SNOWFALL CHEMICAL COMPOSITION: THE ROLE OF SNOW CRYSTAL RIMING

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ABSTRACT

During the winter of 1981-1982, samples of falling snow and cloud water were collected concurrently in clouds which enveloped Storm Peak Laboratory (SPL) at 3156m MSL near Steamboat Springs, Colorado. Analysis of the samples showed that on the average, cloud water contained three times the acidity and four to five times the conductivity of unrimed, diffusionally grown, snow crystals. During single events, these differences approached a factor of ten. Heavily rimed snowfalls consistently were most acidic and had pH values essentially equivalent to the cloud water.

From these measurements, it is estimated that snow crystal riming accounts for up to 86 percent of the total acidity and trace constituent composition of a snowpack. It is proposed that seeding supercooled clouds to convert liquid water to ice for snowpack augmentation could also improve snowfall quality.

INTRODUCTION

The scavenging of trace constituents in the atmosphere by cloud formation can be an efficient process. In contrast, scavenging of particles and gases by snow crystal appears much less efficient (Sood and Jackson, 1970 ; Summers, 1977). This paper presents the results of studies designed to examine the importance of the ice crystal riming process in determining the trace constituent composition of snowfall.

In-cloud scavenging processes have been shown to play a major role in cleansing the atmosphere of pollutants (Engleman and Slinn, 1970 ; Semonin and Beadlek, 1974). The rate limiting step of particle removal from the atmosphere in clouds is most frequently the cloud water removal rate, not the rate of attachment of particles to cloud droplets (Slinn, 1973) . The presence of cloud water can also enhance the removal rates of gases such an SO_2 by increasing the oxidation rate and conversion to sulphate relative to that in clear air (Barrie et. al., 1977 ; Hegg and Hobbs, 1981).

Cloud water chemical composition varies with cloud type, proximity to sources of aerosol particles and gases and whether or not the cloud is precipitating (Petrunchuk and Drozdova, 1966). The chemical composition of cloud water reflects the composition of the aerosol particles and gases present in the air mass within which the cloud formed. Cloud formation concentrates these atmospheric trace constituents (Mrose, 1966). Therefore, any process which removes cloud water directly from the atmosphere would be an efficient mechanism for the removal of aerosol particles and gases.

In wholly warm clouds, the growth of cloud droplets to precipitation-sized partcles is dependent on the collision-coalescence process. The resulting precipitation composition (neglecting below cloud scavenging) closely resembles the cloud water composition. Differences in the composition of precipitation from that of the cloud water may be due to dependen-

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cies of both collision-coalescence efficiency and cloud water chemical composition on cloud droplet size. Precipitation is a mixture of the various sized solution droplets of differing chemical composition.

The cold-cloud precipitation forming process is more complex than that of warm clouds. In this discussion, cold clouds are restricted to those clouds which contain the ice phase and supercooled liquid water. Ice crystals can grow to precipitation-sized particles by diffusional growth by water vapor deposition at the expense of surrounding cloud droplets, by aggregation, or by the accretion of cloud droplets. The diffusional growth process results in a concentration of the solution droplets and a chemical dilution of the ice crystals in cold clouds which are not supersaturated with respect to water. Also, ice nuclei are, in general, insoluble mineral particles, unlike the soluble salts of cloud condensation nuclei. Therefore, precipitation in the form of diffusionally grown snow crystals, or aggregates of these,may have a significantly different chemical composition than the cloud droplets. As a result, the occurrence of ice crystal riming can drastically alter snowfall quality. Scott (1981) addressed the effect of ice crystal riming on the sulfate washout ratio for snowfall. He found that, on the average, cloud water scavenging by ice crystals increased the sulfate washout ratio measured at the surface by a factor of ten. He concluded that additional nucleational scavenging and/or aqueous conversion of SO_2 to $SO_4^=$ in the cloud water in conjunction with the riming mechanism were responsible for the observed increase in the sulfate washout ratio. This scavenging mechanism for atmospheric trace constituents is addressed further in this paper.

EXPERIMENTAL

In order to investigate the role of ice crystal riming to the wet deposition of trace constituents to the surface, concurrent collection of falling snow and cloud water was performed at SPL during the winter of 1981-1982. Snow was collected as it fell into polyethylene bags. The degree of riming on individual ice crystals during the collection was observed visually on black felt or using shadow photography. Cloud water was collected in the form of rime ice deposits on 6.4 mm diameter polyethylene rods exposed to the natural wind. Cloud water contents at SPL ranged from 0.04 to o.42 gm m^{-3} (Hindman et. al., 1982). The rods normally collected 20% to 30% of the total liquid water content based on comparisons to the cloud liquid water contents measured using a roto-rod device described by Rogers et. al.(1982). Snow crystal and rime ice samples were kept frozen until analyses for pH and conductivity were performed. Further analysis of the soluble ion concentrations by ion chromatography are in progress.

