



## PARTICULATE CARBONATE MATTER IN SNOW FROM SELECTED SITES IN THE SOUTH-CENTRAL ROCKY MOUNTAINS

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**Abstract**—Trends in snow acidity reflect the balance between strong acid inputs and reactions with neutralizing materials. Carbonate dust can be an important contributor of buffering capacity to snow; however, its concentration in snow is difficult to quantify because it dissolves rapidly in snowmelt. In snow with neutral or acidic pH, most calcite would dissolve during sample melting if snow samples were processed using standard techniques. Here a method is described for separating particulate carbonate matter from snow. Snow samples were melted in solutions close to saturation with calcite, decreasing the dissolution rate by a factor of 100–200 compared with natural melting of snow. Particulate matter larger than 0.45  $\mu\text{m}$  in diameter was then filtered from solution and analysed for carbonate content. Particulate carbonate matter concentrations are reported for 25 sites in the south-central Rocky Mountains. Results are compared with  $\text{Ca}^{2+}$  and  $\text{H}^+$  concentrations and regional trends are evaluated.

In Colorado, mean particulate carbonate in snow was 43  $\mu\text{g kg}^{-1}$  at sampling sites in the southern mountains and only 4  $\mu\text{g kg}^{-1}$  at sites in the northern mountains. The higher calcite concentrations in the south probably are related to the proximity of sampling sites to major outcrops of limestone. Particulate carbonate at sampling sites in Utah and Wyoming ranged from 3–35  $\mu\text{g kg}^{-1}$ . The levels of particulate calcite measured in snow samples are sufficient to neutralize an average of 0.4  $\mu\text{eq H}^+ \text{kg}^{-1}$  snow.

Strong acid anion concentrations in samples from east of Craig, Colorado, were 30–50% higher than in samples from the Colorado Front Range, but  $\text{H}^+$  concentrations were 400–600% higher east of Craig. Relatively low  $\text{Ca}^{2+}$  concentrations in the samples from east of Craig indicate that the difference in snow acidity was due mostly to lower concentrations of neutralizing materials.

*Key word index:* Eolian, calcite, chemistry, dust, acid.

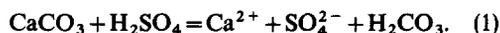
### INTRODUCTION

#### Background

Solutes in precipitation are important inputs to natural ecosystems and can strongly affect the chemistry of streams, lakes, and ground water (Dethier, 1979). Pollutants in precipitation, such as sulfuric and nitric acids, which are the main ingredients in "acid rain", have been linked to declines in fish populations (Wright and Snekvik, 1978; Baker and Schofield, 1982). Alpine and subalpine ecosystems in the western United States of America tend to be sensitive to acidic inputs (Turk and Spahr, 1991) because soils are often thin and patchy, and bedrock minerals are relatively unreactive (Hintze, 1975; Tweto, 1979; Love and Christiansen, 1985). The hydrology of these ecosystems also tends to make them vulnerable. Rapid melting of accumulated snow during the spring causes water to flush quickly through soils, providing little opportunity for neutralization (Baron, 1992). Preferential elution of ions during the first fraction of melt increases the potential for episodic acidification (Williams and Melack, 1991a). Campbell and Turk (1989) reported a springtime decline in acid-neutralizing capacity (ANC) in a Rocky Mountain watershed in 1989 that was attributed to dilution of soil water by snowmelt and a pulse of strong acids from the snow-

pack. The combination of snowmelt-driven hydrology and slow-reacting geologic materials makes alpine-subalpine watersheds in the west susceptible to episodic acidification during the spring should precipitation become more acidic.

The most significant types of acidity in snow are anthropogenically derived sulfuric and nitric acids. Wind-blown carbonate particulate matter may neutralize strong acids in snow via reactions in the atmosphere or the snowpack, providing an important buffering mechanism (Gatz *et al.*, 1986). An example is the reaction of calcite with sulfuric acid, which neutralizes the acidity and produces  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in solution



One mole of calcite neutralizes two moles of  $\text{H}^+$  in this reaction. Other neutralization reactions that have been proposed to affect precipitation acidity include cation exchange on the surfaces of eolian clay particles and buffering reactions involving ammonia aerosols (Munger and Eisenreich, 1983; Gatz *et al.*, 1986). The focus of this paper is to test a method for determination of the buffering capacity of carbonate particulate matter in snow.

In some previous studies, trends among ions dissolved in precipitation have indicated the importance

of alkaline materials in neutralizing strong acids (Murozumi *et al.*, 1969; Messer, 1983; Munger and Eisenreich, 1983; Lewis *et al.*, 1984; Loÿe-Pilot *et al.*, 1986; Williams and Melack, 1991a). Strong positive correlations between alkaline earth elements and alkalinity or inverse correlations between alkaline earth elements and acidity have been cited as evidence that carbonate particulate matter significantly affects precipitation chemistry and provides significant buffering capacity. Williams and Melack (1991b) determined that in an alkaline snowpack in California, ANC was highly correlated with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ( $r=0.83$  and  $0.96$ , respectively), and ANC,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were inversely correlated with  $\text{H}^+$  ( $r=-0.70$  to  $-0.76$ ). In 59 snow samples collected in eastern China, the mean ANC and  $\text{Ca}^{2+}$  concentrations were 50 and  $53 \mu\text{eq l}^{-1}$ , respectively, accounting for about 60% of total ions in solution (Williams *et al.*, 1992). Calcium correlated well with ANC in the samples from China ( $r=0.82$ ,  $n=32$ ), indicating that dissolution of carbonate minerals was an important source of solutes.

The presence of calcite in particulate material filtered from alkaline precipitation samples provides additional evidence supporting the effect of carbonate particulate matter on precipitation chemistry. Red rain, which is rain colored red by particulate matter, commonly occurs in Corsica, an island in the northern Mediterranean Sea (Loÿe-Pilot *et al.*, 1986). Based on X-ray diffraction analysis, Loÿe-Pilot *et al.* (1986) determined that calcite accounted for 5–30% of total particulate matter filtered out of red rain, corresponding to the composition of eolian Saharan dust (Game, 1964; Cross, 1977). Calculations of storm paths indicated that the storm systems containing red rain passed over the Sahara Desert before reaching Corsica, while storms associated with clear rain tracked from the north and northeast. The pH of red rain ranged from 6.0 to 7.0, compared with 4.1–5.6 in clear rain. The average calcium enrichment factor  $[(\text{Ca}^{2+}/\text{Na}^+)_{\text{rain}}/(\text{Ca}^{2+}/\text{Na}^+)_{\text{seawater}}]$  ranged from about 40 to 170 in red rain, compared to 10–20 in clear rain, suggesting that most  $\text{Ca}^{2+}$  in red rain was derived from a non-marine source.

