	1.5	– 0.3	0.145
NO ₃ (μeq l ⁻¹)	12.2	13.3	– 1.1	0.295
SO ₄ (μeq l ⁻¹)	9.4	12.1	– 2.7	0.002

standard deviation of $\delta^{34}\text{S}$ values showed a weak inverse correlation with sulfate concentrations. This pattern may indicate that at low sulfate concentrations, $\delta^{34}\text{S}$ values are influenced by several minor sources and therefore have a greater range of values, whereas at higher concentrations, $\delta^{34}\text{S}$ values tend to approach that of the dominant sulfur source in the area (Newman et al., 1991).

Seasonal variations in $\delta^{34}\text{S}$ and snowpack chemistry were assessed by comparing separate samples collected from the lower and upper portions of the snowpack. Eighteen pairs of samples were collected at 7 sites in Colorado between 1993 and 1995. Mean $\delta^{34}\text{S}$ and major-ion concentrations in the two layers and results of paired *t*-tests between layers are shown in Table 2. $\delta^{34}\text{S}$ values were similar between layers but statistically significant differences were detected for hydrogen-ion and sulfate concentrations, which both increased by an average of 2.7 μeq l⁻¹ in the upper layer. The similarity in $\delta^{34}\text{S}$ values between layers indicates that the source of sulfur remained relatively constant over the winter accumulation period at least for this subset of sites in Colorado. Differences in hydrogen-ion and sulfate concentrations could be affected by variable snowfall amounts over the winter, which would not affect the isotopic composition. Statistically significant differences were not observed for other major solutes (Table 2), however, indicating that snowfall amount probably was not an important factor. Alternatively, higher concentrations of sulfate and hydrogen in the upper half of the snowpack may reflect a seasonal change in the oxidation rate of SO₂ because of longer days and warmer air temperatures in late winter and early spring than in early winter (Saltzman et al., 1983; Faust, 1994).

The chemical composition of snowpack samples collected during the study was extremely dilute and slightly acidic (Table 3); average sulfate concentrations ranged

Table 3

Average major-ion concentrations ($\mu\text{eq l}^{-1}$) for 52 sites in the Rocky Mountain snowpack network, 1993–99 (numbers refer to site locations in Fig. 1)

