CHEMICAL HETEROGENEITY AMONG CLOUD DROP POPULATIONS AND ITS INFLUENCE ON AEROSOL PROCESSING IN WINTER CLOUDS

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by

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ABSTRACT

CHEMICAL HETEROGENEITY AMONG CLOUD DROP POPULATIONS AND ITS INFLUENCE ON AEROSOL PROCESSING IN WINTER CLOUDS

Drop-size resolved measurements of winter cloud composition in the Rocky mountains of northern Colorado revealed significant variations of cloud drop pH, ion $(SO_4^{2-}, NO_3^{-}, NH_4^{+}, Ca^{2+})$ concentrations, and concentrations of trace metal catalysts (Fe and Mn) with drop size.

The observed chemical heterogeneity across the cloud drop size spectrum was used to evaluate its influence on rates of in-cloud sulfate production and scavenging of major inorganic aerosol components by precipitation. The findings indicates that the size-dependent chemical composition of clouds tends to enhance aqueous sulfate production rates and to reduce the efficiency with which accumulation mode aerosol species are scavenged by precipitation.

Simultaneous measurements of snow chemical composition and the degree of cloud drop capture by snow crystals (riming) revealed a significant positive correlation between snow composition and the extent of ice crystal riming in two of four cases studied. In the remaining cases it was found that the variations of snow composition were significantly correlated with air mass changes. Measurements of the size spectra of cloud drops attached on the surface of snow crystals showed that 10-17 μ m and >17 μ m cloud drop size fractions contributed significantly to accreted drop mass; little accreted mass was associated with drops smaller than 10 μ m diameter.

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ABSTRACTii
ACKNOWLEDGMENTSiv
LIST OF TABLESvii
LIST OF FIGURESviii
1. INTRODUCTION
2. EXPERIMENT DESCRIPTION
2.1 Sampling site and observation period8
2.2 Three-stage cloudwater sampling
2.3 Bulk snow sampling10
2.4 Ice crystal replica collection11
2.5 pH analysis and aliquot stabilization12
2.6 Gas phase hydrogen peroxide sampling13
2.7 Cloud drop size spectrum and liquid water content measurement13
2.8 Meteorological data14
2.8 Meteorological data
2.8 Meteorological data
2.8 Meteorological data.142.9 Image analysis of ice crystal replicas.142.10 Sulfur dioxide monitor.153. RESULTS AND DISCUSSION.16
2.8 Meteorological data.142.9 Image analysis of ice crystal replicas.142.10 Sulfur dioxide monitor.153. RESULTS AND DISCUSSION.163.1 Summary of observations.16
2.8 Meteorological data.142.9 Image analysis of ice crystal replicas.142.10 Sulfur dioxide monitor.153. RESULTS AND DISCUSSION.163.1 Summary of observations.163.1.1 Case1.17
2.8 Meteorological data. 14 2.9 Image analysis of ice crystal replicas. 14 2.10 Sulfur dioxide monitor. 15 3. RESULTS AND DISCUSSION. 16 3.1 Summary of observations. 16 3.1.1 Case1. 17 3.1.2 Case 2. 19
2.8 Meteorological data. 14 2.9 Image analysis of ice crystal replicas. 14 2.10 Sulfur dioxide monitor. 15 3. RESULTS AND DISCUSSION. 16 3.1 Summary of observations. 16 3.1.1 Case1. 17 3.1.2 Case 2. 19 3.1.3 Case 3. 20
2.8 Meteorological data. 14 2.9 Image analysis of ice crystal replicas. 14 2.10 Sulfur dioxide monitor. 15 3. RESULTS AND DISCUSSION. 16 3.1 Summary of observations. 16 3.1.1 Case1. 17 3.1.2 Case 2. 19 3.1.3 Case 3. 20 3.1.4 Case 4. 21
2.8 Meteorological data. 14 2.9 Image analysis of ice crystal replicas. 14 2.10 Sulfur dioxide monitor. 15 3. RESULTS AND DISCUSSION 16 3.1 Summary of observations. 16 3.1.1 Case1 17 3.1.2 Case 2 19 3.1.3 Case 3 20 3.1.4 Case 4 21 3.2 Physical factors influencing the snow chemistry. 28
2.8 Meteorological data142.9 Image analysis of ice crystal replicas142.10 Sulfur dioxide monitor15 3. RESULTS AND DISCUSSION 163.1 Summary of observations163.1.1 Case1173.1.2 Case 2193.1.3 Case 3203.1.4 Case 4213.2 Physical factors influencing the snow chemistry283.2.1 The correlation between ion concentrations in snow samples and
2.8 Meteorological data142.9 Image analysis of ice crystal replicas142.10 Sulfur dioxide monitor15 3. RESULTS AND DISCUSSION .163.1 Summary of observations163.1.1 Case1173.1.2 Case 2193.1.3 Case 3203.1.4 Case 4213.2 Physical factors influencing the snow chemistry283.2.1 The correlation between ion concentrations in snow samples and.31

TABLE OF CONTENTS

the equivalent potential temperature θ_e
3.2.3 Discussions of the influence of riming and air mass change on
snow chemistry
3.3 Size distributions of accreted cloud drops
3.4 Influence of chemical heterogeneity on aqueous phase sulfur
oxidation43
3.5 Case 1 study51
3.5.1 Rimed mass size distributions
3.5.2 Influence of chemical heterogeneity on precipitation scavenging
of individual solutes during accretional ice crystal growth (riming)52
3.5.3 Snow chemistry analysis
3.5.4 Relationship between the rimed mass fraction and the degree of
riming69
4. CONCLUSIONS
5. RECOMMENDATIONS FOR FUTURE WORK

REFERENC	ES 77
Appendix A.	Procedures for ice crystal replica collection81
Appendix B.	Analysis of ice crystal replica images
Appendix C.	Meteorological data during study periods105
Appendix D.	Size-resolved cloud drop ion concentration data120
Appendix E.	Diagrams
Appendix F.	Uncertainty analysis of calculated snow chemistry124

LIST OF TABLES

Table 1. Ion concentrations in cloudwater collected by the 3-stage,
supercooled cloudwater collector, FROSTY23
Table 2. Definition of the degree of riming from the work of Mosimann
et al., (1994)
Table 3. Correlation coefficients for regression of chemical (SO $_4^2$ -, NO $_3$ -,
NH4 ⁺) concentrations in snow samples against riming degree (r) and
equivalent potential temperature (θ_e)
Table 4a. The normalized volume size distributions of accreted cloud
drops on individual ice crystals in four cases40
Table 4b Measured masses of individual ice crystals and accreted cloud
drops in three size fractions in case 141
Table 5. Thermodynamic and kinetic data in the calculation of S(IV)
oxidation rates46
Table 6. Summary of the rime drop to cloud drop concentration ratios
$(C_{\rm r}/C_{\rm c})$ for two ice crystal habits (the hexagonal plate and the broad-
branched) during seven time periods in case 1
Table A-1. Proportions of formvar and ethylene dichloride for different
percent solutions

LIST OF FIGURES

Figure 1. Illustration of the three-stage cloudwater sampler (FROSTY)9
Figure 2. Temporal variations of the observed average degree of ice
crystal riming in four cases24
Figure 3. Drop size-resolved spectra of cloud pH, sulfate concentration,
and calcium concentration during sampling periods of four cases25
Figure 4. Temporal variations of snow pH and ion (sulfate, nitrate,
ammonium, and calcium) concentrations during sampling periods of
four cases
Figure 5. The cloud droplet size spectra (FSSP) during the six
consecutive cloudwater sampling periods in case 1 (01/08/1997-
01/09/1997)
Figure 6. Ice crystal images of various rime extent
Figure 7. Regressions of ion (sulfate, nitrate, and ammonium)
concentrations in snow samples against riming degree in cases 1 and 334
Figure 8. Regressions of ion (sulfate, nitrate, and ammonium)
concentrations in snow samples against the equivalent potential
temperature in cases 2 and 4
Figure 9. Observed size distributions of accreted cloud drops on
individual ice crystals or crystal fragments in four cases
Figure 10. Drop size-resolved spectra of total Fe and total Mn
concentrations during sampling periods of four cases

Figure 11. The distribution of S(IV) oxidation enhancement factors for
the three individual oxidation pathways and for the sum of three pathways
Figure 12. The ratio of metal catalyst concentrations in two size ranges
(large and medium) versus the ratio of pH in the same two size ranges50
Figure 13. The mass size spectra of cloud droplets accreted on the surface
of snow crystals during the seven consecutive snowfall sampling periods
in case 1 (01/08/1997-01/09/1997)51
Figure 14. The calculated collision efficiency versus the diameter of
collected cloud droplet for the broad-branched crystal and the hexagonal
plate with various maximum dimensions56
Figure 15. Observed and predicted concentrations of sulfate, nitrate, and
ammonium in snow samples during the first seven consecutive periods
in case 1
Figure 16. Rimed mass fraction (f) versus the degree of riming for planar
ice crystals71
Figure B-1. The ice crystal replica image analysis system
Figure B-2. Observed variations of spreading ratio versus impact velocity
for water drops accreted on ice surface with radius of 10 μ m, 18 μ m and
40 μm92
Figure B-3. The best fit curves of spreading ratio versus impact velocity
for the experimental data in Figure B-2a (T=-10 °C)
Figure B-4. The calculated variation of spreading ratio versus the size of
accreted droplets for an impact velocity of 1.0 m s ⁻¹ and an ambient
temperature of -10 °C93
Figure B-5. Observed total mass size spectrum of accreted cloud droplets
in case 1

Figure B-6. The spreading ratio distribution for accreted droplets (< 25
μm diameter) in the Storm Peak case (April, 1996)97
Figure B-7. The spreading ratio distribution for accreted droplets (> 25
μm diameter) in the Storm Peak case (April, 1996)97
Figure B-8. The observed spreading ratios for 10 droplets accreted on top
of other drops in the Storm Peak case (April, 1996)98
Figure B-9. Illustration of an accreted droplet102
Figure B-10. Observed distribution of the aspect ratio of accreted cloud
drops102
Figure B-11. Variations of relative error S between the measured (D_m)
and true diameter (D) with aspect ratio103
Figure B-12. The calculated maximum relative error S_{max} between the
corrected (f^*D_m) and true diameter (D) versus the cumulative fraction of
total droplets that possesses an error below S _{max} 103
Figure C-1. Temporal profiles of observed liquid water content (LWC)
during three consecutive days (1/8/-1/10/1997) at SPL105
Figure C-2. Temporal profiles of observed liquid water content (LWC)
during two days (1/11/1997 and 1/14/1997) of study periods at SPL106
Figure C-3. Temporal profiles of meteorological data during study
periods of cases 1, 2, and 3107
Figure C-4. Temporal profiles of meteorological data during study
periods of case 4108
Weather maps109
Back trajectories to Storm Peak116
Figure D-1. Drop size-resolved spectra of Na ⁺ , K ⁺ , and Mg ²⁺
concentrations during sampling periods of four cases120
Figure D-2. Drop size-resolved spectra of NH4 ⁺ , NO3 ⁻ , and Cl ⁻

concentrations during sampling periods of four cases	121
Figure E-1. Regressions of ion (sulfate, nitrate, and ammonium)	
concentrations in snow samples against riming degree in cases 2	2 and
4	.122
Figure E-2. Regressions of ion (sulfate, nitrate, and ammonium)	
concentrations in snow samples against equivalent potential temperature	re
in cases 1 and 3	123

1. Introduction

In several ways clouds serve as important processors of atmospheric aerosols and soluble trace gases (Collett et al., 1993). In the presence of low water vapor supersaturations found in the atmosphere, aerosol particles are needed to act as cloud condensation nuclei (CCN) to form clouds. The dissolution of soluble materials contained in these CCN particles determines the initial chemical composition of the newly formed cloud drops. The chemical composition of cloud drops can be subsequently altered by scavenging of soluble gases and interstitial aerosol particles and aqueous phase chemical reactions. The capture of aerosols and gases by cloud drops is an important step in transferring pollutant species to larger precipitation particles through the accretion of cloud drops by falling snow crystals and rain drops. Due to these interactions cloud processing can reduce the atmospheric lifetimes of many atmospheric compounds. In nonprecipitating clouds, these cloud processes can lead to the formation of modified aerosol particles when the cloud evaporates. The new particles may comprise an aerosol distribution with quite different chemical and physical properties than found prior to the cloud formation.