Snowfall intensity (mm/hr water equivalent), ice crystal habit and degree of ice crystal riming were recorded at a site at the base of Storm Peak. These observations were used to determine both the effect of riming on the overall precipitation rate and the frequency of occurrence of riming events. In combination with the chemical analyses, these observations permitted an estimate to be made of the contribution of riming to the overall snowfall chemistry at this location.

RESULTS AND DISCUSSION

Preliminary resultsfrom this data set can be summarized in four parts. First, the role of ice crystal riming in the total water deposition to the surface is determined. The second part summarizes what fraction of the total hydrogen ion concentration and conductivity measured in the snowfall is due to rime deposits on the ice crystals. These first two results are then combined to estimate the role of the riming process on wet deposition of trace constituents from the atmosphere. Finally, the potential effects of cloud seeding (for snowfall augmentation) on the riming process, and thus snowfall chemistry, are briefly discussed in light of these results.

Water deposition and ice crystal riming

Hindman et. al.(1983) estimated the water flux to the surface at Steamboat Springs, Colorado which was due to ice crystal riming. They showed, based on the data of Feng and Grant (1982), that the measured precipitation rate was positively related to the ice crystal number flux. The data was also stratified into rimed and unrimed snowfall cases. An example is given in Figure 1. The result was that rimed snowfall precipitation rates were about a factor of two larger than the precipitation rates of unrimed snowfall for a given ice crystal number flux. Scott (1981) found similar results in a study conducted on the east coast of Lake Michigan. Interpretation of his results showed that precipitation rates (mm/hr water equivalent) for rimed snowfalls were 2.4 times the precipitation rates of unrimed snowfalls. Further interpretation of the data from Scott (1981) and Hindman et. al. (1983) indicates that 58% of the observed precipitation events consisted of rimed snow crystals. Ohtake (personal communication) reports 75% of Colorado mountain snowfalls are rimed. Combining the observations of water deposition and the frequency of riming events indicates that as much as 38% of the water content of a snowpack may be in the form of cloud water scavenged by snow crystals. Additionally, Hindman et. al. (1983) report that 4% to 11% of the water deposited to a snowpack results from direct surface riming in mountainous areas.

pH and conductivity of cloud water and ice crystals

The concurrent samples of cloud water (rime) and snowfall collected at SPL during the period December, 1981 to February, 1982 were analyzed for pH and conductivity. In addition