Although previous work has established that eolian calcite probably contributes alkalinity to precipitation, there are no published reports of carbonate dust concentrations in rain or snow, or of the buffering capacity that might be expected from carbonate particulate matter in precipitation. This information is especially critical for sensitive alpine ecosystems because buffering by eolian calcite may provide a first line of defense against acidic snowmelt. Quantification of calcite dust concentrations in snow is difficult because of the fast dissolution kinetics of calcite, especially in acidic solutions. In snow samples with neutral or acidic pH and low concentrations of carbonate dust, virtually all carbonates would quickly dissolve during melting of snow samples processed by standard methods (see Williams and Melack, 1991b, for example).

Here we report development and testing of a method for separating calcite dust from snow. Results are reported for measurements of calcite dust concentrations in snow from 3 sites in Utah, 4 sites in Wyoming, and 18 sites in Colorado. Calcite dust concentration trends were compared to  $\text{Ca}^{2+}$  and  $\text{H}^+$  dissolved in snow, and likely sources of  $\text{Ca}^{2+}$  in snow were evaluated.

## METHODS

### Sample collection

Snow samples were collected at 3 sites in Utah and 4 sites in Wyoming in 1988, and at 18 sites in Colorado in 1992 (Fig. 1). Most sampling sites were located in level forest clearings near snowpack-monitoring sites operated by the Soil Conservation Service (Soil Conservation Service, 1992). Sites ranged from 2521 to 3627 m in elevation. Samples were obtained during peak snow accumulation, which occurred between the last week of March and the middle of April in both sampling years. Sampling prior to the onset of melt was deemed essential because of the propensity of calcite to dissolve quickly in liquid water. Snowpack depths were recorded, and measurements of temperature and density were performed in 15 cm increments at most sites. Snowpack depths ranged from 0.84 to 2.23 m, and densities ranged from 200 to  $400 \text{ kg m}^{-3}$ . Snowpack temperature measurements indicated that snow at most of the sites was subfreezing.

At each site, two snow samples representing the entire snowpack were collected from freshly dug snow pits. One sample was collected for particulate calcite analysis, and a second was obtained for analysis of dissolved solutes (Turk *et al.*, 1992). Samples ranged in mass from 0.4 to 1.3 kg. Care was taken to exclude the bottom few centimeters of snow to preclude contamination from soil water. At each of the sites in Utah and Wyoming, nine additional cores were collected for replicate particulate carbonate and chemical analyses. Six of the extra cores were analysed for particulate carbonate and three were analysed for dissolved solutes. Prior to use, sampling equipment and laboratory apparatus contacting samples were washed with 5% HCl, followed by at least four rinses with deionized distilled water (DDW). Samples were placed in pre-cleaned plastic bags, packed in ice for transport, and stored at  $-20^\circ\text{C}$  within 48 h of sampling.

### Snow chemistry

Snow samples analysed for dissolved solutes were melted at room temperature in covered plastic containers. Complete chemical analyses for major cations and anions were performed, but only results for  $\text{Ca}^{2+}$ ,  $\text{H}^+$ , and alkalinity will be discussed here. Detailed methodology and results concerning solute chemistry and sulfur isotopes in snow from the Colorado sites are presented in Turk *et al.* (1992).

$\text{Ca}^{2+}$  was analysed on filtered aliquots by inductively coupled plasma, pH was measured using an electrode designed for low ionic-strength waters, and alkalinity was measured by autotitration using Gran-plot analysis. Precision, taken as two times the standard deviation of 20 analyses of an internal standard run throughout the sampling season, was better than  $2 \mu\text{eq l}^{-1}$  for  $\text{Ca}^{2+}$ , 0.1 units for pH, and  $3 \mu\text{eq l}^{-1}$  for alkalinity. Accuracy was better than 3% for  $\text{Ca}^{2+}$  and 5% for alkalinity, based on the mean of 15 analyses of U.S. Geological Survey standard reference samples. Mean charge imbalance, calculated as  $(\sum \text{anions} - \sum \text{cations})/(\sum \text{anions} + \sum \text{cations})$ , was +3% and analyses with charge imbalances greater than 25% were rejected.

### Particulate carbonate matter processing

Because most particulate carbonate matter in acidic or neutral pH snow would dissolve while melting and filtering

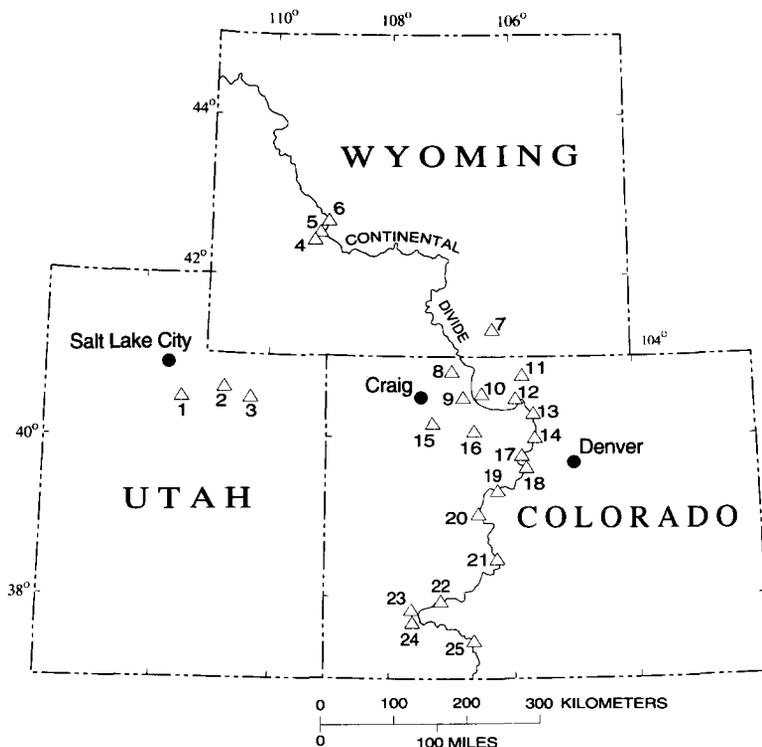


Fig. 1. Location of sampling sites in Utah, Wyoming, and Colorado. Sampling locations are indicated by open triangles.