No.	Site name	H ⁺	Ca	Mg	Na	K	NH ₄	Cl	SO ₄	NO ₃
1	Gallegos Peak, NM	4.1	15.1	2.4	1.4	2.5	4.8	1.3	9.8	9.5
2	Hopewell, NM	5.8	14.1	2.0	1.6	1.3	4.6	1.4	10.1	12.0
3	Wolf Creek Pass, CO	5.4	12.7	1.9	2.1	1.2	3.6	1.9	8.3	9.1
4	Molas Lake, CO	3.8	13.3	1.4	1.5	1.7	2.6	1.4	5.9	7.9
5	Red Mountain Pass, CO	3.8	15.1	2.2	1.8	1.8	2.5	1.5	6.3	8.5
6	Slumgullion Pass, CO	3.2	10.9	1.7	2.1	2.7	1.9	1.9	5.5	6.1
7	Monarch Pass, CO	3.6	11.4	1.9	1.2	1.2	3.3	1.2	6.4	8.9
8	Grand Mesa, CO	5.2	12.7	2.0	1.7	1.7	4.7	1.3	9.2	9.0
9	Brumley, CO	6.2	5.6	1.1	1.7	0.9	2.3	1.0	4.7	7.6
10	Fremont Pass, CO	3.6	9.3	2.0	1.9	1.6	2.4	1.7	4.7	7.7
11	Sunlight Peak, CO	5.7	11.6	1.7	1.2	1.1	4.4	1.0	7.0	9.1
12	Loveland Pass, CO	5.0	7.3	1.6	2.7	1.1	2.7	2.4	5.3	8.7
13	Berthoud Pass, CO	7.2	4.9	1.0	2.9	0.7	2.5	2.4	5.1	8.1
14	Niwot Snotel, CO	7.9	6.9	1.4	1.4	0.8	7.5	1.1	9.0	11.8
15	University Camp, CO	8.0	6.8	1.7	1.3	1.9	4.7	1.3	8.6	9.8
16	Lynx Pass, CO	10.6	6.2	1.3	1.1	0.5	2.9	1.0	6.6	11.4
17	Dunckley Pass, CO	4.8	14.2	2.3	1.4	4.2	3.4	1.9	7.9	9.5
18	Loch Vale, CO	8.7	7.2	1.6	1.6	1.2	4.3	1.3	8.7	11.2
19	Phantom Valley, CO	11.0	6.3	1.6	1.7	1.3	3.9	1.2	8.4	10.6
20	Rabbit Ears Pass, CO	12.5	4.5	0.9	1.8	0.5	4.7	1.1	10.3	10.8
21	Lake Irene, CO	8.3	4.7	0.9	1.4	0.7	2.7	< 1.0	6.3	8.5
22	Cameron Pass, CO	8.7	7.3	1.6	2.3	1.6	3.5	1.9	8.2	9.4
23	Buffalo Pass, CO	11.6	6.2	1.3	1.3	0.5	5.3	1.3	11.7	11.3
24	Dry Lake, CO	15.3	6.7	1.5	1.5	0.9	5.2	1.3	12.2	14.8
25	Deadman Pass	5.7	9.0	2.2	1.1	2.4	4.5	1.5	8.4	10.7
26	Elk River, CO	10.6	7.5	1.4	1.5	0.6	3.8	1.4	8.5	13.4
27	Old Battle, CO	9.9	6.3	1.5	1.4	0.9	4.6	1.3	9.6	10.8
28	Divide Peak, CO	10.9	8.3	1.8	1.9	< 0.5	4.9	1.5	10.1	14.3
29	Brooklyn Lake, WY	8.4	6.0	1.5	1.3	0.9	4.1	1.3	8.3	10.1
30	South Pass, WY	7.8	6.2	1.3	2.6	0.7	4.0	1.2	8.9	8.7
31	Elkhart Park, WY	5.4	3.8	0.9	2.0	0.5	4.4	1.3	6.1	6.5
32	Gypsum Creek, WY	6.0	3.9	1.2	1.5	1.1	3.5	1.2	5.1	6.9
33	Teton Pass, WY	2.0	10.0	3.4	4.0	1.7	6.4	2.9	6.7	7.6
34	Rendevous Mtn., WY	4.8	3.7	1.3	1.3	< 0.5	3.4	1.0	5.1	5.1
35	Garnet Canyon, WY	6.0	2.4	0.8	1.1	0.5	4.0	1.0	4.7	5.1
36	Togwotee Pass, WY	3.9	3.8	0.9	2.1	0.5	2.9	1.0	4.2	4.6
37	Four Mile Meadow, WY	4.2	3.6	1.2	1.8	1.0	3.5	1.3	3.9	5.7
38	Lewis Lake Divide, WY	4.7	2.1	0.6	0.9	< 0.5	6.2	1.1	4.3	5.7
39	Sylvan Lake, WY	5.2	2.1	0.5	1.3	0.5	4.8	1.0	4.3	4.9
40	West Yellowstone, MT	5.6	3.0	0.9	1.2	0.8	7.7	2.0	5.1	8.8
41	Canyon, WY	4.3	2.3	0.5	1.5	0.5	4.6	1.2	4.0	5.6
42	Lionshead, MT	5.6	4.2	1.2	1.3	1.6	12.9	2.3	8.8	10.5
43	Twenty-one Mile, MT	6.7	2.7	0.7	1.9	0.8	6.2	2.0	4.9	7.3
44	Daisy Pass, MT	5.0	2.2	0.6	0.7	0.6	3.5	< 1.0	3.8	4.4
45	Big Sky, MT	3.6	4.8	1.0	1.8	0.5	4.0	1.0	4.3	5.6
46	Chief Joseph Pass, MT	4.4	1.5	0.3	0.9	0.5	3.0	< 1.0	2.8	3.7
47	Red Mountain, MT	4.1	4.0	0.9	1.5	0.6	4.6	< 1.0	4.2	5.5
48	Granite Pass, MT	4.8	0.9	0.3	1.1	0.6	1.3	1.0	2.4	2.4
49	Kings Hill, MT	5.2	4.6	0.8	0.8	0.6	5.5	1.0	6.2	6.4
50	Snow Bowl, MT	6.2	1.4	0.5	1.3	0.6	2.7	1.0	3.7	3.9
51	Noisy Basin, MT	6.6	1.6	0.4	1.1	1.7	3.9	1.0	4.2	5.0
52	Big Mountain, MT	7.2	1.4	0.3	1.0	< 0.5	3.0	< 1.0	3.9	4.6