The existence of liquid water in clouds also provides an environment conducive to new aerosol mass formation. For example, it is well known that clouds promote the oxidation of dissolved sulfur dioxide to sulfate. In the presence of oxidants such as ozone, hydrogen peroxide or oxygen catalyzed by trace metals (Fe(III) and Mn(II)), sulfur dioxide can be oxidized much more rapidly in the aqueous phase than in the gas phase (Seinfeld and Pandis, 1998; Calvert et al., 1985; Snider and Vali, 1994). The sulfate which is formed is nonvolatile and, consequently, remains in the aerosol when the cloud drops evaporate.

In many environments precipitation is formed initially as ice crystals in mixed-phase (ice plus supercooled water) clouds. The ice crystals can grow by three mechanisms: water vapor deposition, accretion of cloud drops (an inertial capture process also known as riming), and crystal aggregation (Pruppacher and Klett, 1997). Vapor depositional growth of the crystals is analogous to a distillation process. Since the equilibrium vapor pressure of water over ice is lower than the equilibrium vapor pressure over supercooled water at the same temperature, water evaporates from supercooled cloud droplets and is deposited on the surface of growing ice crystals. Consequently, nonvolatile solute concentrations rise in the shrinking cloud drops while solute contents are diluted in the ice crystal. As a result pollutant concentrations in cloudwater tend to be much higher than

those in unrimed ice crystals. This mechanism of ice crystal growth is sometimes referred to as the Wegener-Bergeron-Findeisen precipitation mechanism (Pruppacher and Klett, 1992). In contrast, the riming process transfers both solutes and water mass to the growing ice crystals. Recent work has illustrated that ice crystal growth by riming can be an important step in the effective scavenging of atmospheric aerosol particles during precipitation events (Borys et al., 1988; Mitchell and Lamb, 1989; Collett et al., 1991; Devulapalli and Collett, 1994; Kalina and Puxbaum, 1994; Dixon et al., 1995; Takahashi et al., 1996).

Traditional approaches to the study of cloud chemistry have usually assumed a homogeneous distribution of chemical species concentrations across a population of cloud drops within a cloud parcel. Recently experimental studies (Munger et al., 1989; Carter and Borys, 1993; Collett et al., 1994; Bator and Collett, 1997; Collett et al., 1998a, 1998b; Rao and Collett, 1998; Laj et al., 1998) have revealed the presence of substantial variations in drop chemistry across the cloud drop size spectrum. These variations, also predicted by a number of recent cloud chemistry models (e.g., Pandis et al., 1990; Hegg and Larson, 1990; Roelofs, 1993), can result from a variety of causes, including the chemically heterogeneous nature of the CCN population, different condensation growth rates for different drop sizes, different chemical reaction rates between drops of disparate

composition and drop size-dependent rates of soluble gas scavenging (Ogren and Charlson, 1992). For example, chemical species associated with the accumulation mode of aerosol particles (e.g., sulfate, nitrate, and ammonium) produced from gas-to-particle conversion processes often are found at higher concentrations in small cloud drops. Species found primarily in larger, mechanically generated aerosol particles tend to be enriched in large cloud drops. Some previous work (see, e.g., Collett et al., 1994, 1998b; Laj et al., 1998) also revealed that smaller drops usually, but not always, possess higher acidity than larger drops.

Variations in cloud drop composition as a function of drop size can influence sulfate production rates in clouds. In cases where the ozone or trace metal catalyzed autooxidation (oxidation by O₂) pathways contribute significantly to aqueous phase sulfate production, the presence of chemical heterogeneity in a population of cloud drops can alter the average rate of sulfate production in the cloud from the rate expected based on the average cloud drop composition (Collett et al., 1994; Gurciollo and Pandis, 1997). The effect, which usually acts to increase average sulfate production rates, results from the nonlinear dependence of the sulfur oxidation rates on cloud drop composition, including the hydrogen ion concentration. Since the rate of S(IV) oxidation by hydrogen peroxide is essentially independent of drop pH, and is linear in the aqueous hydrogen peroxide concentration, it is

unlikely to be affected by chemical heterogeneity present among the cloud drop population. The effect of drop size-dependent variation in cloud drop composition on sulfate production, therefore, is likely to be greatest at high pH, where oxidation by ozone or by metal-catalyzed autooxidation is typically faster than oxidation by hydrogen peroxide. This situation is also more likely to occur in winter when peroxide formation is reduced due to shorter days and lower solar intensities. In a previous study of warm clouds (Collett et al., 1994), it has been demonstrated that the difference of acidity between small and large drops can significantly accelerate sulfur oxidation. A newly developed cloud impactor capable of sampling several independent drop size fractions under harsh winter conditions enabled us to extend this investigation to winter cloud systems.

Precipitation scavenging of individual chemical species during ice crystal riming can also be influenced by the distribution of those species across the cloud drop size spectrum. The collision efficiency between an ice crystal and a cloud drop typically increases with drop size. Consequently, it is expected that chemical species which are enriched in large cloud drops will be incorporated into rimed ice crystals more efficiently than species which tend to be enriched in small cloud drops. For very large drop sizes ($d > 40-50 \mu m$ for hexagonal plate or broad-branched ice crystals), the collision efficiency decreases with increasing drop size

(Pruppacher and Klett, 1997). In the present study these large drops were not observed to be important. Although a series of available work (see, e.g., Borys et al., 1988; Mitchell and Lamb, 1989; Collett et al., 1991; Dixon et al., 1995) has illustrated the importance of accretional ice crystal growth (riming) in raising the efficiency of pollutant scavenging by wet deposition, no one has investigated to any significant extent how the non-uniform distribution of chemical composition across the cloud drop size spectrum affects these processes. Since the species contained in accumulation mode aerosol particles are only inefficiently removed by below-cloud scavenging processes (Seinfeld and Pandis, 1998), the atmospheric lifetimes of these species may be different than expected based on the assumption of their uniform distribution over the cloud drop size spectrum. Most likely their lifetimes will be increased as a result of preferential enrichment in small cloud drops.

The present study was aimed at (1) examining winter clouds in the Rocky Mountains of northern Colorado to determine whether cloud drop composition varied significantly across the drop size spectrum; (2) assessing the influence of the observed chemical heterogeneity on sulfate production rates and scavenging of individual solutes during accretional ice crystal growth. These findings along with an analysis of the snow chemistry are conducive to our understanding of how various microphysical

processes influence snow and cloud chemistry in winter cloud systems. As complementary work we also investigated the mass size spectra of accreted cloud drops on rimed ice crystals and the relationship between the rimed mass fraction and the visually determined (Mosimann et al., 1994) extent of ice crystal riming. As another complementary work we attempted to predict ion concentrations in snow using cloud chemistry and ice crystal riming observations and compared them with observed snow chemistry.

2. Experiment Description

2.1 Sampling site and observation period

Ground-based sampling of clouds and ice crystals was conducted during winter 1996-97 at the Storm Peak Laboratory (SPL) (Borys and Wetzel, 1997), located at 3210 m elevation in the Rocky Mountains of northern Colorado (40.45N, 106.74W). The laboratory is situated on a peak of a 70km-long north-south mountain barrier, oriented perpendicular to the prevailing west winds. When winter storm systems influence northern Colorado, SPL is often enveloped by clouds containing supercooled liquid water. During this project, frontal and orographic clouds and snow were sampled from January 1-17, 1997. Sampling was conducted in four main events. Time periods for each event are: 21:00, January 8 to 05:00, January 9; 17:00 to 22:00, January 9; 16:00, January 10 to 02:00, January 11; and 13:30 to 20:30, January 14. (From here through all following sections, time refers to the local time unless specified).

2.2 Three-stage cloudwater sampling

Cloudwater was collected during the study using a new, 3-stage cloud collector (FROSTY) designed in our laboratory for use in supercooled



(a) FROSTY collector in operation at Storm Peak Lab, Steamboat Springs, CO



(b) Top View of Collector

Figure 1. Illustration of the three-stage cloudwater sampler (FROSTY).

clouds. Designed for use at the altitude and typical winter conditions experienced at SPL, FROSTY features three jet impaction stages in series (see Figure 1), with 50% cut sizes of 4, 10, and 17 µm. Each stage features a single rectangular jet followed by a Teflon impaction surface. The impaction surfaces are removable to permit easy retrieval of the rime deposits that accumulate as impacting supercooled droplets freeze on each stage. Air is drawn through the collector at 1500 l min⁻¹, providing sufficient sample on the three stages to permit sample collection at one hour intervals. Collected cloud samples were melted on-site for pH measurement and preservation of unstable chemical species as described below. The impactor is cleaned prior to use with deionized (DI) water. Blanks are taken for the impaction surfaces by pipetting a small volume of DI water onto each surface and then removing the water for chemical analysis.

2.3 Bulk snow sampling

Snow was collected for chemical analysis at intervals of 15-30 minutes. Samples were collected in polyethylene bags mounted on a frame and directed into the wind. Because the snow sampling was made in clouds, the recognizable rimed cloud drops collected around the edge of each bag were

carefully removed before the snow samples in the bag were collected. Collected snow samples were melted for on-site pH measurement and preservation of unstable chemical species as described below. Blanks were taken for polyethylene bags by rinsing several new bags with DI water and collecting the rinse water for chemical analysis.