snow samples using standard techniques, a new method was developed to separate carbonate particles from snow. Calcite dissolution kinetics are much faster in solutions far from saturation, such as snowmelt, than in solutions near saturation. The approach taken in this study was to reduce the carbonate dissolution rate by a factor of 100–200 by melting snow samples in 0.1 M  $\text{CaCl}_2$  solutions brought to saturation with respect to calcite by using  $\text{Na}_2\text{CO}_3$ . A 0.1 M  $\text{CaCl}_2$  solution was made from reagent grade  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and deionized distilled water. Sufficient  $\text{Na}_2\text{CO}_3$  powder was added to the solution to bring it to saturation with respect to calcite at 22°C. After allowing the solution to equilibrate for 5 days, the solution was filtered to remove any undissolved carbonate salts. Snow samples to be analysed for particulate carbonate matter were weighed and then placed in 1ℓ of  $\text{CaCl}_2/\text{Na}_2\text{CO}_3$  salt solution at 22°C. Snow samples ranged from 0.25 to 1.3 kg in mass. Melting snow decreased the solution temperature to between 0 and 2°C within 5 min. Immediately after the snow was completely melted, particulate matter was removed by filtering through a pre-cleaned 0.45- $\mu\text{m}$  acetate filter. The time required to melt and filter the samples ranged from 5 to 8 h. The inorganic carbon content of particulate matter on filters was measured by coulometric titration, which involves reaction of samples with dilute HCl, yielding  $\text{CO}_2$  gas. The  $\text{CO}_2$  evolved is then coulometrically titrated. Precision, taken as two standard deviations of the results for four filter blanks, was 1  $\mu\text{g}$   $\text{CaCO}_3$ . A relative accuracy of <2% was estimated by analysing seven weighed aliquots of reagent grade  $\text{CaCO}_3$  powder ranging in mass from 2.04 to 4.92 mg. For simplicity, it was assumed that all inorganic carbon on the filters was derived from calcite. In reality, a small fraction may have been derived from dolomite. The possibility is addressed in the "Discussion" section. To test whether any carbonate was left on the filters by the salt solution, five filters were tested for inorganic carbon

after 1ℓ of the  $\text{CaCl}_2/\text{Na}_2\text{CO}_3$  salt solution was passed through them. No measurable inorganic carbon was detected on these filters.

Although snow samples were melted in solutions close to saturation with respect to calcite, some mineral dissolution was unavoidable because as the snow melted, the solutions became slightly undersaturated due to the addition of snowmelt. The amount of calcite that dissolved during sample processing was calculated using the calcite dissolution model developed by Plummer *et al.* (1978, 1979).

In simple systems without chemical inhibitors, the dissolution rate of calcite is a function of solution composition, temperature, and  $P_{\text{CO}_2}$  (Plummer *et al.*, 1979). According to Plummer *et al.* (1979), the rate of calcite dissolution,  $R$ , can be described by the equation

$$R = k_1 a_{\text{H}^+} + k_2 K_{\text{H}} P_{\text{CO}_2} + k_3 a_{\text{H}_2\text{O}} - k_4 a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-} \quad (2)$$

where  $a_{\text{H}^+}$ ,  $a_{\text{H}_2\text{O}}$ ,  $a_{\text{Ca}^{2+}}$ , and  $a_{\text{HCO}_3^-}$  are the activities of solutes in the bulk fluid;  $K_{\text{H}}$  is the Henry's Law constant for  $\text{CO}_2$ ;  $P_{\text{CO}_2}$  is the partial pressure of  $\text{CO}_2$ ; and  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are reaction rate constants. Rate constants  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are dependent on temperature, and  $k_4$  is also dependent on  $P_{\text{CO}_2}$  (Plummer *et al.*, 1978). We calculated appropriate values for the rate constants at 1°C and  $P_{\text{CO}_2}$  equal to  $10^{-3.5}$ , based on the procedures outlined in Plummer *et al.* (1978). Although solution  $P_{\text{CO}_2}$  may have varied somewhat, the variations were not enough to change calcite dissolution rates appreciably (Plummer *et al.*, 1978). It was assumed that the activity of water was equal to 1.

The mass of calcite that dissolved ( $C_d$ ) while melting the snow samples was calculated in hourly increments using the following equation:

$$C_d = SA \cdot T \cdot R \quad (3)$$

where  $SA$  ( $\text{cm}^2$ ) is the surface area of calcite remaining in the sample,  $T$  (h) is the amount of time required to melt and filter the snow, and  $R$  ( $\text{mg cm}^{-2} \text{h}^{-1}$ ) is the dissolution rate of calcite. We assumed that during melting,  $SA$  decreased as dissolution decreased the size of the particles, and  $R$  increased as the solution became more dilute. Working backwards from the time when melting was complete, the amount of calcite dissolved in each hour was calculated on the basis of computed values for  $SA$  and  $R$  at the end of that hour.

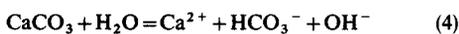
Surface areas for each hour were calculated from the sum of masses of calcite dissolved in all later hours plus the mass of calcite detected on the filters, assuming a specific surface area of  $2.22 \text{ cm}^2 \text{ mg}^{-1}$ . Specific surface area was calculated on the basis of the density of calcite and the assumption that calcite crystals were rhombohedrons with an average diameter of  $10 \mu\text{m}$ , a reasonable approximation of the size of common eolian material (Barrie, 1985).

Hourly dissolution rates (equation (2)) were calculated on the basis of solution composition, which changed over time due to the addition of snowmelt. For simplicity, a linear snowmelt rate was assumed. The total mass of calcite dissolved while processing the samples was obtained by summing the  $C_d$  values for each hour of melt.