from 2.4 to 12.2 $\mu\text{eq l}^{-1}$ and pH ranged from 4.82 to 5.70. The highest sulfate concentrations and lowest pH values were consistently measured in samples collected in the northwestern part of Colorado at Dry Lake, Buffalo Pass, and Rabbit Ears Pass. Pearson rank-correlation coefficients were calculated for the average values at each site to determine associations among $\delta^{34}\text{S}$ and major-ion concentrations. The $\delta^{34}\text{S}$ values showed no relation to sulfate concentrations ($r = 0.303$, $p = 0.027$) but showed a weak positive correlation with hydrogen ion ($r = 0.584$, $p = < 0.001$) and inverse correlation with calcium ($r = -0.354$, $p = 0.010$). The lack of a correlation between $\delta^{34}\text{S}$ values and sulfate concentrations indicates that sulfate in the snowpack likely is derived from several isotopically distinct sources. This is not unexpected considering that the sampling network spans a distance of more than 1500 km and is influenced by a number of different source areas of sulfur. Sulfate concentrations were strongly correlated with concentrations of nitrate ($r = 0.895$, $p = < 0.001$), hydrogen ion ($r = 0.627$, $p = < 0.001$), calcium ($r = 0.545$, $p = < 0.001$), and magnesium ($r = 0.577$, $p = < 0.001$). Strong correlations with nitrate and hydrogen are indicative of anthropogenic sources of sulfate, whereas positive correlations with base cations suggest sulfate originates either from sulfate salts or from sulfuric acid that is neutralized by carbonate dust in the atmosphere (Sievering, 1987; Baron and Denning, 1993).

3.2. Geographic variations in $\delta^{34}\text{S}$ and major ions

Because the snowpack network is roughly aligned along a north–south transect, geographic variations in isotopic composition are best illustrated by plotting $\delta^{34}\text{S}$ values as a function of latitude (Fig. 2). In the southern part of the network, there is a nearly linear trend of increasing $\delta^{34}\text{S}$ values with increasing latitude for sites between northern New Mexico and the southern end of the Wind River Mountains at South Pass, Wyoming. In the northern part of the network, the geographic pattern in $\delta^{34}\text{S}$ is not as pronounced. The $\delta^{34}\text{S}$ values appear to decrease with increasing latitude across Wyoming but then increase slightly towards the US–Canadian border. There are a few notable exceptions from these general geographic patterns. For example, the three sites near the Mount Zirkel Wilderness Area in northwestern Colorado (Rabbit Ears Pass, Buffalo Pass, and Dry Lake) plot distinctly above the pattern defined by the southern subgroup of sites. Among the northern sites, Daisy Pass, Sylvan Lake, and Canyon were lighter than sites at similar latitudes, and Kings Hill was significantly heavier. All four of these sites are located east (open symbols) of the Continental Divide, whereas within the southern subgroup, there were no distinct differences between sites on the west (closed symbols) and east sides of the Continental Divide.