2.4 Ice crystal replica collection

Ice crystal formvar replicas (Van der Hage, 1969) were made on glass slides at intervals of five to ten minutes. A solution of formvar dissolved in ethylene dichloride (either 2% or 4% by weight) was used to coat a glass microscope slide by dipping the slide into a glass vessel containing the formvar solution. The coated slide was exposed to falling ice crystals outside the lab for 10-30 seconds. The formvar polymerizes on contact with water and forms a thin plastic coating over the ice crystal surface. After a short period of drying the replicas in a cold enclosure containing a drying agent, the replicas are stable, allowing for later careful analysis of ice crystal habit and the size of rime drops attached to the ice crystal under a microscope. The slides, formvar solution and drying materials were stored under ambient atmospheric conditions for at least a few hours prior to sampling to avoid melting collected ice crystals (For a detailed description of ice crystal collection see appendix A).

2.5 pH analysis and aliquot stabilization

Measurement of cloudwater and snow pH were made on-site following sample collection using a portable pH meter and glass combination microelectrode (Microelectrodes, Inc. mode MI-250A) calibrated with pH 4 and 7 buffers. Individual cloud sample aliquots for analysis of unstable species were prepared by the following procedures. Hydrogen peroxide was stabilized by addition of a buffered solution of parahydroxyphenylacetic acid for later analysis by fluorescence (Lazrus et al., 1985). Formaldehyde was preserved by reaction with ammonium acetate and 2,4-pentanedione to form 3,5-diacetyl-1,4-dihydrolutidine which was later analyzed by fluorescence (Dong and Dasgupta, 1987). Trace metals were stabilized by addition of nitric acid and later analyzed by Zeeman-corrected graphite furnace atomic absorption. S(IV) was stabilized as HMS by adding buffered CH₂O, plus catalase to destroy hydrogen peroxide in the sample, and analyzed on a visible spectrophotometer by the pararosaniline method (Dasgupta et al., 1980). Separate aliquots of the cloud and snow samples were also made for major ion (Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, NO₃⁻, and SO₄²⁻) analysis using standard techniques of ion chromatography. Samples and preserved aliquots were refrigerated prior to analysis in our laboratory.

2.6 Gas phase hydrogen peroxide sampling

The gas phase total soluble hydrogen peroxide concentration was continuously measured using a single-channel enzyme based peroxide analyzer (Lazrus et al., 1986). Analysis using this method consists first of quantitatively transferring soluble gaseous peroxides into distilled water flowing through a coiled glass tube. The hydroperoxides in the collected solution are reacted with p-hydroxyphenylacetic acid under conditions of enzymatic catalysis to produce a fluorescent biphenyl derivative. Spectroscopic monitoring of the fluorescence emission at 420 nm permits

quantitative determination of hydroperoxides in the aqueous solution. The instrument was calibrated periodically by injection of liquid standards of known concentration.

2.7 Cloud drop size spectrum and liquid water content measurement

The cloud drop size spectrum was continuously monitored by SPL's Particle Measurement Systems aspirated FSSP-100 forward scattering spectrometer probe. The calibrated bin midpoints for the FSSP on Range 1 $(2 - 32 \mu m)$ for this study were 3.2, 5.4, 7.5, 9.7, 11.8, 13.9, 16.1, 18.2, 20.4, 22.5, 24.7, 26.8, 28.9, 31.1, and 33.2 μm . Continuous measurements of the cloud liquid water content (LWC) were made using a Gerber Scientific Particulate Volume Monitor (PVM-100) (Gerber, 1991), calibrated with an optical disk provided by the manufacturer.

2.8 Meteorological data

Meteorological data were continuously recorded using SPL's roof-top meteorological system. The system includes temperature sensor (temperature), barometer (pressure), relative humidity sensor (relative humidity), deiced wind vane (wind direction), and deiced anemometer (wind speed). Data were recorded at intervals of 10 minutes.

2.9 Image analysis of ice crystal replicas

A PC-based image analysis system was used to analyze the size distribution of accreted droplets on ice crystal replicas. The image analysis system consists of three parts: optical microscope, image capture system and the image analysis software. Ice crystal replicas are viewed using a Nikon SMZ-U stereo zoom microscope with a magnification ranging from 30 to 300. Detail is sufficient to resolve features as small as 1 µm. A video camera attached to the microscope sends pictures of the replicas to a personal computer equipped with a frame grabber to digitize the images. A

commercial image processing package (Image-Pro Plus, Version 1.2) was used to process the digitized ice crystal photos and to determine the habits and sizes of the ice crystals and measure size distributions of attached cloud (rime) drops. A correction factor of 0.9 was applied to account for effects of the spreading of accreted drops on the ice crystal surfaces. This correction is based on some previous field observations and experimental studies (Brownscombe and Hallett, 1967; Dong and Hallett, 1988, 1989; Mosimann, 1994). A detailed description of the image analysis system, image analysis procedures and the spreading of accreted cloud drops is provided in appendix B.

2.10 Sulfur dioxide monitor

A continuous SO_2 monitor was installed at the site for ambient SO_2 measurement. Unfortunately no SO_2 concentrations could be measured due to failure of the instrument at the start of the study.

3. Results and discussion

3.1 Summary of observations

During the period January 1-17, 1997, 30 cloudwater samples, 68 snow samples, and 265 ice crystal replica slides were collected during 4 extended sampling periods. Both snow and cloudwater composition were dominated by sulfate, nitrate, ammonium, calcium, and hydrogen ion. Cloud pH ranged from 3.6 to 6.5 during the study. Cloudwater concentrations of sulfate ranged from 27 to 376 microequivalents l^{-1} (µN); nitrate concentrations ranged from 11 to 254 µN; ammonium concentrations ranged from 34 to 438 µN; calcium concentrations ranged from undetectable to 175 µN. The high concentrations of calcium observed in the snow and cloudwater were somewhat surprising given the extensive snowcover found over the entire region which presumably suppressed regional dust emissions. Gas phase soluble peroxide concentrations measured during the study were typically a few tenths of a ppby, with some periods below the instrument detection limit (~0.05 ppbv). The general characteristics of each event are summarized below.

3.1.1 Case 1. Cloud interception at SPL occurred in conjunction with a frontal system approaching from the north on January 8. As shown in weather maps in Appendix C, during the periods of January 7-11, a cold frontal system built up and moved through the sampling site. Frontal clouds intercepting the site during this event (and cases 2 and 3) were enhanced by orographic lifting of the air flow over the mountain. Sampling of cloudwater, snow, and ice crystal replicas began at 21:00, January 8, and continued until 05:00 on January 9. The cloud drop size spectrum was continuously measured by the FSSP starting from 22:00, January 8. Heavy snow occurred throughout this event until 04:30 on January 9. Almost all snow crystals collected at the site were planar types (sector-like, broadbranched, stellar with broad arms, hexagonal plates, etc.) with characteristic dimensions of 0.1-1.3 mm. The collected ice crystals were lightly to densely rimed (see Figure 2a). The degree of riming increased from 1.0 to 3.0 on Mosimann's (1994) scale of 0 to 5 where riming degree 0 corresponds to no riming and riming degree 5 corresponds to graupel (refer to Table 2 in the next section).

During the event, strong west winds (20-25 m s⁻¹) and cold temperatures (-15 °C) were observed. The measured LWC (Liquid Water Content) increased from 0.01 to 0.3 g m⁻³ during the event with visibilities decreasing

to approximately 40-50 meters. Temporal profiles of meteorological data during all study periods are given in Appendix C.

Chemical species concentrations measured in the three FROSTY cloud drop size ranges are listed in Table 1; cloud pH and concentrations of sulfate and calcium are depicted in Figure 3. Concentrations of other species during all study periods are depicted in Appendix D. During most sampling periods smaller cloud drops contain higher concentrations of $SO_4^{2^-}$, NO_3^- , and NH_4^+ than found in larger cloud drops. Ca^{2+} concentrations increase with drop size for some case 1 sampling periods, but this trend is reversed early and late in the event. Cloud pH also varies with drop size, generally increasing with increasing drop size. Cloud pH values between 3.5 and 5.5 were observed during this case.

Concentrations of several species measured in snowfall during case 1 are shown in Figure 4a. Concentrations of NO_3^- , SO_4^{-2-} , and Ca^{2+} are generally between 10 and 20 microequivalents/liter (μ N), with the exception of higher Ca^{2+} concentrations at the start of the event. NH_4^+ concentrations are generally below 10 μ N. Snow pH declines from approximately 6.5 to 5.5 over the course of the event.

The cloud drop size spectra (FSSP) during the six case 1 cloudwater sampling periods are plotted in Figure 5. A recognizable shift of the drop size spectrum toward larger cloud drop sizes with time is apparent, with the

peak concentration droplet size approximately doubling from 8 to 16 μ m diameter over the course of the event.

3.1.2 Case 2. This case featured continued cloud interception from the same frontal system producing case 1. Sampling of cloudwater, snow, and ice crystal replicas was conducted from 17:00 until 22:00 on January 9. Moderate to heavy snow was observed through this event. Most ice crystals collected were broken planar types, with the average degree of riming between 2.0 and 3.0 (see Figure 2b). It was very windy throughout this sampling period, with west winds up to 30 m s⁻¹. The air temperature at Storm Peak was -11 to -12 °C. Cloud LWC was approximately 0.3 g m⁻³. The drop size-dependent cloud chemistry observations are listed in Table 1 and illustrated in Figure 3. Again, these samples show a tendency for SO_4^{2-} , NO_3^- , and NH_4^+ concentrations to increase with decreasing drop size. Significant differences in pH (exceeding one pH unit) are also seen between large and small cloud drop fractions, while Ca²⁺ concentrations show a variable dependence on drop size. Snow composition for case 2 is depicted in Figure 4b. Snow pH remains between 4.5 and 5.5 during this period and concentrations of all ions are below 20 µN.

3.1.3 *Case 3.* The same frontal system producing the case 1 and case 2 studies continued to produce cloud interception and snow at SPL into January 11th. Case 3 sampling occurred from 16:00 on January 10 until 02:00 on January 11. Most snow crystals observed during this period were planar types with some columns. The ice crystals were typically moderately to heavily rimed, with observed degrees of riming between 2.5 and 4.0 (Figure 2c). During this period the wind blew from the northwest, with typical wind speeds of approximately 10-25 m s⁻¹. The air temperature at the site was approximately -11 °C. Cloud LWC ranged from 0.1 to 0.6 g m⁻³. Concentrations of major species in the cloudwater and snow are depicted in Table 1 and Figures 3 and 4. Cloudwater pH values during this period ranged from 3.9 to 6.5, with the highest values observed in the large drop fraction. Differences in pH between large and small drop fractions as large as 2.5 pH units were observed during this period. Cloud composition during this period is dominated by sulfate and ammonium, both of which tend to be enriched in smaller drops. The drop size-dependence of calcium concentrations is again variable, but many samples exhibit a U-shaped profile, with the lowest concentrations in drops of intermediate size. Ion concentrations in snow increased over the course of case 3, with sulfate dominating the composition. Snow pH during case 3 varied between approximately pH 4.5 and 6.