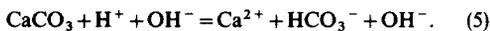
#### Calcite dissolution rate experiments

Three types of experiments were performed to test the validity of the model (Plummer *et al.*, 1978) used to calculate calcite dissolution rates during snow sample processing. First, to facilitate comparisons with previous studies, an experiment was performed using methods similar to those outlined in Plummer *et al.* (1978) and Busenberg and Plummer (1986). A small, weighed quantity (1–2 mg) of 10–20  $\mu\text{m}$  diameter optically clear calcite crystals was added to 1  $\ell$  of 0.1 M  $\text{CaCl}_2$  solution brought close to saturation with  $\text{Na}_2\text{CO}_3$ . Air was bubbled through the solution using a diaphragm pump to maintain equilibrium with the atmosphere, and the solution was kept at  $1^\circ\text{C}$  by using an ice-water bath. The duration of the experiment was 3 h. pH was monitored every few minutes *in situ* and 10 ml aliquots were collected from the salt solution every 15–30 min for determination of alkalinity. pH ranged from 6.7 to 6.9, and alkalinity ranged from 50 to 100  $\mu\text{eq } \ell^{-1}$ . The experiment was replicated twice.

Dissolution rates were calculated from changes in pH and bicarbonate concentration, which were assumed equal to changes in alkalinity. Calcite dissolution in water at pH 6.7 to 6.9 and  $P_{\text{CO}_2}$  less than 0.05 atmospheres can be described by the following equation (Plummer *et al.*, 1978)



which can be rewritten as



The charge balance equation for this reaction is

$$2(\Delta m_{\text{Ca}^{2+}}) = \Delta m_{\text{HCO}_3^-} - \Delta m_{\text{H}^+} \quad (6)$$

where  $m$  denotes the molarity of each constituent and  $\Delta$  denotes the change in concentration between time steps. Since the number of moles of  $\text{Ca}^{2+}$  released is equal to the moles of calcite dissolved,  $m_{\text{calcite dissolved}}$  is substituted for  $\Delta m_{\text{Ca}^{2+}}$ , giving

$$m_{\text{calcite dissolved}} = \frac{\Delta m_{\text{HCO}_3^-} - \Delta m_{\text{H}^+}}{2} \quad (7)$$

The degree of undersaturation at each time step was calculated from  $\text{H}^+$  and  $\text{HCO}_3^-$  which were measured as noted above, and  $\text{Ca}^{2+}$  concentrations which were assumed constant at 0.1 molar.  $P_{\text{CO}_2}$  was assumed constant at  $10^{-3.5}$  atmospheres.

To test the effect of bubbling on dissolution rates in the salt solutions used in this study, the experiment described above was repeated, except without bubbling. Plummer *et al.* (1978) noted that in solutions with low pH and low  $P_{\text{CO}_2}$ ,

$\text{CO}_2$  could become depleted in a thin layer near the mineral surface, and as a result, dissolution rates in their experiments increased with stirring rate in solutions that had pH less than 5 at  $35^\circ\text{C}$  and  $P_{\text{CO}_2} = 10^{-3.5}$ . In this study, stirring and bubbling were deemed undesirable and were not employed during sample processing because low dissolution rates were sought. This experiment was replicated three times.

A third type of experiment was conducted to determine whether the presence of snow affected calcite dissolution rates. A small, weighed quantity (1–2 mg) of optically clear calcite was added to 1 kg of snow obtained from one of the sampling sites (site 7). The calcite was sprinkled on top of the snow sample, which was in a Teflon bowl. One liter of the  $\text{CaCl}_2/\text{Na}_2\text{CO}_3$  solution was poured over the snow sample. Immediately after the snow sample melted, the solution was filtered. Filters were dried at  $80^\circ\text{C}$  overnight. Inorganic carbon was measured on the particulate matter collected on the filter and converted to mass of calcite. The calcite dissolution rate was calculated from the decrease in mass of calcite and the time required to melt the snow sample. The experiment was replicated five times.

## RESULTS

#### Dissolution rate experiments

Results for the three dissolution rate experiments are presented in Fig. 2 along with rates predicted from the model of Plummer *et al.* (1978). A pronounced decrease in rates as solutions approached saturation is clearly evident. The results for unbuffered solutions (experiment 2) show much more scatter than those for buffered solutions (experiment 1). Rates from these experiments are in good agreement with those predicted by the model of Plummer *et al.* (1978) (Fig. 2) and with the experiments conducted in  $\text{CaCl}_2$  by Busenberg and Plummer (1986). In this study, measured rates tended to be slightly lower than predicted (Plummer *et al.*, 1978), but the difference was not significant.

#### Particulate carbonate matter

Concentrations of particulate carbonate matter measured in snow samples ranged from  $<2$  to  $83 \mu\text{g CaCO}_3 \text{ kg}^{-1}$  snow (Fig. 3). Concentrations referred to here and in following sections include only particulate carbonate matter measured on filters and do not include the fraction estimated to have dissolved during sample processing or any fine particulate matter ( $<0.45 \mu\text{m}$ ) that may have passed through the filters. Carbonate dust concentrations were highest at sites in southern Colorado (sites 20–25), averaging  $43 \mu\text{g kg}^{-1}$  and ranging from 24 to  $83 \mu\text{g kg}^{-1}$ . Concentrations at sites in northern Colorado (sites 8–19) ranged from less than 2 to  $21 \mu\text{g kg}^{-1}$ , with a mean of  $4 \mu\text{g kg}^{-1}$ . Mean particulate carbonate in snow from sites in Utah and Wyoming was  $16 \mu\text{g kg}^{-1}$  and ranged from 3 to  $35 \mu\text{g kg}^{-1}$ . Intrasite variation, calculated as the standard deviation of results from six cores from each site in Utah and Wyoming that were analysed for particulate carbonate matter, ranged from 3 to  $17 \mu\text{g kg}^{-1}$ , corresponding to 35–100% of sample concentrations.