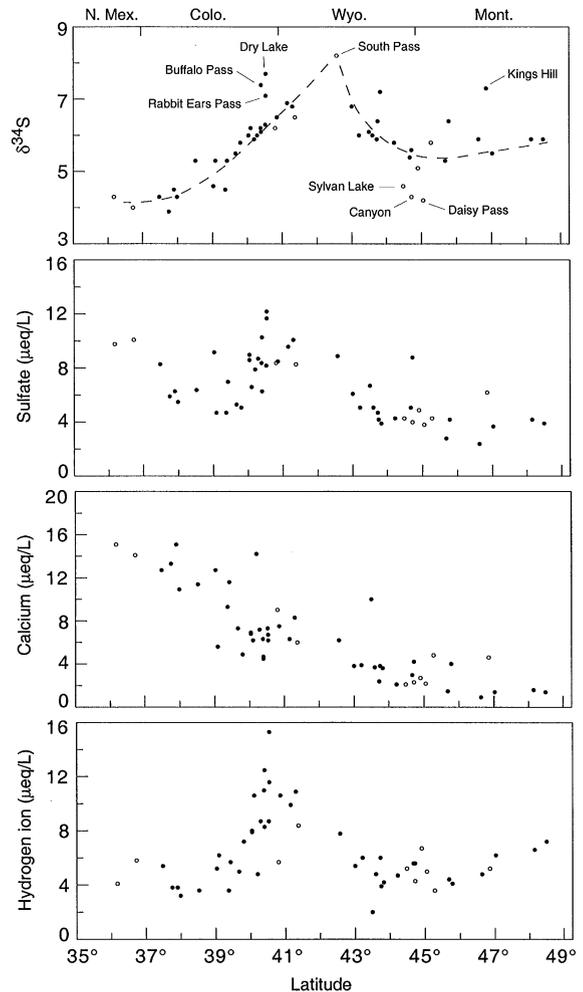


Fig. 2. Variations in average snowpack $\delta^{34}\text{S}$ values and sulfate, calcium and hydrogen-ion concentrations as a function of sampling-site latitude. Open symbols indicate sites situated east of the Continental Divide and closed symbols indicate sites situated on or west of the Continental Divide.

Strong geographic trends also are apparent in the major-ion concentrations, particularly sulfate, calcium, and hydrogen ion (Fig. 2). Calcium concentrations are highest at the southern end of the network (13–15 $\mu\text{eq l}^{-1}$) and show a striking decrease across the network to very low concentrations ($< 2 \mu\text{eq l}^{-1}$) in northwestern Montana. Sulfate and hydrogen-ion concentrations show slightly more complex patterns. The highest concentrations of both ions consistently were measured at sites near the Colorado–Wyoming border. To the north, concentrations of both ions generally decreased, although hydrogen ion showed a slight increase in concentration at the northern Montana sites similar to $\delta^{34}\text{S}$. To the south of the Colorado–Wyoming border, hydrogen-ion concentrations decreased strikingly. Sulfate

concentrations declined towards central Colorado but increased again near the Colorado–New Mexico border.

3.3. Sources of snowpack sulphate

Sulfate in snow can be derived from a variety of natural sources such as biogenic emissions, sea-salt aerosols, and entrained dust particles and anthropogenic sources such as fossil-fuel combustion and nonferrous metal smelting. Biogenic emissions from wetlands have been identified as an important source of airborne sulfur in remote and rural areas of southern Canada (Nriagu et al., 1987). Because contributions of biogenic sulfur are most important during summer and the isotopic signature is relatively light $\delta^{34}\text{S}$ (-2.4%), biogenic sources should have little influence on the $\delta^{34}\text{S}$ values of winter precipitation in the Rocky Mountains. Likewise, marine aerosols probably are a minor contributor to the solute composition of the snow, considering the heavy $\delta^{34}\text{S}$ value of sea spray ($\sim +20\%$) compared to that of the snow ($+4.0$ to $+8.2\%$). This also is consistent with low snowpack chloride and sodium concentrations (average $1.5\ \mu\text{eq l}^{-1}$), which indicate that marine-derived sulfate accounts for 2–5% of the dissolved sulfate in snow.