3.1.4 Case 4. The final case study of this campaign occurred on the afternoon and early evening of January 14. As shown in weather maps in Appendix C, in contrast to above three cases, no front built up and moved through the sampling site during the sampling period of this case. Strong upslope flow during the afternoon resulted in formation of an orographic cloud at the SPL monitoring site. Sampling started at 13:30 and continued until 20:30. Typical values of cloud LWC at SPL during the period ranged from 0.2 to 0.4 g m⁻³. Light to moderate snow was observed throughout the event. Many planar ice crystals (hexagons, stellar crystals, dendrites and aggregates) and a few needles were observed. Moderate (2.0) to heavy (4.0) riming was observed on the ice crystals during most of the event (see Figure 2d). The wind blew from the west at approximately $10-15 \text{ m s}^{-1}$ while air temperatures at the site were approximately -12 °C. The cloudwater during case 4 was more polluted than seen in most of the previous sampling periods. The pH was close to 4 and showed little variation with drop size in most samples (see Figure 3). Nitrate, sulfate and ammonium concentrations increased with decreasing drop size in most, but not all, case 4 sampling periods and showed a tendency to increase over the course of the event. Calcium concentrations again showed a variable dependence on drop size (see Table 1 and Figure 3). Snow samples were

also found to be more polluted than most collected earlier in the study. The snow pH varied between approximately pH 4 and pH 6.5 (Figure 4d). High concentrations of calcium during the middle of the event appear to have provided significant alkalinity to the snow and kept the snow pH high during that period (Figure 4d).

Date	Start	End	pH Value			[Ammonium] (µN)			[Ca2+] (µN)			[Nitrate] (µN)			[Sulfate] (µN)			Total Iron (µg/l)			Total Manganese (µg/l)		
Case 1	Time	Time	Large	Medium	Small	Large	Medium	Small	Large	Medium	Small	Large	Medium	Small	Large	Medium	Small	Large	Medium	Small	Large	Medium	Small
01/08/97	21:00	21:57	4.5	4.1	3.6	243.8	331.6	438.4	44.7	71.1	70.5	130.3	174.9	254.0	164.7	250.6	375.6	N/A	N/A	N/A	N/A	N/A	N/A
01/08/97	22:02	23:00	4.2	3.9	3.6	252.9	266.0	291.5	32.7	30.5	20.5	140.9	164.7	191.8	173.6	213.9	252.4	N/A	N/A	N/A	N/A	N/A	N/A
01/08/97	23:02	00:00	4.3	4.1	3.9	148.9	178.4	176.8	40.8	42.8	18.0	94.0	125.2	141.5	127.4	154.9	183.1	229.7	N/A	N/A	3.4	N/A	N/A
01/09/97	00:03	01:01	4.5	4.1	3.9	77.4	101.1	130.1	38.1	37.4	25.0	56.5	78.2	93.8	70.3	99.5	143.6	538.0	65.5	N/A	5.2	2.8	N/A
01/09/97	01:02	02:00	5.0	4.3	4.1	53.8	50.5	72.8	31.5	29.8	45.6	33.1	39.6	53.8	43.6	59.9	80.7	131.1	70.7	N/A	2.3	1.6	N/A
01/09/97	02:03	03:00	4.6	4.3	4.4	47.9	56.2	58.8	20.3	20.7	37.0	29.8	38.7	42.3	40.1	52.6	70.3	329.1	N/A	N/A	13.2	N/A	N/A
01/09/97	03:02	04:00	5.4	4.5	4.6	39.2	69.8	76.0	23.2	23.7	54.1	39.0	46.5	43.4	35.0	45.6	59.0	35.0	95.1	N/A	1.3	20.1	N/A
01/09/97	04:02	05:00	3.8	3.9	5.5	36.2	66.1	84.1	16.2	9.0	55.4	32.2	40.6	46.9	31.4	41.3	66.3	174.3	163.4	N/A	1.4	3.1	N/A
Case 2																							
01/09/97	17:02	18:00	4.9	5.0	5.6	37.4	42.6	88.7	23.3	53.1	67.3	20.4	25.2	37.6	45.4	64.6	102.5	261.9	163.6	N/A	5.2	35.1	N/A
01/09/97	18:02	19:00	5.7	5.8	5.5	44.0	49.4	54.2	27.5	28.5	56.8	16.7	20.1	24.2	31.8	41.0	57.1	219.5	N/A	N/A	4.3	N/A	N/A
01/09/97	19:02	20:00	6.2	5.8	6.2	44.5	42.1	53.4	68.6	29.5	58.8	14.0	17.4	18.6	26.7	32.0	44.1	205.5	N/A	N/A	3.4	N/A	N/A
01/09/97	20:02	21:00	6.4	5.3	5.2	43.3	52.9	105.8	79.2	47.1	66.4	16.4	21.3	27.9	40.8	56.9	81.5	605.0	N/A	N/A	4.6	N/A	N/A
01/09/97	21:02	22:00	5.6	5.0	4.5	71.7	71.2	120.6	42.5	46.0	53.5	19.8	23.3	31.3	61.6	86.7	140.5	211.4	N/A	N/A	1.8	N/A	N/A
Cuse 3														Nue Contra	C-11								
01/10/97	16:00	17:00	5.6	5.2	4.2	33.5	119.4	122.6	98.2	31.2	51.9	14.7	11.3	19.0	87.4	125.0	217.5	188.6	161.1	N/A	1.3	2.1	N/A
01/10/97	17:02	18:00	6.2	4.9	4.2	63.6	56.0	81.5	136.2	58.5	43.4	18.8	16.1	21.3	90.8	119.6	150.2	501.0	104.9	N/A	1.7	1.8	N/A
01/10/97	18:02	19:00	6.4	5.1	3.9	81.5	118.6	69.0	170.6	39.6	121.5	22.5	17.3	22.8	91.9	121.6	177.0	174.2	N/A	N/A	0.7	N/A	N/A
01/10/97	19:02	20:00	6.1	5.2	5.3	37.5	89.6	87.2	147.6	43.6	49.1	18.5	14.2	16.2	57.8	66.5	96.5	227.8	N/A	N/A	1.7	N/A	N/A
01/10/97	20:02	21:03	6.5	4.8	5.8	60.2	67.5	169.3	175.0	51.2	59.1	24.4	21.7	25.1	79.1	98.3	159.1	219.6	55.1	N/A	2.0	1.0	N/A
01/10/97	21:05	22:00	6.3	5.0	4.8	39.8	101.5	38.3	127.6	38.3	70.4	25.4	25.3	25.6	65.3	84.9	107.6	185.3	30.6	N/A	3.6	1.4	N/A
01/10/97	22:02	23:00	6.0	4.7	4.8	60.9	94.9	127.0	93.1	36.7	51.3	25.8	29.4	36.6	66.3	86.8	124.0	161.7	394.1	N/A	1.4	2.7	N/A
01/10/97	23:02	00:00	6.2	4.5	5.2	43.0	77.3	112.0	135.5	25.8	46.1	29.5	28.9	29.9	58.0	75.4	101.7	416.5	36.6	N/A	3.1	0.6	N/A
01/11/97	00:02	01:00	6.1	4.6	5.6	47.4	49.1	136.8	104.1	24.8	81.6	31.7	31.2	43.4	49.8	58.9	77.2	125.5	241.5	N/A	1.4	0.7	N/A
01/11/97	01:01	02:02	5.6	4.5	6.1	64.4	91.8	201.0	69.4	28.5	42.1	35.0	41.6	37.9	69.8	85.9	90.4	210.5	47.9	N/A	1.6	1.1	N/A
Case 4																							
01/14/97	13:30	14:30	4.3	4.2	4.0	46.2	46.7	68.1	30.7	28.1	22.9	57.6	67.1	97.1	58.1	66.2	97.6	46.6	12.2	50.6	4.4	0.7	2.2
01/14/97	14:33	15:30	4.3	4.1	3.8	72.1	52.8	47.3	42.6	53.1	24.4	79.0	87.2	98.6	70.7	81.8	96.9	127.1	93.5	N/A	1.5	0.8	N/A
01/14/97	15:32	16:30	4.0	4.0	3.9	119.5	115.3	151.8	23.8	23.2	13.9	92.5	96.3	133.2	125.9	130.4	169.4	20.0	34.8	N/A	1.0	1.3	N/A
01/14/97	16:32	17:30	4.0	4.0	4.0	88.1	129.5	203.8	21.5	20.8	0,0	79.9	93.8	112.9	116.0	136.1	190.0	52.2	23.4	N/A	1.1	1.2	N/A
01/14/97	17:32	18:30	4.1	3.9	4.2	72.5	93.4	175.5	20.3	19.8	52.8	85.8	121.7	105.6	86.8	121.0	156.0	218.6	170.1	N/A	3.1	2.2	N/A
01/14/97	18:32	19:30	3.9	4.0	4.1	82.1	124.1	199.7	25.2	24.1	43.3	126.3	139.6	130.3	91.9	123.1	144.7	194.1	155.8	N/A	1.9	2.2	N/A
01/14/97	19:32	20:30	4.5	5.6	N/A	230.6	N/A	N/A	61.2	N/A	N/A	165.7	N/A	N/A	144.7	N/A	N/A	83.9	N/A	N/A	4.1	N/A	N/A

Table 1. Ion Concentrations in Cloudwater Collected by the 3-Stage, Supercooled Cloudwater Collector, FROSTY (Large Drops: dia. > 17µm; Medium Drops: dia. between 10-17µm; Small Drops: dia. between 4-10µm)



Figure 2. Temporal variations of the observed average degree of ice crystal riming in four cases.


Figure 3. Drop size-resolved spectra of (a) cloud pH; (b) sulfate concentration; (c) calcium concentration during the consecutive cloud sampling periods in each of four cases. The eight consecutive periods in case 1, the five consecutive periods in case 2, and the ten consecutive periods in case 3 correspond to those listed in Table 1. The six consecutive periods in case 4 correspond to the first six periods of case 4 listed in Table 1. For each period the data are presented as a three-stage ion concentration spectrum.



Figure 4. Temporal variations of snow pH and ion (sulfate, nitrate, ammonium, and calcium) concentrations for: (a) case 1; (b) case 2; (c) case 3; (d) case 4.



Figure 5. The cloud droplet size spectra (FSSP) during the six consecutive cloudwater sampling periods in case 1 (01/08/1997-01/09/1997).