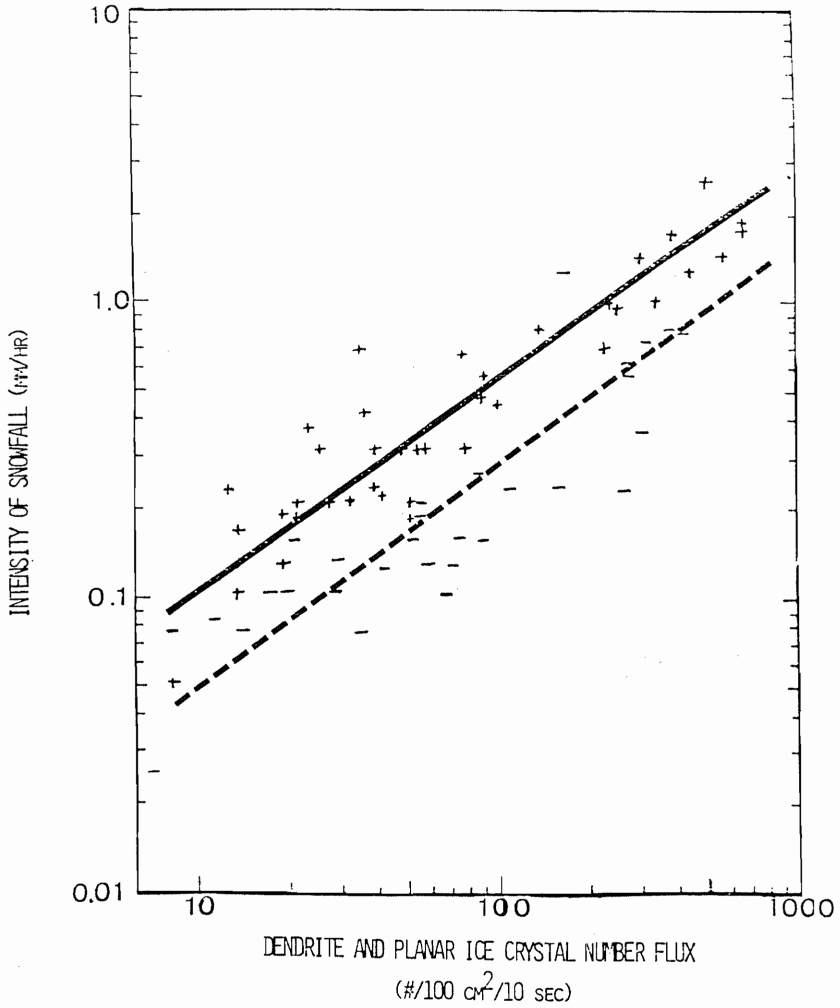

Figure 1. Intensity of snowfall (mm/hr water equivalent) as a function of crystal number flux (N/100 cm^2/10 s) for rimed (solid line, + symbols) and unrimed (dashed line, - symbols) dendritic and planar snow crystals. Ice amounts on the crystals ranged from light to heavy. From Feng and Grant (1982).

to these collections, observations were made of the snow crystal habit and degree of rime on the crystals. The data were separated into four categories indicating the degree of riming observed. These were none, light, moderate and heavy. A total of twelve sample pairs were collected and analyzed. The data are presented in Table 1 in several forms. 1) The rime (cloud water) and snow samples that were collected concurrently are presented as paired data using the format: $(H^+)_{snow}/(H^+)_{rime}$. 2) The paired rime and snow samples are categorized according to the amount of riming observed on the crystals. 3) The pH and conductivity values in each ice crystal riming category are averaged and listed. 4) The differences between the average pH for the paired rime and snow samples and the differences between the average conductivity values are listed for each rime category. 5) The average hydrogen ion concentrations (determined from the pH values) in the snow and rime samples were calculated and the ratios of these concentrations are listed for each rime category.

STORM PEAK LABORATORY RIME AND SNOW pH AND CONDUCTIVITY (µmho cm^{-1}) MEASUREMENTS - WINTER 1981-82

ICE CRYSTAL RIME AMOUNT CLASSIFICATION

MEASUREMENTS	NONE	LIGHT	MODERATE	HEAVY
(pH/COND.)snow (pH/COND.)rime	6.82/4.62 6.89/6.01	5.79/3.61 5.32/9.75	4.66/6.54 4.42/11.6	4.37/6.95 4.40/15.8
"	6.59/6.63 5.54/31.5	5.61/3.19 5.51/11.2	5.50/3.86 5.29/4.15	4.29/7.68 4.40/15.8
"	6.03/4.50 4.96/37.2			4.54/6.79 4.43/13.5
"	5.44/5.75 5.20/15.9			
"	5.81/1.48 5.75/12.4			
AVERAGES	6.14/4.60 5.67/20.6	5.70/3.40 5.41/10.5	5.08/5.20 4.86/7.85	4.40/7.14 4.41/15.0
$(\overline{pH}_{snow} - \overline{pH}_{rime})$ $(\overline{COND}_{rime} - \overline{COND}_{snow})$	0.47/16.0	0.29/7.10	0.22/2.65	- 0.01/7.86
$(\overline{H^+})_{snow}/(\overline{H^+})_{rime}$	0.34	0.51	0.60	1.0

Table 1. pH and conductivity of the twelve paired samples of snow and rime collected at Storm Peak Laboratory from December, 1981 to 1 February, 1982.

Figure 2 is a plot of the twelve paired samples of snow pH versus cloud water pH. The categories of ice crystal riming are differentiated by various symbols. The solid line represents a 1:1 relation between cloud water and snow crystal pH, while the dashed line is the best fit linear regression line through the data points. The correlation coefficient of these data is 0.88, significant at the 99% level.