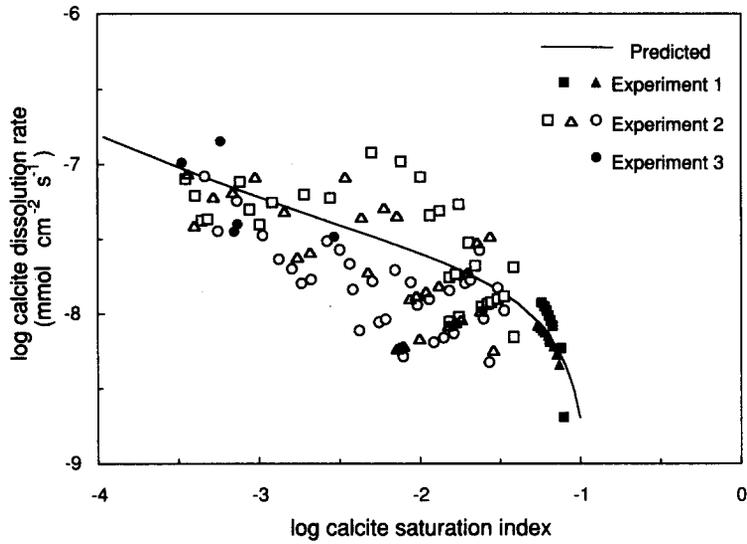


Fig 2. Data from dissolution rate experiments showing dissolution rates as a function of saturation index, which is the ion activity product/solubility constant of calcite. Two replicate runs from the first experiment are shown as closed triangles and squares. Three replicate runs from the second experiment are shown as open symbols. Five replicate runs from the third experiment are shown as individual closed circles. Dissolution rates predicted from model developed by Plummer *et al.* (1978) are shown as solid line.

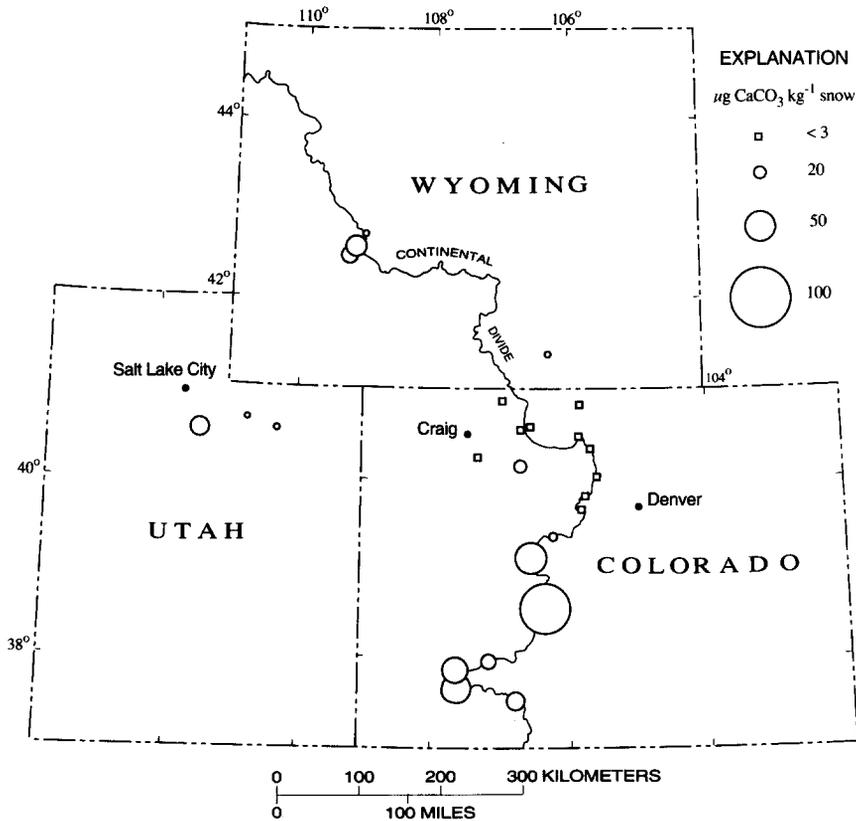


Fig 3. Particulate carbonate concentrations (as  $\text{CaCO}_3$ ) in snow from sampling sites in the south-central Rocky Mountains.

Calculations using equations 2 and 3 indicate that the amount of calcite dissolved during processing ranged from 1 to 24%, with a mean of 9%. Similar calculations using snow chemistry alone as input to the model (Plummer *et al.*, 1978) indicate that an average of 91% of calcite in the snow samples would have dissolved during processing if snow had been melted without using the salt solution. Virtually all calcite in the snow samples with no alkalinity would have dissolved.

#### Solute chemistry

The mean  $\text{Ca}^{2+}$  concentration in snow samples from Colorado was  $6 \mu\text{eq } \ell^{-1}$ , and ranged from 3 to  $13 \mu\text{eq } \ell^{-1}$  (Fig. 4). Sites in the northern Colorado Front Range (sites 11–14), northwest of Denver, had relatively high concentrations, averaging  $9 \mu\text{eq } \ell^{-1}$ , as did sites in Utah and Wyoming, which averaged  $10 \mu\text{eq } \ell^{-1}$ . Relatively low  $\text{Ca}^{2+}$  levels were measured in samples from sites 8–10, east of Craig, Colorado, with an average of  $5 \mu\text{eq } \ell^{-1}$ . Intrasite variation for  $\text{Ca}^{2+}$  ranged from 1 to  $2 \mu\text{eq } \ell^{-1}$ , or 10–20% of sample concentrations on the basis of the standard deviation of results from the three cores analysed from each site in Utah and Wyoming.

Snow samples from sites in Colorado were slightly acidic and contained no alkalinity, but snow samples

from sites in Utah and Wyoming were generally slightly alkaline, with alkalinities ranging from 0 to  $10 \mu\text{eq } \ell^{-1}$ . Dissolved  $\text{H}^+$  concentrations in snow from the Colorado sites ranged from 1 to  $14 \mu\text{eq } \ell^{-1}$ , and were highest at sites east of Craig, where they ranged from 9 to  $14 \mu\text{eq } \ell^{-1}$  (Fig. 5). Snow acidity was about 2.5-times higher east of Craig than in the southern Colorado Rocky Mountains (Turk *et al.*, 1992).  $\text{H}^+$  concentrations in snow from the northern Colorado Front Range ranged from 4 to  $6 \mu\text{eq } \ell^{-1}$ . Acid levels in Utah and Wyoming were low, with a maximum of  $3 \mu\text{eq } \ell^{-1}$   $\text{H}^+$ . Intrasite variation in  $\text{H}^+$  was less than  $0.5 \mu\text{eq } \ell^{-1}$  at the Utah and Wyoming sites.