3.2 Physical factors influencing the snow chemistry

Various physical factors may influence the chemistry of snow such as the mechanism of ice crystal growth and changes in the identity (and composition) of the air mass in which snow is formed (see, e.g., Collett et al., 1991; Devulapalli and Collett, 1994). In the present study we adopted Mosimann's (1994) riming scale to describe the extent of accretional ice crystal growth, as given in Table 2 and visualized in Figure 6. The extent of riming on each ice crystal is determined by visually comparing its riming pattern with the reference patterns as described and shown in Table 2 and Figure 6. Sometimes a scaling value between those reference values was chosen when it was thought more relevant. We used the equivalent potential temperature, θ_e , as an air mass tracer to help determine whether the snow chemistry is influenced by air mass changes since this parameter remains relatively constant for several hours as a given air mass undergoes transport (see, e.g., Collett et al., 1991). It is expected that different air masses may contain aerosol particles and clouds of different chemical and physical properties. For example pollutant concentrations in the warm air present at a monitoring site preceding the arrival of a cold frontal may be quite different from those present in the post-frontal cold air mass. These differences may arise from a variety of sources including different pollutant

source contributions to the two air masses or different precipitation

histories. Since \mathcal{P}_e is an effective air mass tracer in winter frontal systems and in winter orographic storms, changes in cloud and snow chemistry due to the air mass changes can often be correlated with changes in \mathcal{P}_e . Use of \mathcal{P}_e is more practical than use of back-trajectories for our purpose, since \mathcal{P}_e can be monitored at much higher time resolution. Changes in cloud and precipitation chemistry occur in time scales as short as minutes during frontal passage.

Degree of riming	Description of riming
0	(unrimed). No cloud drops are found on the ice crystal surface.
1	(lightly). There are a few cloud drops scattered on the crystal surface. Uncovered surface dominates. The percentage of the crystal's surface covered by rime is less than 25%.
2	(moderately). For planar ice crystals the edges and branches are undoubtedly covered with droplets, whereas the inner part of the crystal is only lightly rimed or even unrimed. There are a lot of droplets stacked at edges. For columnar crystals the rime coverage of the surface is approximately 50%.
3	(densely). The whole crystal surface is nearly or completely covered with one layer of droplets. The crystal shape is not deformed and can still be identified. More than one layer of accreted droplets can be found at edges of planar ice crystals.
4	(heavily). A large amount of drops are accreted on the crystal surface and the original crystal shape is barely recognizable. The crystal surface is no longer visible due to multiple layers of accreted cloud drops.
5	(graupel). This group contains all kinds of graupel. Original crystal shape cannot be recognized due to extensive riming.

Table 2. Definition of the degree of riming from the work of Mosimann et al., (1994).



Figure 6. Ice crystal images representing the first five degrees of riming. From top to bottom riming degrees are 0, 1, 2, 3, and 4. All these planar ice crystal images were obtained from 4 cases of the present study.

3.2.1 The correlation between ion concentrations in snow samples and the observed degree of riming

Ion (NH_4^+, NO_3^-) , and SO_4^{2-}) concentrations in snow samples were regressed against the degree of riming observed during the snow sample periods to determine whether changes in riming could explain changes in snow chemistry during each of the four events. Cases 1 and 3 yielded a significant positive correlation between snow composition and riming degree (see Figure 7). In case 1 R-squared values for sulfate, nitrate and ammonium are 0.36, 0.09 and 0.05, respectively. The confidence levels by T-test for the significance of these R-squared values are 99.7%, 86.8% and 75.0% for sulfate, nitrate and ammonium, respectively. In case 3 R-squared values for sulfate, nitrate and ammonium are 0.38, 0.38 and 0.34, respectively. The confidence levels by T-test for the significance of these R-squared values are 99.0%, 99.3% and 98.9% for sulfate, nitrate and ammonium, respectively. Cases 2 and 4 yielded only a poor correlation between snow composition and riming degree (see Figure E-1 in Appendix E). This result is consistent with our expectation that riming is one of several factors that can strongly influence snow chemistry. Previous work has found similar positive correlations between snow chemistry and degree

of riming (e.g., Mitchell and Lamb, 1989; Collett et al., 1991; Devulapalli and Collett, 1994).

3.2.2 The correlation between ion concentrations in snow samples and the equivalent potential temperature θ_e

Ion (NH₄⁺, NO₃⁻, and SO₄²⁻) concentrations in snow samples were regressed against the equivalent potential temperature θ_e observed at Storm Peak Laboratory during the snow sample periods to determine whether air mass composition changes might account for changes in snow chemistry during each of the four events. The equivalent potential temperature is defined as the final temperature θ_e which an air parcel attains when it is lifted dry adiabatically to its lifting condensation level (LCL), then pseudowet adiabatically (with respect to water saturation) to a great height (dropping out all condensed water as it is formed), then finally brought down dry adiabatically to the 1000 mb level. θ_e is calculated by (Holton, 1972; Bolton, 1980):

$$\theta_e \cong T_K (\frac{1000}{P})^{0.2854(1-0.00028m_r)} \tag{1}$$

where T_K , P and m_r are the absolute temperature, pressure and water vapor mixing ratio at the initial air level (SPL). This is an approximated

expression for the formula used by Bolton (1980). It yields only a few percent deviation from Bolton's formula.

Unlike the correlation between snow chemistry and degree of riming, a stronger correlation between ion concentrations in snow samples and the equivalent potential temperature was revealed in cases 2 and 4 instead of cases 1 and 3 (Figure 8 and Figure E-2 in Appendix E). In case 2 Rsquared values for sulfate, nitrate and ammonium are 0.26, 0.67 and 0.06, respectively. The confidence levels by T-test for the significance of these R-squared values are 89.3%, 99.1% and 55.2% for sulfate, nitrate and ammonium, respectively. In case 4 R-squared values for sulfate, nitrate and ammonium are 0.33, 0.62 and 0.31, respectively. The confidence levels by T-test for the significance of these R-squared values are 94.1%, 99.1% and 93.7% for sulfate, nitrate and ammonium, respectively. This result suggests that the air mass change in cases 2 and 4 is a more important factor influencing the chemical composition of snow samples. Previous work has in some cases revealed stronger correlations between changes in snow chemistry and changes in equivalent potential temperature. (e.g., Collett et al., 1991; Devulapalli and Collett, 1994).



Figure 7. Ion (sulfate, nitrate, and ammonium) concentrations in snow samples are regressed against riming degree in: (a) case 1; (b) case 3. The scattered points are sample data. The solid lines are regression fits for nitrate. The long dashed lines are regression fits for sulfate. The short dashed lines are regression fits for ammonium. Both cases yielded a significant positive correlation: (a) R-squared=0.36, 0.09, and 0.05 for sulfate, nitrate, and ammonium, respectively; (b) R-squared=0.38, 0.38, and 0.34 for sulfate, nitrate, and ammonium, respectively.



Figure 8. Ion (sulfate, nitrate, and ammonium) concentrations in snow samples are regressed against the equivalent potential temperature in: (a) case 2; (b) case 4. The scattered points are sample data. The solid lines are regression fits for nitrate. The long dashed lines are regression fits for sulfate. The short dashed lines are regression fits for ammonium. Both cases yielded a significant correlation: (a) R-squared=0.26, 0.67, and 0.06 for sulfate, nitrate, and ammonium, respectively; (b) R-squared=0.33, 0.62, and 0.31 for sulfate, nitrate, and ammonium, respectively.

3.2.3 Discussion

Either of two important physical factors (riming and air mass change) strongly influenced the chemical composition in the snow during the four cases. As shown in former sections, the changes of chemical composition in snow appear to be strongly influenced by changes in riming degree in cases 1 and 3, while the air mass change is a more important factor in cases 2 and 4. To examine the combined importance of these two factors in influencing the snow chemistry during each of the four cases, we computed multiple linear regressions of ion (SO₄²⁻, NO₃⁻, NH₄⁺) concentrations against both riming degree (r) and equivalent potential temperature (θ_e). Results are summarized in Table 3. We note that combined factors sometimes can explain significantly more than the dominant factor by itself. For example, the nitrate concentration was correlated significantly with both r and θ_e in case 3 and together these factors can explain nitrate concentration variations significantly better than either factor alone. But for sulfate and ammonium in case 3, riming alone appeared to be a significant factor in influencing their concentration variations in snow samples.

In addition, we also looked at back trajectories (see Appendix C) to SPL during the periods of all cases. Each plot shows two trajectories: one ending at SPL at 00 UTC and one at 12 UTC. It appears that there was

rapid transport from the Pacific Northwest during January 8-10 and from Pacific Southwest during January 14 (~1 to 2 days long). However, these back-trajectory data could not be quantitatively used in our study since the time resolution cannot match the time resolution of our sampling.

Table 3. Correlation coefficients (R²) for chemical (SO₄²⁻, NO₃⁻, NH₄⁺) concentrations in snow samples against riming degree (r) and equivalent potential temperature (θ_e), individually and multiply.

	SO4 ²⁻				NO ₃ ⁻		$\mathbf{NH_4}^+$		
	regression with r	regression with θ_{e}	regression with both r and θ_e	regression with r	regression with θ_e	regression with both r and θ_e	regression with r	regression with θ_e	regression with both r and θ_e
case 1	0.36	0.14	0.37	0.09	0.01	0.17	0.05	0.01	0.11
case 2	0.00	0.26	0.26	0.00	0.67	0.67	0.08	0.06	0.17
case 3	0.38	0.10	0.35	0.38	0.43	0.56	0.34	0.14	0.36
case 4	0.11	0.33	0.38	0.18	0.62	0.67	0.02	0.31	0.32

3.3 Size distributions of accreted cloud drops

Ice crystal replicas on slides were observed and the accreted drops on each crystal or crystal fragments were sized using the image analysis system. We have determined for case 1 the habit and size of 70 ice crystals and measured size distributions of attached cloud (rime) drops. The rimed mass size distribution for each ice crystal has also been derived. For cases 2, 3 and 4, we measured only size distributions, and subsequently calculated the normalized volume size distributions, of rimed cloud drops on the single ice crystals or crystal segments observed. Selected size distributions of accreted cloud drops in the four cases are plotted in Figure 9. The rimed mass size distributions and the normalized volume size distributions of accreted cloud drops on the single ice crystals or crystal fragments during each of the four cases are summarized in Table 4. The data have been binned in three size fractions to match the size cuts for the cloud chemistry measurements. Generally most contributions of the mass (volume) of accreted cloud drops come from 10-17 μ m and >17 μ m size fractions; little accreted mass (volume) was associated with drops smaller than 10 µm, although drops in this size range were observed on some ice crystals.



Figure 9. Observed size distributions of accreted cloud drops on single ice crystals or single crystal fragments in four cases. Y-axis is the normalized number fraction divided by each bin size.