Dust is perhaps the most likely natural source of solutes to the snow, particularly considering the proximity of the Rocky Mountains to vast expanses of arid soils in the Western United States (Litaor, 1987; Schlesinger and Peterjohn, 1988). Because airborne calcium tends to be associated with terrestrial particulate materials (Lewis et al., 1984; Braaten and Cahill, 1986), the geographic pattern in snowpack calcium concentrations suggests that sites in the southern part of the network are more strongly influenced by airborne dust than sites to the north (Fig. 2). Similar to calcium, the pattern of increasing sulfate concentrations at the very southern end of the network could be due to an increased contribution of sulfate from dust-derived sources. If dust contributes significant amounts of sulfate to the snowpack, it should be reflected in the $\delta^{34}\text{S}$ values as well as the concentrations.

In the desert Southwest, gypsum or anhydrite in sedimentary rocks, dry lakebeds, and soils are the sources most likely to contribute sulfate-rich aerosols to the atmosphere (Popp et al., 1986; Schlesinger and Peterjohn, 1988). Holser and Kaplan (1966) reported $\delta^{34}\text{S}$ values of $+9.0$ to $+16.5\%$ for marine evaporites and $+11.3$ to $+15.0\%$ for nonmarine evaporites at selected sites in the Western United States. Schlesinger and Peterjohn (1988) measured the $\delta^{34}\text{S}$ values of water soluble sulfate from arid regions of the southwestern US and reported median values of $+6.2\%$ for soils and $+7.5\%$ for dry lakebeds. If a large amount of snowpack sulfate were derived from these types of terrestrial materials, the isotopic composition of snowpack sulfate at sites in northern New Mexico and southern Colorado might be expected to be heavier than those actually measured ($+4.0$ to $+4.3\%$). A similar

observation was made by Popp et al. (1986), who determined that the $\delta^{34}\text{S}$ of precipitation in mountainous areas of New Mexico did not reflect substantial inputs of soil-derived sulfate, which led them to conclude that precipitation sulfate was primarily derived from distant anthropogenic sources. Comparing ion ratios and $\delta^{34}\text{S}$ in soils and precipitation, Schlesinger and Peterjohn (1988) also concluded that wind erosion of undisturbed desert soils was not a major source of sulfate in precipitation of remote areas of the Southwestern United States.

Given that biogenic sources, marine aerosols, and terrestrial dust do not appear to contribute significantly to the sulfate composition of the snowpack, it seems reasonable that anthropogenic sources are the greatest contributors of sulfate to snowpacks in the Rocky Mountains. This is consistent with air-quality studies that show that nearly all SO_2 emissions in the Rocky Mountain region are produced by fossil-fuel combustion and other industrial processes (Peterson et al., 1998). Similar results also have been found during winter in remote areas of southern Canada and as far north as the Canadian Arctic (Nriagu et al., 1987, 1991). Because of the strong geographic pattern in $\delta^{34}\text{S}$, it may be possible to distinguish different source regions of atmospheric sulfur in the Rocky Mountains. Although isotopic tracers more typically are used to identify local air-pollution sources (Krouse and Grinenko, 1991), lead isotopes have been used to discriminate between regional emission sources in the United States and Canada (Sturges and Barrie, 1987).