Several observations can be made from Table 1 and Figure 2. 1) The average pH values for the cloud water (rime) were lower than the pH values for the snow. 2) The greatest difference between the pH values of the snow crystals and cloud water occured for ice crystals with no riming. The average pH of the cloud water in the unrimed cases was 5.67, approximately the natural pH for precipitation at equilibrium with CO$_2$ in the atmosphere. The snow meltwater pH indicates a neutralization which can be attributed to the natural nuclei at the centers of the snow crystals. These particles are comprised mainly of aluminosilicates and carbonates. As a crude example, a 0.8µm diameter spherical CaCO$_3$ particle at the center of a 600µm ice crystal (hexagonal plate) would produce the observed neutraliza-

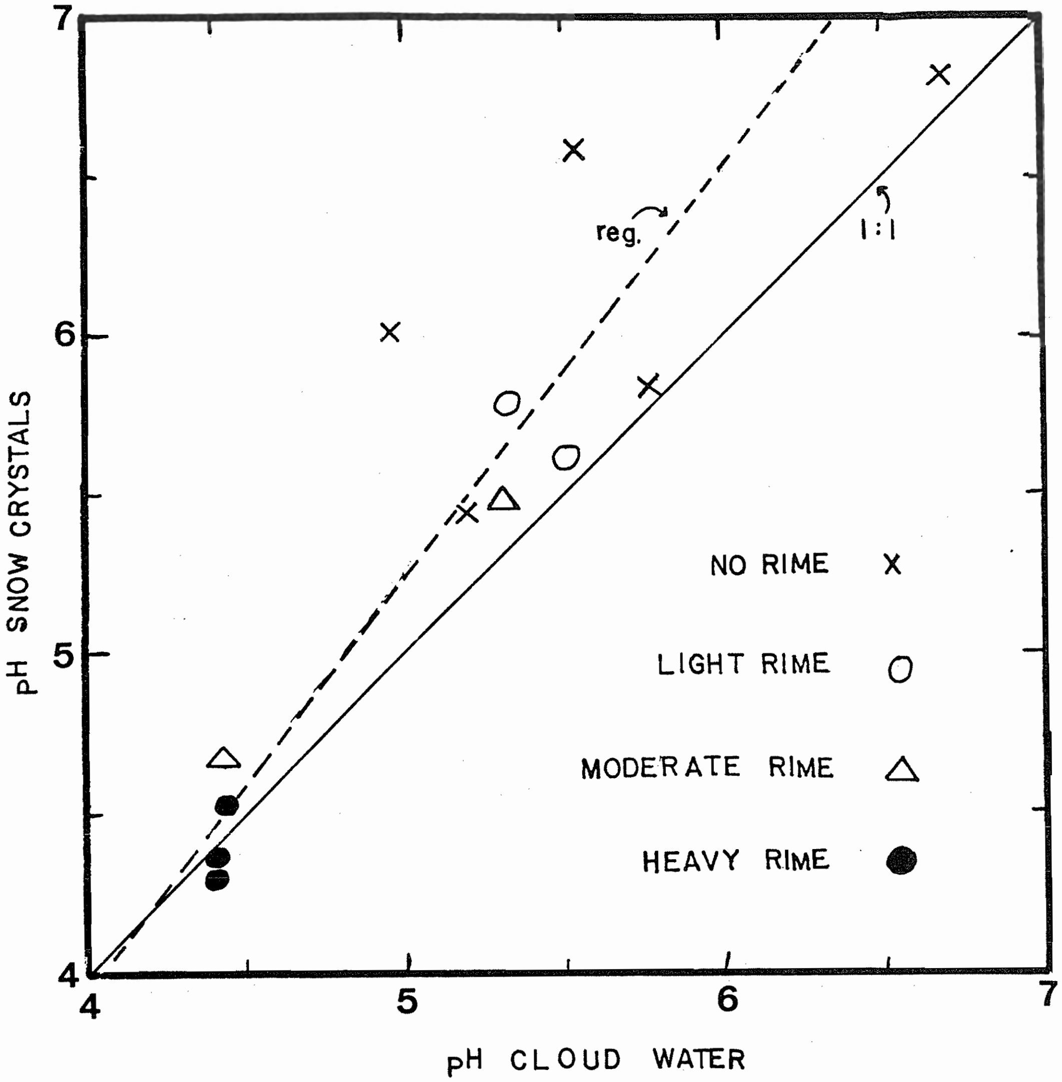

Figure 2. Summary of the pH analyses of twelve paired snow and rime samples from Storm Peak Laboratory. Paired samples were collected concurrently at the same location.

tion. This size particle is consistent with the 0.4 - 1.0μm modal diameter of natural particles observed at the center of ice crystals reported by Pruppacher and Klett (1981). 3) The difference between the pH values of the snow crystals and the cloud water decreased with increasing deposits of rime on the snow crystals. A simple calculation shows that the heavy accretion of acidic cloud droplets onto a pristine snow crystal to produce a graupel-like particle would be sufficient to change the snow crystal pH from 6.14 to the observed 4.40 value (with heavy riming). 4) The average conductivity for the cloud water was higher than the conductivity of the snow. However, the dependence of conductivity on the degree of riming was not as clear as that of pH. This suggests that the same soluble species are not necessarily responsible for both the pH and conductivity of a sample. 5)Finally, the average pH values of both the snow crystals and the cloud water decreased as the degree of ice crystal riming increased. This strong correlation is most visible in Figure 2. This suggests that the snow crystal riming process is most effective when the pH of cloud water is lowest.