Crystal ID #	Sampling time/date	Crystal type	Volume faction 4-10 µm	Volume faction 10-17 µm	Volume fraction >17 µm
Case 1					
9706401*	1/8/97 20:35	Dendrite (BRKN)	0.1%	11.2%	88.7%
9706402	1/8/97 20:35	Stellar (BRKN)	0.0%	11.5%	88.5%
9706403	1/8/97 20:35	Dendrite (BRKN)	0.1%	14.8%	85.2%
976605_9	1/8/97 20:50	BRKN Dendrite	0.1%	11.2%	88.7%
9706701	1/8/97 20:55	Stellar (BRKN)	2.3%	93.1%	4.6%
9706702	1/8/97 20:55	Stellar (BRKN)	0.1%	19.1%	80.8%
9706901	1/8/97 21:05	Stellar (BRKN)	0.0%	5.3%	94.7%
9706902	1/8/97 21:05	Stellar w/end plt	0.0%	64.9%	35.1%
9707001	1/8/97 21:10	Broad-Brchd	0.0%	12.4%	87.6%
9707002	1/8/97 21:10	Stellar w/end plt	0.0%	14.7%	85.3%
9707901	1/8/97 21:55	Stellar	0.0%	2.6%	97.4%
9707902	1/8/97 21:55	Plt w/simple ext	0.0%	1.0%	99.0%
9707903	1/8/97 21:55	Stellar w/end plt	0.0%	11.0%	89.0%
971051_3	1/9/97 0:05	Stellar w/end plt	0.7%	78.8%	20.5%
9710504	1/9/97 0:05	BRKN Plate	0.6%	92.2%	7.2%
9710505	1/9/97 0:05	Stellar w/end plt	9.2%	90.8%	0.0%
9710506	1/9/97 0:05	Stellar	1.4%	98.6%	0.0%
9714401	1/9/97 4:35	Fat Stellar	0.9%	46.3%	52.8%
9714402	1/9/97 4:35	Broad-Brchd	0.6%	56.7%	42.7%
9714403	1/9/97 4:35	Hex Plt	1.3%	98.7%	0.0%
9714404	1/9/97 4:35	Broad-Brchd	0.0%	54.1%	45.9%
9714405	1/9/97 4:35	Fat Stellar	2.9%	62.4%	34.8%
9714406	1/9/97 4:35	Broad-Brchd	0.7%	49.1%	50.2%
9714407	1/9/97 4:35	Broad-Brchd	0.7%	73.6%	25.6%
Case 2					
9715001	1/9/97 18:25	Fragment	1.8%	90.9%	7.3%
9715002	1/9/97 18:25	Hex. Plt	0.5%	45.6%	54.0%
9715003	1/9/97 18:25	Fragment	0.0%	40.3%	59.7%
9715004	1/9/97 18:25	Fragment	0.4%	49.1%	50.5%
9715005	1/9/97 18:25	Fragment	0.7%	75.5%	23.8%
9715006	1/9/97 18:25	Fragment	0.5%	46.3%	53.2%
9715007	1/9/97 18:25	Fragment	1.0%	92.6%	6.4%
9718001	1/9/97 21:55	Hex. Plt	0.0%	64.7%	35.3%
9718002	1/9/97 21:55	Fragment	0.6%	68.0%	31.3%
9718003	1/9/97 21:55	Fragment	0.0%	50.3%	49.7%
9718004	1/9/97 21:55	Fragment	0.0%	79.3%	20.7%
9718005	1/9/97 21:55	Fragment	0.0%	83.5%	16.5%
9718006	1/9/97 21:55	Fragment	0.0%	100.0%	0.0%
Case 3					
9718501	1/10/97 16:05	Fragment	0.4%	69.7%	29.9%
9718502	1/10/97 16:05	Fragment	0.0%	100.0%	0.0%
9718503	1/10/97 16:05	Fragment	0.0%	52.3%	47.7%
9718504	1/10/97 16:05	Fragment	0.8%	51.7%	47.5%
9718505	1/10/97 16:05	Fragment	0.5%	44.9%	54.6%
9718506	1/10/97 16:05	Fragment	1.0%	24.6%	74.3%
9723201	1/10/97 20:40	Fragment	0.0%	45.1%	54.9%
9723202	1/10/97 20:40	Fragment	1.5%	51.6%	46.9%
9723203	1/10/97 20:40	Fragment	0.9%	50.7%	48.4%
9723204	1/10/97 20:40	Hex. Plt	2.6%	66.0%	31.4%
9723205	1/10/97 20:40	Fragment	0.6%	83.7%	15.6%

Table 4 (a) The normalized volume size distributions of accreted cloud drops on single ice crystals in four cases.

9727201	1/11/97 1:20	Fragment	0.0%	100.0%	0.0%
9727202	1/11/97 1:20	Fragment	0.6%	92.4%	7.1%
9727203	1/11/97 1:20	Fragment	0.0%	67.0%	33.0%
9727204	1/11/97 1:20	Hex. Plt	1.3%	82.3%	16.3%
9727205	1/11/97 1:20	Hex. Plt	3.3%	96.7%	0.0%
9727206	1/11/97 1:20	Column	6.3%	93.7%	0.0%
9727207	1/11/97 1:20	Needle	0.0%	20.3%	79.7%
9727208	1/11/97 1:20	Needle	0.0%	54.7%	45.3%
Case 4					
9728101	1/14/97 14:10	Hex. Plt	0.0%	34.8%	65.2%
9728102	1/14/97 14:10	Hex. Plt	0.0%	11.0%	89.0%
9728103	1/14/97 14:10	Fragment	0.0%	12.4%	87.6%
9728104	1/14/97 14:10	Fragment	0.2%	11.0%	88.7%
9728105	1/14/97 14:10	Fragment	0.3%	35.3%	64.4%
973121_3	1/14/97 17:25	Broad-Brchd	0.9%	78.6%	20.5%
9731204	1/14/97 17:25	Fragment	1.8%	83.5%	14.7%
9731205	1/14/97 17:25	Broad-Brchd	0.8%	71.2%	27.9%

* Crystal ID # in the format 97SSSNN, where 97 represents the year 1997, SSS the slide number, NN the crystal number.

Table 4 (b) Masses of	single ice crysta	als and accreted cloud	drops in three size	fractions in case 1.
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lce Crystal ID	Sampling Time/Date	Ice Crystal Type	Crystal Dia. Mm	Crystal Mass mg	Rime mass 4-10µm mg	Rime mass 10-17µm mg	Rime mass >17µm mg	Riming Degree
06404*	1/8/97 20:35	Stellar	0.69	9.45E-04	3.90E-07	2.67E-05	8.03E-05	1
06405	1/8/97 20:35	plate w/simple extensions	0.74	2.85E-03	0	0	0	0
06406	1/8/97 20:35	1 or 2? **	0.9	3.41E-03	0	0	0	0
06407	1/8/97 20:35	Stellar	1.6	8.34E-03	5.57E-06	6.41E-05	6.62E-05	0.8
06501	1/8/97 20:45	Stellar	1.11	3.24E-03	3.87E-06	2.92E-05	5.53E-05	0.5
06502	1/8/97 20:45	Dendrite(BRK)	3.32	4.90E-02	2.44E-05	1.28E-03	4.45E-03	1.5
06601	1/8/97 20:50	Stellar w/end plt	1.55	1.89E-02	5.68E-06	8.87E-05	1.72E-04	0.5
06602	1/8/97 20:50	Broad-Brchd	0.48	7.87E-04	5.75E-06	3.70E-05	0	1
06603	1/8/97 20:50	Broad-Brchd	0.52	9.84E-04	1.69E-06	5.42E-05	1.28E-04	1
06703	1/8/97 20:55	Stellar w/end plt	1.38	1.41E-02	3.44E-04	1.65E-03	2.30E-03	1.5
06801	1/8/97 21:00	plate w/simple extention	0.99	6.46E-03	2.71E-05	4.16E-04	2.48E-04	2
06802	1/8/97 21:00	Stellar(BRK)	0.71	1.02E-03	9.35E-06	3.34E-05	1.60E-05	0.5
06903	1/8/97 21:05	5 or 6?	0.78	3.85E-03	1.08E-05	1.78E-05	0	0.5
06904	1/8/97 21:05	Stellar w/end plt	0.65	2.09E-03	7.69E-06	1.41E-04	2.43E-04	2.2
06905	1/8/97 21:05	plate w/simple extensions	0.53	1.12E-03	1.76E-06	2.20E-05	3.43E-05	0.5
07003	1/8/97 21:10	Broad-Brchd	0.62	1.61E-03	9.57E-06	3.17E-04	2.71E-04	1.5
07101	1/8/97 21:15	Stellar w/end plt	0.82	3.77E-03	1.06E-05	8.87E-05	1.08E-04	1.2
07301	1/8/97 21:25	Stellar	0.41	2.45E-04	2.37E-05	4.96E-05	8.72E-05	1.5
07302	1/8/97 21:25	Stellar	0.78	1.30E-03	2.48E-05	5.17E-04	6.27E-05	1.5
07401	1/8/97 21:30	Stellar	1.28	4.68E-03	7.94E-06	3.48E-04	7.66E-04	2
07601	1/8/97 21:40	Dendrite	2.09	1.70E-02	4.93E-05	1.16E-03	6.95E-04	1.8
07602	1/8/97 21:40	Stellar	0.67	8.75E-04	8.09E-06	6.36E-05	1.26E-04	0.8
07801	1/8/97 21:50	Broad-Brchd	1.02	6.45E-03	2.23E-05	5.88E-04	2.18E-03	2
08001	1/8/97 22:00	Stellar w/end plt	0.92	5.05E-03	6.98E-05	6.82E-04	1.23E-03	2
08002	1/8/97 22:00	Dendrite	1.15	4.32E-03	1.48E-05	3.62E-04	2.34E-04	1
08201	1/8/97 22:10	Stellar w/end plt	0.69	2.44E-03	7.97E-05	7.97E-04	1.96E-04	1.5
08202	1/8/97 22:10	plate w/simple extensions	0.47	7.96E-04	0	0	0	0
08401	1/8/97 22:20	Broad-Brchd	0.38	4.10E-04	2.37E-05	1.29E-04	4.67E-05	1.5
08501	1/8/97 22:25	Broad-Brchd	0.56	1.21E-03	1.73E-05	2.25E-04	1.93E-04	1.8
08502	1/8/97 22:25	Hex. Plate	0.48	4.47E-03	1.52E-05	2.58E-04	1.49E-04	1.5
08601	1/8/97 22:30	plate w/simple extensions	0.59	1.51E-03	1.97E-05	2.16E-04	1.75E-04	1.5
08801	1/8/97 22:40	Broad-Brchd	0.56	1.21E-03	2.87E-05	1.42E-04	4.76E-05	1.5
09101	1/8/97 22:55	4 or 5?	0.75	2.87E-03	2.77E-06	1.79E-04	4.29E-05	1
09102	1/8/97 22:55	Sector-Brchd	0.66	2.90E-03	5.86E-05	4,84E-04	1.39E-04	1.5
09201	1/8/97 23:00	Sector-Brchd	0.37	5.64E-04	6.70E-06	7.45E-05	7.14E-04	1
09401	1/8/97 23:10	5 or 2?	0.81	3.53E-03	2.38E-05	8.51E-04	2.79E-04	2
09501	1/8/97 23:15	5 or 2?	0.44	6.39E-04	3.80E-05	4.81E-05	8.03E-05	1.8
09601	1/8/97 23:20	5 or 2?	0.47	7.69E-04	2.51E-05	2.73E-04	8.71E-05	2.2

Table 4 (b) continued.