In the southern part of the snowpack network (New Mexico to southern Wyoming), the nearly linear trend in $\delta^{34}\text{S}$ with latitude suggests that snowpack sulfate is a mixture of sulfur from two isotopically distinct source regions, a lighter source in the south and a heavier one in the north. Because the predominant upper air flow in the Rocky Mountains during winter is from the west to east (Changnon et al., 1990), most winter deposition should be most strongly influenced by sources located on the west side of the Continental Divide (Heuer et al., 2000). At the southern end of the network, the largest point sources are two coal-fired powerplants near the Four Corners region and another farther west along the Arizona–Utah border (Fig. 1). Malm et al. (1990) investigated the dominant source regions of fine sulfur aerosols in remote areas of the Western United States and concluded that powerplants in the Four Corners region had the strongest influence on sulfur concentrations in northern New Mexico and southern Colorado, particularly during the winter. If these facilities are the largest contributors of airborne sulfur, then the $\delta^{34}\text{S}$ of the southern snowpack sites might reflect the $\delta^{34}\text{S}$ of coals burned by the powerplants, which primarily come from the San Juan Basin in northwestern New Mexico and the Black Butte area in northern Arizona. Published values on the isotopic composition of these coals are extremely sparse. In fact, the

authors are aware of only one study that has published values for coal samples from the Four Corners region, which ranged from -16.7 to $+8.3\text{‰}$ (Popp et al., 1986). The wide range of values for coal makes it difficult to establish any relation between sulfate in precipitation and powerplant emissions based on the isotopic data available. An additional emission source that may influence sites in the southern part of the snowpack network is the smelter region of southern Arizona and New Mexico (Malm et al., 1990). The isotopic composition of massive sulfide deposits in Arizona, which cluster tightly near 0‰ (Eastoe et al., 1990), is light relative to the snowpack. Assuming the isotopic signature of smelter emissions is similar to that of sulfide deposits in the region, the isotopic data indicate that smelters are not the dominant source of snowpack sulfate. This is consistent with emissions data for Arizona and New Mexico, which indicate that around 20% of current SO_2 emissions from point sources in these two States are derived from smelters (<http://www.epa.gov/airsdata>). This does not dismiss the possibility, however, that lighter sulfur from smelters mixes with heavier sulfur from sources, such as power plants or terrestrial dust, to produce the lower snowpack $\delta^{34}\text{S}$ values measured at the southern end of the network.

Farther north towards the Colorado–Wyoming border, the isotopic composition of the snowpack is distinctly heavier than in the south, indicating that a different source area of sulfur is influencing snowpack chemistry in this part of the network (Fig. 2). The largest point sources to the west are two coal-fired powerplants in northwestern Colorado and two in southwestern Wyoming. There are also a large number of smaller industrial sources including oil and gas extraction facilities, refineries, and mining operations in the Red Desert Basin across southwestern Wyoming, and farther to the west is the Salt Lake City urban corridor. Emission sources along the Front Range urban corridor in Colorado can influence precipitation chemistry in remote areas on the east side of the Continental Divide, although the effect is most pronounced during upslope weather events in late spring and summer (Hueur et al., 2000). The source of the isotopically heavy snowpack sulfate is difficult to determine because of the large number of potential anthropogenic sources in this part of the network. Powerplants in southwestern Wyoming and northwestern Colorado probably burn coal primarily from the Green River Coal Region. Hackley and Anderson (1986) reported an average value of $+6.0\text{‰}$ ($n = 11$) for organic sulfur ($> 80\%$ of the total sulfur) in coal from two areas in southern Wyoming. Coal from the Williams Fork Formation sampled from two different mines in northwestern Colorado had average $\delta^{34}\text{S}$ values of $+9.9\text{‰}$ ($n = 29$) and $+11.1\text{‰}$ ($n = 16$) (Holmes and Brownfield, 1992). Although the isotopic compositions of other industrial sources are not well defined, the range of $\delta^{34}\text{S}$ in

coal suggests that powerplant emissions are not an unreasonable explanation of the heavier isotopic values at sites in the central part of the network. The shift towards heavier values at the Rabbit Ears Pass, Buffalo Pass, and Dry Lake sites (Fig. 2) supports the idea that powerplants are the primary source of heavier sulfur as these three sites are located less than 50 km downwind from two large coal-fired powerplants. These three sites also have the highest hydrogen-ion and sulfate concentrations in the entire snowpack network (Table 3), providing additional evidence that the powerplants are affecting snow chemistry at these sites (Turk and Campbell, 1997).