## DISCUSSION

#### Dissolution rate experiments

The good agreement between results from experiments conducted during this study and previous data reported by Plummer *et al.* (1978) and Busenberg and Plummer (1986), indicate that use of the model developed by Plummer *et al.* (1978) is appropriate for estimating losses of calcite during snow sample processing due to dissolution. The relatively large scatter in results from unbuffered experiments indi-

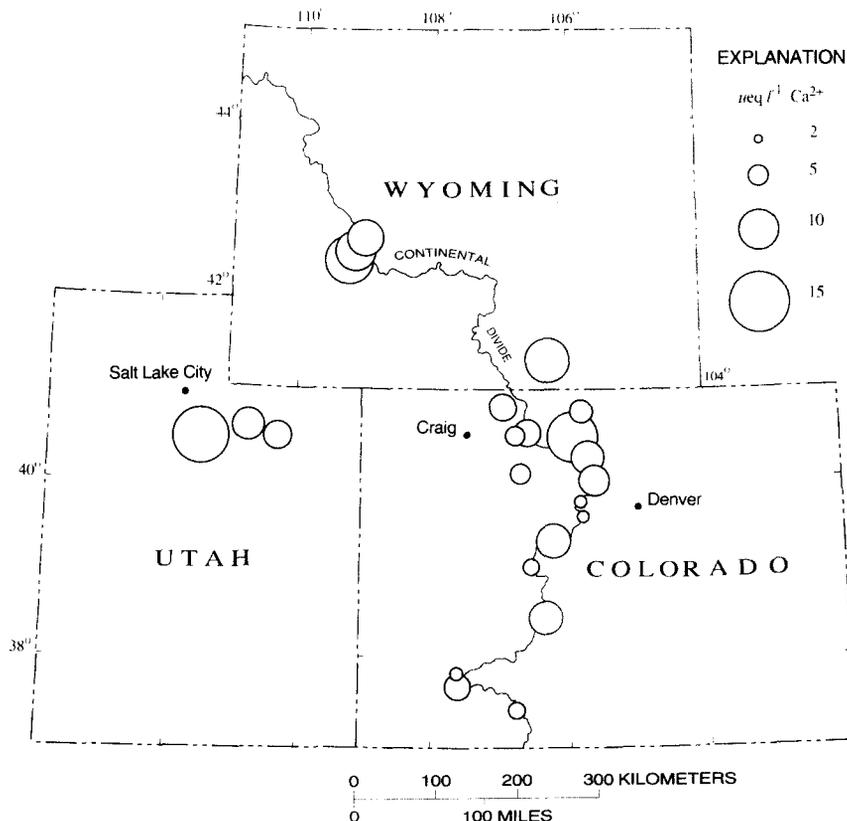


Fig 4. Dissolved  $\text{Ca}^{2+}$  concentrations in snow from sampling sites in the south-central Rocky Mountains.

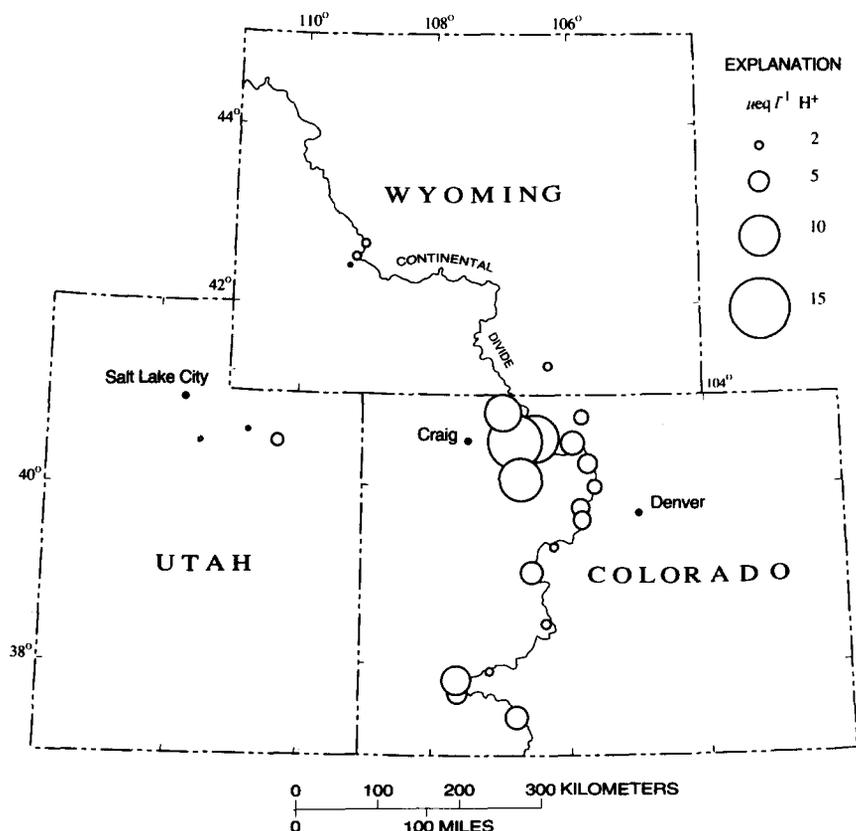


Fig 5. Dissolved  $H^+$  concentrations in snow from sampling sites in the south-central Rocky Mountains.

cates that melting snow samples in unbubbled solutions contributes to the uncertainty in the particulate carbonate matter results. Because results from the experiments did not indicate an increase in dissolution rates in solutions that were bubbled, it may be beneficial to bubble the salt solutions during sample melting to decrease the uncertainty in calcite dissolution rates. Another method modification that might be considered is to add minor amounts of phosphate to the salt solution. Phosphate ions severely inhibit dissolution of calcite by binding to high-energy sites on crystal faces (Berner and Morse, 1974). However, additional work is needed to better define dissolution rates in the presence of phosphate ions.

#### Particulate carbonate matter

The amount of acid that could be neutralized by particulate carbonate matter measured in snow in this study is minimal compared to measured snow acidity. Particulate carbonate matter concentrations measured in this study averaged  $0.2 \mu\text{mol calcite kg}^{-1}$  snow, corresponding to mean neutralization capacity of  $0.4 \mu\text{eq } H^+ \text{ kg}^{-1}$  snow. The maximum neutralization capacity was  $1.7 \mu\text{eq } H^+ \text{ kg}^{-1}$  snow. In comparison, the mean  $H^+$  concentration was  $5.8 \mu\text{eq kg}^{-1}$  snow.