A possible explanation for the final observation above can be seen in the relationship between the cloud droplet size distribution and the age of the cloud. A newly formed cloud usually has a narrow range of droplet sizes and small diameter droplets (less than 10um). This would be especially true in the stable orographic clouds (with little turbulent mixing) that commonly form about SPL. Droplets of this size have very poor collision efficiencies. It has generally been accepted that 20um is the threshold droplet diameter required for ice crystal riming. With time, a cloud droplet distribution boradens to such sizes as a result of collision-coalescence and diffusional growth processes. During this time, the cloud droplets will have had more time to interact with aerosol particles and gases. As a result, snow crystal riming may occur preferentially when droplets are more concentrated solutions. This is of course only one possible mechanism which can explain the observed decrease in both snow crystal and cloud water pH with an increase in ice crystal riming. Adequate droplet size measurements were not available to support this hypothesis.

The role of ice crystal riming in the wet deposition of trace constituents

Estimates of the magnitude of water deposition by snow crystal riming and the measured dependence of snow crystal pH and conductivity on the degree of snow crystal riming can be combined to assess the role of the riming process on the wet deposition of trace constituents from the atmosphere. During individual rimed snowfalls, 50% to 60% of the water deposited to the surface is due to scavenged cloud water. Due to the high frequency of rimed snowfalls in some areas, as much as 38% of the water content of a snowpack may be scavenged cloud water. The first column in Table 1 indicates that 8 to 10 times greater hydrogen ion concentrations and conductivity can occur in cloud water than in unrimed snow water. Combining these observations, it is estimated that the rime (cloud water) deposits on ice crystals can explain up to 94% of the total conductivity and hydrogen ion concentration of a snowfall and as much as 86% of the total conductivity and hydrogen ion concentration of a seasonal snowpack (neglecting below cloud scavenging and dry depositional processes).

Potential cloud seeding effects on snow quality

The previous discussion suggests that if the snow crystal riming process could be inhibited, and the diffusional growth of ice crystals enhanced, then the acidity of the resulting snowfall would be reduced. The method of weather modification for precipitation augmentation from cold-clouds by seeding with artificial ice nucleating agents is based upon the conversion of cloud liquid water to ice in clouds where the condensation rate exceeds the rate of ice formation. From a weather modification standpoint, the occurrence of ice crystal riming is indicative of an inefficient ice phase growth process, with potential for enhancement . Ice crystals which form as a result of seeding grow in the ice supersaturated environment at the expense of the surrounding cloud droplets and fall out as snow. If the sizes of cloud droplets are reduced by the greater ice crystal concentrations, riming would be inhibited and the snowfall would be less acidic (where below cloud scavenging of acidic components of aerosol particles and gases is not important). This speculative hypothesis could be readily tested by the inclusion of snowfall chemical studies in association with future winter snowfall augmentation programs. The already large economic benefits of a successful program would be multiplied if snow quality were simultaneously improved. In areas where precipitation quantity is not a problem, but precipitation acidity is a problem, overseeding might be an acceptable technique for inhibiting ice crystal riming and improving snow quality.

SUMMARY

On the average, at SPL, cloud water contains 3 times the acidity and 4-5 times the conductivity of unrimed snow crystals. The enhancement factor of trace constituents in rime ice was a factor of 10 in some cases. Rime deposits on ice crystals can contribute 50% to 60% of the total water content in a snowfall and 38% of the water content of a snowpack. Combining these results, up to 94% and 86% of the total trace constituents in a snowfall and snowpack respectively may be due to rime ice deposits, excluding below cloud and dry depositional processes. It is suggested that cloud seeding with artificial ice nucleating agents might serve to inhibit ice crystal riming and thus improve snow quality.

The data set is small and preliminary. General agreement with other observations suggests that results may be applicable in other regions. Further studies are needed to broaden the data base and to include soluble ion and trace element chemistry of the snow and cloud water. Efforts should be made in the future to address the cause of the observed variability in snowfall chemistry by linking in-cloud scavenging processes with sources of natural and man-made aerosol particles and gases.

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