09801	1/8/97 23:30	5 or 2?	0.54	1.13E-03	5.86E-05	4.66E-04	5.69E-05	3
09802	1/8/97 23:30	Hex. Plate	0.59	7.49E-03	1.52E-06	4.63E-05	1.69E-03	1.8
09901	1/8/97 23:35	5 or 2?	0.71	2.44E-03	6.76E-05	6.58E-04	1.55E-04	2.5
10101	1/8/97 23:45	Hex. Plate	1.07	3.32E-02	2.50E-05	1.46E-03	2.89E-03	2.2
10301	1/8/97 23:55	Hex. Plate	0.5	4.95E-03	1.45E-04	2.54E-04	3.16E-04	2.2
10401	1/10/97 0:00	5 or 2?	0.4	4.90E-04	2.57E-05	9.93E-05	1.73E-05	1.7
10402	1/10/97 0:00	plate w/simple extensions	0.67	2.15E-03	9.25E-05	2.69E-04	2.20E-05	1.7
10701	1/10/97 0:15	Broad-Brchd	0.79	3.16E-03	6.85E-05	3.31E-04	2.01E-05	1.5
10801	1/10/97 0:20	Sector-Brchd	1.17	1.47E-02	6.75E-05	2.15E-03	2.61E-03	2
11101	1/10/97 0:40	Stellar	0.92	1.99E-03	1.88E-04	4.02E-04	9.71E-05	2.5
11301	1/10/97 0:50	Hex. Plate	0.47	4.24E-03	1.57E-05	2.43E-04	1.54E-04	2
11501	1/10/97 1:00	Hex. Plate	0.55	6.28E-03	3.25E-05	3.18E-04	2.07E-05	1.8
11502	1/10/97 1:00	5 or 2?	0.51	9.67E-04	2.98E-05	2.70E-04	4.46E-05	2
11601	1/10/97 1:05	Broad-Brchd	0.3	2.12E-04	1.02E-05	1.01E-04	4.27E-05	2
11602	1/10/97 1:05	Broad-Brchd	0.51	9.32E-04	8.01E-06	1.90E-04	2.43E-05	1.8
11701	1/10/97 1:10	Hex. Plate	0.45	3.80E-03	4.97E-05	6.83E-04	1.65E-04	2.5
11901	1/10/97 1:20	Hex. Plate	0.39	2.66E-03	2.86E-05	6.87E-04	8.69E-05	2.5
12001	1/10/97 1:25	5 or 2?	0.42	5.61E-04	9.53E-06	2.11E-04	5.02E-05	2
12201	1/10/97 1:35	Broad-Brchd	0.14	2.53E-05	1.58E-06	5.77E-05	3.20E-05	2.5
12301	1/10/97 1:40	Hex. Plate	0.25	8.75E-04	1.28E-05	1.18E-04	8.03E-05	2
12401	1/10/97 1:45	Hex. Plate	0.19	4.41E-04	9.05E-06	6.77E-05	1.37E-05	2.2
12701	1/10/97 2:00	Hex. Plate	0.2	5.01E-04	2.44E-05	1.26E-04	5.90E-05	2.5
12801	1/10/97 2:05	5 or 2?	0.49	8.64E-04	2.43E-05	1.38E-04	4.91E-05	2.5
13001	1/10/97 2:15	Hex. Plate	0.49	4.71E-03	5.41E-05	2.86E-04	6.35E-04	2.5
13201	1/10/97 2:35	Sector-Brchd	0.16	5.26E-05	2.33E-06	6.19E-05	5.14E-05	2.5
13301	1/10/97 2:45	Hex. Plate	0.12	1.40E-04	4.02E-06	1.02E-04	8.03E-05	2.5
13401	1/10/97 2:55	Broad-Brchd	0.25	1.28E-04	1.86E-05	7.96E-05	9.12E-05	2.7
13601	1/10/97 3:15	Hex. Plate	0.24	7.90E-04	9.75E-06	1.67E-04	1.31E-05	2.5
13801	1/10/97 3:35	Broad-Brchd	0.33	2.77E-04	9.95E-06	2.76E-04	1.10E-05	2.7
14001	1/10/97 3:55	Hex. Plate	0.53	5.73E-03	2.81E-05	1.01E-03	1.25E-03	3
14101	1/10/97 4:05	Broad-Brchd	0.22	8.93E-05	5.00E-06	5.24E-05	1.00E-04	2.5
14201	1/10/97 4:15	Broad-Brchd	0.39	4.41E-04	1.74E-05	3.35E-04	2.11E-05	2.7

* Crystal ID # in the format SSSNN, where SSS the slide number, NN the crystal #. ** Type 1 is the stellar, 2 the plate w/simple extension, 3 dendrite, 4 the stellar w/end plate, 5 the broad-branched, 6 the sector-branched.

3.4 Influence of chemical heterogeneity on aqueous phase sulfur oxidation

It is well known that aqueous phase sulfur dioxide (S(IV)) can be oxidized by hydrogen peroxide, by ozone, and by oxygen (autooxidation) catalyzed by Fe(III) and Mn(II) (see e.g., Seinfeld and Pandis, 1998). Although oxidation by hydrogen peroxide is largely independent of pH over the range observed in atmospheric liquid water, rates of S(IV) oxidation by ozone and trace metal catalyzed S(IV) autooxidation depend strongly on pH. Since the oxidation rate by ozone and autooxidation depends nonlinearly on the drop composition, it is not possible to correctly predict the average oxidation rate, in a population of chemically heterogeneous cloud drops, from the average cloud drop hydrogen ion concentration (Collett et al., 1994; Gurciullo and Pandis, 1997). For the ozone pathway, the presence of chemical heterogeneity among the cloud drop population always yields a faster average oxidation rate in the cloud than expected from the average droplet composition (Gurciullo and Pandis, 1997). The situation is more complex for the metal-catalyzed autooxidation pathway, since the oxidation rate depends nonlinearly on concentrations of hydrogen ion, Fe(III) and Mn(II). Rao and Collett (1998) have demonstrated that the S(IV) autooxidation rate is often enhanced due to positive correlations

between drop pH and catalyst concentrations (increasing pH and catalyst concentrations both tend to favor faster S(IV) autooxidation over a wide pH range); suppression of S(IV) autooxidation was predicted in some cases where lower than average pH drops possessed higher than average catalyst concentrations. The effects of chemical heterogeneity on S(IV) autooxidation and oxidation by ozone are most important when these pathways are faster than oxidation by hydrogen peroxide. This situation is more likely to occur in winter when peroxide formation is reduced due to shorter days and lower solar intensities.

In the current study, we observed significant variations in pH and concentrations of iron and manganese (see Table 1 and Figures 2 and 10) across the cloud drop size spectrum. Using the observed variations in composition vs. drop size, we can use established rate laws to predict how S(IV) oxidation varies with drop size and compare the net rate of sulfate production in the observed, chemically heterogeneous cloud with the rate that would be predicted based on the average cloud drop composition. The latter comparison will yield information about how much the presence of chemical heterogeneity among the cloud drop population enhances (or suppresses) aqueous phase sulfate production. Our estimate of this effect should be considered conservative, however, as there are certainly more than three independent droplet compositions present in the studied clouds.

The greater the chemical heterogeneity present, the larger the possible effect on S(IV) oxidation.

The following rate laws were taken from the literature for determining S(IV) oxidation rates by the three oxidation pathways. Oxidation by hydrogen peroxide was predicted by (Hoffmann and Calvert, 1985):

$$-dS(IV)/dt = k_1[H^+][HSO_3][H_2O_2]/(1+13.0[H^+])$$
(2)

Oxidation by ozone was predicted according to (Hoffmann, 1986):

$$-dS(IV)/dt = (k_2[SO_2H_2O] + k_3[HSO_3] + k_4[SO_3])[O_3]$$
(3)

where H_{03} and P_{03} are the Henry's law coefficient and partial pressure of ozone, respectively. Rates of trace metal catalyzed S(IV) autooxidation were predicted using the expression by Ibusuki and Takeuchi (1987):

$$dS(IV)/dt = k_5[Fe(III)][Mn(II)][S(IV)][H^+]^{-0.74}$$
 for pH<4.2 (4a)

$$-dS(IV)/dt = k_6[Fe(III)][Mn(II)][S(IV)][H^+]^{0.67} \text{ for } pH>4.2$$
(4b)

Rate expressions were adjusted, using published thermodynamic data (see Table 5), to temperatures measured at the site (-10 to -20 °C) during the sample periods. The H⁺ concentration was taken from sample pH measurements. The concentrations of Fe(III) and Mn (II) were assumed equal to 25% and 100% of the total measured Fe and Mn concentrations, respectively. Because the concentrations of total Fe and Mn in the smallest cloudwater stage were not available due to insufficient sample volumes, we assumed concentrations equal to the maximum concentrations determined

from the other two stages. As we will see below, the assumptions concerning metal speciation and small drop metal concentrations are not critically important, since the metal catalyzed autooxidation pathway does not appear to contribute significantly to aqueous phase sulfate production in these clouds. Aqueous hydrogen peroxide concentrations were calculated by assuming equilibrium with the gas phase H_2O_2 concentrations measured in the cloud. No ozone measurements were available, so a typical background concentration of 30 ppbv was assumed. The average ozone concentration measured during the period from January 8-15, 1997 at 2743 m elevation in Rocky Mountain National Park (approximately 100 km east of SPL) was 36 ppb (USEPA, 1998).