Although particulate calcite concentrations measured in the samples were insufficient to provide much ANC to snow, there is evidence that infrequent, widespread eolian deposition events occur in the Colorado Rocky Mountains that may strongly affect snow chemistry. Such an event occurred in early February, 1990, when a widespread dust layer was deposited on the snow surface (Olsson and Denning, 1990). Precipitation samples collected in the Rocky Mountain region for the week of 6–13 February, 1990 by the National Atmospheric Deposition Program (NADP) contained high concentrations of  $\text{Ca}^{2+}$  and had high pH values (Olsson and Denning, 1990). For example, the weekly sample at Buffalo Pass, CO (site 10) contained  $57 \mu\text{eq } \ell^{-1} \text{Ca}^{2+}$  and the pH was 6.6, compared to the 1990 annual average of  $11 \mu\text{eq } \ell^{-1} \text{Ca}^{2+}$  and a pH of 6.0 (National Atmospheric Deposition Program, 1991). As a result, the winter quarter of 1990 had higher  $\text{Ca}^{2+}$  concentrations than any of the other quarters for the year. Usually,  $\text{Ca}^{2+}$  concentrations are relatively low during the winter quarter (National Atmospheric Deposition Program, 1991). Snow was reported to be discolored, and calcite and dolomite were observed using X-ray diffraction and scanning electron microscopy in particulate matter filtered from the snow (A. Mast, U.S. Geological Survey, 1993, personal communication).

Intrasite variation in particulate carbonate matter concentrations was relatively large compared to the concentrations in the samples. Variations in local snow surface topography could strongly affect deposition of wind-blown carbonate matter. Depressions in the snowpack would be more likely to capture eolian particulate matter than high points.

The regional trends in particulate carbonate reflect the proximity to calcareous bedrock upwind of the sampling sites. The geologic map of Colorado (Tweto, 1979) shows significant exposures of limestone west of the Continental Divide in southern Colorado. Prevailing winds in the study area generally are west to east in the winter. Sites 22–23 and 25–26 are within 10–25 km of large exposures of limestone. No large limestone outcrops are indicated on the geologic map within 50 km of the northern Colorado sampling sites, except for site 16. Limestone is exposed 10 km northeast of site 16, which had the highest particulate carbonate concentration of the northern Colorado sites. In Utah and Wyoming, particulate carbonate levels were highest at sites 1, 4, and 5, which are close to large, arid valleys that contain evaporite deposits (Hintze, 1975; Love and Christiansen, 1985).

Another possible source of particulate carbonate matter is dust from limestone-surfaced unpaved roads (Gatz *et al.*, 1986). However, in the high-elevation Rocky Mountain region, dust from unpaved roads is more likely to contribute particulate matter to precipitation in the summer than in the winter, when most unpaved roads are closed or snow-covered.

#### Solute chemistry

Trends in  $\text{Ca}^{2+}$  concentrations do not follow those of particulate carbonate (Figs 3 and 4), indicating that much of the dissolved  $\text{Ca}^{2+}$  measured in snow was derived from a different source than the particulate carbonate matter. (It should be noted that the  $\text{Ca}^{2+}$  measured in snow includes both that which was present as an ionic species in the snowpack and that which was derived from dissolution of carbonate particulate matter during sample processing). Further evidence for the difference in sources includes the fact that the amount of calcite required to produce the  $\text{Ca}^{2+}$  levels measured in snow is an order of magnitude greater than the amount that can be inferred from particulate carbonate matter results. A maximum of  $1 \mu\text{mol}$  of  $\text{Ca}^{2+}$  could have been derived from dissolution of the particulate carbonate matter detected in the snow samples. Most particulate carbonate matter probably is derived from local sources, since eolian dust generally is  $> 10 \mu\text{m}$  in diameter and tends to fall out of the atmosphere relatively quickly (Fennelly, 1976). Much of the  $\text{Ca}^{2+}$  dissolved in snow may be derived from reactions involving finer grained particulate matter ( $< 10 \mu\text{m}$  diameter), which tends to be lofted higher into the atmosphere and travel longer distances (Fennelly, 1976).

Precipitation plays an important role in scavenging fine particulate matter from the atmosphere. Fine particulate matter can act as condensation nuclei in clouds, and can also be removed from the atmosphere by precipitation as it falls (Barrie, 1985). Pruppacher and Klett (1978) reported that particulates as small as  $0.2 \mu\text{m}$  in diameter could act as condensation nuclei. Barrie (1985) reported that except in cases of low annual snow accumulation or when exceptionally large particles predominate, most particulate matter is deposited with wet deposition. This is primarily because fine particles are usually present in much higher concentrations than coarse particles (Barrie, 1985; Parungo *et al.*, 1990).

The relative contributions of  $\text{Ca}^{2+}$  from wet vs dry deposition were calculated for two of the sites sampled in 1992. Wet-only deposition was measured by the National Atmospheric Deposition Program at sites 10 and 13 (NADP, 1992). At those sites the volume-weighted mean  $\text{Ca}^{2+}$  concentration in wet deposition from 1 November, 1991 through 19 May, 1992 was 3.5 and  $4.0 \mu\text{eq} \ell^{-1}$  (NADP, 1992), respectively. This compares with bulk snowpack  $\text{Ca}^{2+}$  concentrations of 6.7 and  $8.2 \mu\text{eq} \ell^{-1}$  at the same sites.

There are several reasons why particulates scavenged from the atmosphere may not have been detected using our method for separating and analysing particulate carbonate matter. Fine particulate carbonate matter less than  $0.45 \mu\text{m}$  would not have been removed from the snowmelt/salt solutions used in this study because that was the pore size of the filters used to process the samples. Using a filter with a smaller pore size may provide the opportunity to detect greater amounts of particulate carbonate matter.

Another possible explanation for the small amounts of particulate carbonate matter detected is that carbonate particles may have dissolved or been modified through snowpack metamorphism processes. Prior to melt, water within the pack goes through the vapor phase a few times. During the process, solutes tend to be excluded from the ice crystal structure and end up coating the ice grains. Intergranular solute concentrations may become high enough to lower the freezing point of water, creating a quasi-liquid layer, especially where three crystals meet in a triple-junction (Davies *et al.*, 1987; Mulvaney *et al.*, 1988).