Sites in northern Wyoming and Montana show a much weaker geographic pattern in $\delta^{34}\text{S}$ relative to the southern subgroup of sites. In this part of the network, there are few large point sources to the west, which reflected in the lower hydrogen-ion and sulfate concentrations at these sites compared to sites in the south (Table 3). The $\delta^{34}\text{S}$, which averages about 6.0‰ , may represent regional background sulfur that has been transported from sources as distant as the Pacific Northwest. This is not unreasonable given that the average transport distance of SO_2 ranges from 400 to 1200 km (Alewell et al., 2000). One notable difference between the southern and northern subgroups is that there appear to be more outliers among the northern sites. The influence of local sulfur sources may be more important at the northern sites because of the low sulfate concentrations in this part of the network. For example, the Kings Hill site in central Montana has a substantially heavier $\delta^{34}\text{S}$ value as well as elevated sulfate and calcium concentrations relative to sites at similar latitudes. One possible explanation for this anomalous chemistry is that the snowpack chemistry is affected by a large lead smelter located about 100 km west of the sampling site. Sylvan Lake, Canyon, and Daisy Pass all show lighter than expected $\delta^{34}\text{S}$ values, although their chemistry is similar to nearby sites. There are no large point sources in this area; however, all three sites are located on the east side of Yellowstone National Park and might be influenced to some degree by sulfur emissions from geothermal features in the park. The cause of the heavy value at South Pass, Wyoming, is unclear. Because the site is located at the southern end of the Wind River Range, it may be influenced by a variety of different industrial sources in the Red Desert Basin in southwestern Wyoming.

4. Conclusions

Stable sulfur isotope ratios and major ions in snowpack samples were monitored at a network of high-elevation sites along the Continental Divide to improve understanding of atmospheric deposition to remote areas of the Rocky Mountains. Contributions of sulfur to the snowpack from sources such as biogenic emissions,

marine aerosols, and continental dust were found to be negligible, indicating that anthropogenic SO₂ emissions were the primary contributor of sulfate to the snowpack. This is consistent with recent air-quality studies, which indicate that nearly all SO₂ emissions in the Western United States are related to urban areas and industrial sources. Although dust was found to be an important source of calcium to the snowpack, particularly at sites in the southern part of the network, the δ³⁴S values of snow were lower than common terrestrial materials, suggesting that airborne dust was not the dominant source of snowpack sulfate. This result is important because chemical data alone cannot discriminate between calcium sulfate minerals as a source of sulfate in precipitation and sulfuric acid from anthropogenic sources that is neutralized by carbonate minerals in the atmosphere.

Geographic trends in snowpack δ³⁴S revealed distinct differences in the dominant source regions of snowpack sulfate through the region. The nearly linear trend in δ³⁴S relative to latitude for sites in the southern part of the network suggests that snowpack sulfate is a mixture of sulfur from two isotopically distinct source regions, a lighter source to the south and a heavier one to the north. The largest emitters of SO₂ are coal-fired powerplants in the Four Corners area and farther north in northwestern Colorado and southwestern Wyoming. Because the powerplants in these two areas are located in two different coal-producing regions, the isotopic variation in snowpack δ³⁴S may reflect variations in the isotopic composition of types of coal burned by the powerplants. The geographic pattern in δ³⁴S for sites farther to the north in Wyoming and Montana was much weaker, perhaps reflecting the paucity of major point sources of SO₂ in the northern part of the network.

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