A minor amount of particulate carbonate matter may have dissolved in the snowpack due to reaction with liquid water on the snowpack surface or in near-surface layers. Liquid water can form in surface and near-surface layers of subfreezing snowpacks by several mechanisms. Surface layers of snow can melt during warm, sunny days, which are common during the spring. Surficial melting was observed and melt-freeze layers were noted well below the snow surface in snowpits at a number of the sites sampled in Colorado in 1992. Subsurface melting can occur in subzero snowpacks due to absorption of solar radi-

ation (Clow, 1987; Colbeck, 1989). Temperature measurements taken at the sites sampled in 1992 indicated that most of the melt-freeze layers were subfreezing at the time of sampling. Particulates that dissolved in those layers may have reprecipitated or been sequestered in the postulated quasi-liquid layer mentioned above.

Although particulate carbonate matter and  $\text{Ca}^{2+}$  dissolved in snow may have largely originated from different sources, it is likely that they were both ultimately derived from carbonate minerals. Munger and Eisenreich (1983) noted that soil materials, including calcite, dolomite, and gypsum, are the only plausible source of  $\text{Ca}^{2+}$  in snow. Mineral dissolution and cation exchange have been suggested as two processes that could possibly affect precipitation chemistry (Gatz *et al.*, 1986). Cation exchange can be ruled out for samples collected in Utah and Wyoming in this study, however, based on the mass, composition, and exchange capacity of minerals filtered from snow. Particulate mass averaged  $1.8 \text{ mg } \ell^{-1}$ , and X-ray diffraction analyses indicate the mineralogy included mostly quartz and feldspar, and minor quantities of mica and smectite. Of these minerals, only mica and smectite have appreciable cation exchange capacity. As an extreme example, if snow contained  $1 \text{ mg } \ell^{-1}$  smectite with an exchange capacity of  $1 \text{ } \mu\text{eq mg}^{-1}$  (Drever, 1988), and all the exchange sites were loaded with  $\text{Ca}^{2+}$ , a maximum of  $1 \text{ } \mu\text{eq } \ell^{-1}$   $\text{Ca}^{2+}$  could be released to solution by cation exchange.

Gypsum can be ruled out as a significant source of dissolved  $\text{Ca}^{2+}$  in samples collected in this study because the correlation between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  typically was poor ( $r^2 = 0.04$ ,  $p = 0.45$ ), although their concentrations generally were similar.  $\text{Mg}^{2+}$  was strongly correlated with  $\text{Ca}^{2+}$  ( $r^2 = 0.83$ ,  $p = 0.0001$ ), and concentrations were 20–30% of  $\text{Ca}^{2+}$  levels ( $1\text{--}4 \text{ } \mu\text{eq } \ell^{-1}$ ), indicating that a small fraction of particulate matter that reacted with snow was dolomitic in composition. This leaves calcite as the most likely significant source of  $\text{Ca}^{2+}$ . This conclusion is important because of the implications for acid neutralization. Calcite and dolomite will neutralize acidity; gypsum will not.

Trends in snow acidity reflect the balance between strong acids and neutralizing materials. Mean concentrations of strong acid anions ( $\text{SO}_4^{2-}$  plus  $\text{NO}_3^-$ ) were 35% higher in snow from sites east of Craig ( $23 \text{ } \mu\text{eq } \ell^{-1}$ ; Turk *et al.*, 1992) than in snow samples from Utah, Wyoming, and the northern Colorado Front Range ( $17 \text{ } \mu\text{eq } \ell^{-1}$ ), but  $\text{H}^+$  concentrations were four to six times higher in snow samples from east of Craig (Fig. 5). Low concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in snow from sites east of Craig indicate that alkaline particulate matter provided less buffering capacity in that region. If significant neutralization occurs in the atmosphere, differences in the distance between sites of acidic inputs and snow deposition could account for some of the trends in snow acidity.

## CONCLUSIONS

A method was developed for separating particulate carbonate matter larger than  $0.45 \text{ } \mu\text{m}$  from snow, allowing quantification of the buffering capacity contributed by dry-deposited eolian carbonates. Loss of carbonate matter during the separation process was minimized by melting snow in salt solutions near saturation with respect to calcite. Calculations indicated that 1–24% of the  $>0.45 \text{ } \mu\text{m}$  particulate carbonate matter in snow dissolved during sample processing. If standard melting and filtration methods had been used, an average of 91% of  $>0.45 \text{ } \mu\text{m}$  particulate carbonate matter would have dissolved from samples in this study.

Concentrations of particulate carbonate matter detected in snow collected at 25 sites in the south-central Rocky Mountains ranged from  $<2$  to  $83 \text{ } \mu\text{g kg}^{-1}$  snow as  $\text{CaCO}_3$ . Mean particulate carbonate matter concentrations were 10 times higher in snow from the southern Colorado Rockies than from the northern mountains of Colorado. The higher particulate carbonate matter concentrations in the south were probably related to the proximity of sampling sites to major outcrops of limestone. Particulate carbonate matter concentrations in snow from Utah and Wyoming ranged from 3 to  $35 \text{ } \mu\text{g kg}^{-1}$ . Even the highest levels of particulate calcite measured in snow samples are sufficient to neutralize only minimal amounts of strong acids. Neutralizing capacity of particulate carbonate matter averaged  $0.4 \text{ } \mu\text{eq H}^+ \text{ kg}^{-1}$  snow and the maximum neutralization capacity was  $1.7 \text{ } \mu\text{eq H}^+ \text{ kg}^{-1}$  snow.

Dissolved  $\text{Ca}^{2+}$  concentrations measured in bulk snowpack samples were relatively high compared to the amount of particulate carbonate matter detected on filters used to process samples. Much of the dissolved  $\text{Ca}^{2+}$  was probably deposited with wet deposition in the form of fine-grained particulate matter ( $<0.4 \text{ } \mu\text{m}$ ).

A poor correlation between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  indicates that contributions from gypsum were insignificant. The cation exchange capacity of noncarbonate minerals was insufficient to contribute significant buffering to snow samples collected in Utah and Wyoming.

Trends in snow acidity reflect the balance between strong acid inputs and reactions with neutralizing compounds. Among sites with similar strong acid anion concentrations, those with low concentrations of dissolved  $\text{Ca}^{2+}$  had much higher acidity than sites with average dissolved  $\text{Ca}^{2+}$ .

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