K _H (M/atm) or K (M ⁿ) (298 [°] K)	∆H (KJ/mol)	Reference
1.10E-02	-21.3	Snider and Vali, 1994
7.45E+04	-55.0	Snider and Vali, 1994
1.20E+00	-26.3	Snider and Vali, 1994
1.29E-02	-16.3	Snider and Vali, 1994
6.40E-08	-11.9	Snider and Vali, 1994
k _i (M ⁿ /S) (298 [°] K)	∆H (KJ/mol)	Reference
7.45E+07	39.5	Snider and Vali, 1994
2.40E+04	0.0	Snider and Vali, 1994
3.70E+05	46.0	Snider and Vali, 1994
1.50E+09	43.9	Snider and Vali, 1994
3.72E+07	70.1	Snider and Vali, 1994
2.51E+13	70.1	Snider and Vali, 1994
	K _H (M/atm) or K (M ⁿ) (298 [°] K) 1.10E-02 7.45E+04 1.20E+00 1.29E-02 6.40E-08 k _i (M ⁿ /S) (298 [°] K) 7.45E+07 2.40E+04 3.70E+05 1.50E+09 3.72E+07 2.51E+13	K_H (M/atm) or K (M ⁿ) ΔH (KJ/mol) (298 *K) ΔH (KJ/mol) 1.10E-02 -21.3 7.45E+04 -55.0 1.20E+00 -26.3 1.29E-02 -16.3 6.40E-08 -11.9 k _i (M ⁿ /S) (298 *K) ΔH (KJ/mol) 7.45E+07 39.5 2.40E+04 0.0 3.70E+05 46.0 1.50E+09 43.9 3.72E+07 70.1 2.51E+13 70.1

Table 5. Thermodynamic and kinetic data

The calculated S(IV) oxidation enhancement resulting from the drop size-dependent cloud composition is summarized in Figure 11. Results are presented for the three oxidation pathways individually and for the overall oxidation rate. The data are presented as frequency distributions of samples with various ranges of oxidation rate enhancement. Oxidation enhancement factors are calculated with the averaged (LWC-weighted) rate of S(IV) oxidation in the three chemically distinct drop size ranges divided by the rate of oxidation predicted using the averaged (LWC-weighted) cloud drop composition. For the H_2O_2 pathway, no oxidation enhancement is predicted, since the oxidation rate is essentially independent of the H⁺ concentration and is linear in the H₂O₂ concentration. For the ozone pathway, approximately, 32% of samples experience enhancement less than 20%, 33% of samples experience enhancement between 20% and 500%. and 35% of samples experience enhancement larger than 500%. A maximum enhancement factor of 217 is predicted for the ozone pathway in one sample with a large pH gradient. For the metal-catalyzed autooxidation pathway, 27% of samples experience enhancement between 0% and 20%, 41% are between 20% and 200%, and 18% of samples experience enhancement between 200% and 500%; the remaining 14% of samples experience oxidation rate suppression between 0 and 25%. As demonstrated by Rao and Collett (1998), the S(IV) autooxidation rate is

often enhanced due to positive correlations between drop pH and catalyst concentrations. Here we also found positive correlations between drop pH and catalyst concentrations for most samples studied (see Figure 12).

When the total oxidation rate (the sum of the three individual pathway rates) is considered, 59% of the samples are predicted to experience enhancement less than 20% and 27% of the samples experience enhancement larger than 500%. S(IV) oxidation in these samples was dominated either by hydrogen peroxide or by ozone. The metal-catalyzed autooxidation pathway was never predicted to be the fastest. Even if all of the iron present was assumed to be catalytically active Fe(III), the metal-catalyzed autooxidation pathway is expected to be the fastest for only one sample.



Figure 10. Drop size-resolved spectra of (a) total Fe concentration and (b) total Mn concentration during the consecutive cloud sampling periods in each of four cases. The eight consecutive periods in case 1, the five consecutive periods in case 2 and the ten consecutive periods in case 3 correspond to those listed in Table 1. The six consecutive periods in case 4 correspond to the first six periods of case 4 listed in Table 1. For each period the data are presented as a two-stage ion concentration spectrum (except when data for one or two stages were not available due to the lack of sufficient sample volumes to permit these analyses).



Figure 11. The distribution of S(IV) oxidation enhancement factors for the three individual oxidation pathways and for the overall oxidation rate. 22 samples in all four cases are considered.





3.5 Case 1 study:

3.5.1 Rimed mass size distributions

The total mass size spectra of rimed cloud drops during each of the seven consecutive snow sampling periods in case 1, determined from image analysis of the ice crystal replicas, are plotted in Figure 13. The data have been binned to match the size cuts for the cloud chemistry measurements. Significant contributions to total rimed mass come from both the 10-17 and >17 μ m drop size fractions; little of the accreted mass is associated with drops smaller than 10 μ m. As discussed in the following section of "snow chemistry analysis", the data obtained here will be used to calculate the snow chemistry in case 1.



Figure 13. The mass size spectra of cloud droplets accreted on the surface of snow crystals during the seven consecutive snowfall sampling periods in case 1 (01/08/1997-01/09/1997).

3.5.2 Influence of chemical heterogeneity on precipitation scavenging of individual solutes during accretional ice crystal growth (riming)

The efficiency with which an individual chemical species is incorporated into ice crystals during the riming process depends on the distribution of that species across the cloud drop size spectrum. This dependence results from the fact that the impaction efficiency of cloud drops by falling ice crystals increases with increasing drop size. If a particular chemical species concentration increases with drop size, it will be scavenged more efficiently than predicted from the average cloud drop composition. If its concentration decreases with drop size, its incorporation into precipitation by riming will be less efficient than expected from the average cloud drop composition. This effect can be expressed using the ratio C_r/C_c , where C_r and C_c represent the average concentrations of a species in rimed cloud drops and in ambient cloudwater, respectively. Cr is calculated from the theoretical collision efficiencies between drops and an ice crystal, the observed cloud drop size spectrum, and our observations of cloud composition vs. drop size. Cc is calculated as the weighted average of the chemical compositions of the three cloud drop size fractions collected by FROSTY, where the weighting factors are the fractions of total LWC in

each FROSTY drop size interval as determined from the ambient drop size distribution measurements.

To calculate the collision efficiencies of cloud drops with ice crystals, we adopted Hall's (1980) formulation:

$$E_{d} = \{1-0.20[\log(K)-\log(K_{crit})-2.236]^{2}\}^{1/2}$$
 (for Re<40) (5)

where,

$$K=2(V_t-v_t) v_t /(Dg)$$
 (6)

and

Re>5.0

 $K_{crit} = \{$

 V_t is the ice particle terminal velocity, v_t is the cloud drop terminal velocity, g is the gravitational constant, D is the ice particle maximum dimension, and Re is the Reynolds number for flow around the ice crystal. Terminal velocities (V_t and v_t) and Reynolds number are evaluated following Mitchell's (1996) approach. The ambient drop size distributions are taken from the FSSP measurements.

The calculated collision efficiencies versus the diameters of accreted cloud drops for the broad-branched crystal and the hexagonal plate are presented in Figure 14. These curves predict that no cloud drops of diameter smaller than 10 µm are collected by these ice crystals. This is

generally consistent with our observations shown in former sections that little accreted mass (volume) was associated with drops smaller than 10 μ m, although drops in this size range were observed on some ice crystals. We also see from the collection efficiency curves that ice crystals with diameter (maximum dimension) of 0.1 mm or smaller are predicted not to collect drops in any size ranges. Our observations (see, e.g., Table 4 (a)) suggest that this is not true, since some of the observed ice crystals of size close to 0.1 mm did collect significant amounts of cloud drops (rimed mass fraction >50%).

The calculated ratio of rimed cloud composition to ambient cloud composition, C_r/C_c , for each sampling period in case 1 is summarized in Table 6. The ratios have been determined using collision efficiencies computed for ice crystal habits (hexagonal plate and broad-branched crystal) and size (0.5 mm) typical of those observed during the study. C_r/C_c ratios for sulfate, nitrate and ammonium generally fall between 0.70 and 1.00, implying somewhat lower efficiencies exist for incorporating these species into snow than expected based on average cloud drop composition. This is a result of the larger drops, which are collected efficiently by the ice crystals, having lower than average concentrations of these species. C_r/C_c ratios for Ca²⁺ are somewhat higher, and more variable (a range of 0.83 to 1.15), than those for the other species. The ratios larger than 1.0 represent

periods where Ca²⁺ concentrations increased with drop size. The large range of ratio values reflects the variability in how Ca²⁺ concentrations were distributed across the cloud drop size spectrum.

For the case studied, use of the average cloud composition for determining solute incorporation into riming ice crystals will result in a modest overestimate of the scavenging of nitrate, sulfate, and ammonium and a slight positive or negative error in estimating Ca²⁺ scavenging. Although these results are based on a limited number of observations, they suggest that modeling the transfer of solutes from cloud drops to ice crystals may not suffer great errors if the size-dependent cloud drop chemistry is ignored.



Figure 14. The calculated collision efficiency versus the diameter of collected cloud droplet for: (a) the broad-branched crystal; (b) the hexagonal plate with various maximum dimensions.

Table 6

Summary of the rime drop to cloud drop concentration ratios (Cr/Cc) for two									
ice crystal habits during seven time periods in case 1.									
	Hexago	nal Plate			Broad-E	Branched			
	0.5	mm			0.5	mm			
SO4 ²⁻	NO ₃	NH4 ⁺	Ca ²⁺	SO4 ²⁻	NO ₃ -	NH4 ⁺	Ca ²⁺		
0.82	0.84	0.87	0.94	0.74	0.78	0.81	0.83		
0.92	0.93	0.97	1.12	0.87	0.89	0.95	1.14		
0.93	0.93	0.98	1.15	0.88	0.86	0.92	1.13		
0.89	0.92	0.92	1.05	0.82	0.85	0.86	1.05		
0.93	0.95	0.99	0.98	0.89	0.93	0.99	0.99		
0.95	0.96	0.97	0.97	0.91	0.92	0.95	0.97		
0.95	0.98	0.92	0.96	0.92	0.96	0.85	0.96		

3.5.3 Snow chemistry analysis

As shown in Figure 7, the extent of ice crystal riming exerted a significant influence on snow chemistry in case 1. As a complementary work we have chosen this event for further analysis to see whether it is feasible to estimate snow composition using information about cloudwater composition and ice crystal riming. In this section we present a simple model scheme for calculating ion concentrations in snow samples along with an uncertainty analysis for the estimated concentrations. To calculate ion concentrations in snow samples, we used the observed ion concentrations in cloudwater of three size fractions (4-10 μ m, 10-17 μ m, and >17 μ m), masses of accreted cloud drops in the same three size ranges and masses of ice crystals at Storm Peak laboratory during simultaneously sampled periods.

Calculation of ion concentrations in snow samples

(1) Description of the calculation model:

We assume that the riming process is the unique (or at least dominant) source of individual trace species to snow crystals and the mass-weighted average ion concentration for bulk snow is given by the following equation:

$$C_{P} = \frac{M_{S}C_{S} + M_{M}C_{M} + M_{L}C_{L}}{M_{S} + M_{M} + M_{L} + M_{I}}$$
(8)

where C_j (j=S, M or L) is the ion concentration in each size range of accreted cloud drops. M_j (j=S, M, or L) is the mass of accreted drops in each size range, and M_I is the mass of the unrimed ice crystal. Here "S", "M", and "L" denote the drop diameter ranges of 4-10 µm (small), 10-17 µm (medium), and >17 µm (large), respectively.

The masses of accreted drops and unrimed ice crystals were calculated using the mass-dimensional relationships:

$$M = \rho_d \times \frac{\pi D^3}{6} \text{ (for a spherical drop)}$$
(9)

where ρ_d is the density of a single accreted droplet (920 kg m⁻³, Mosimann, 1994) and *D* is the droplet diameter.

 $M = \alpha L^{\beta}$ (for an ice crystal, Mitchell, 1996) (10)

where L is the maximum dimension of the ice crystal particles. a and β are empirical parameters derived from the nonlinear fit of M against L. The sizes of accreted cloud droplets and ice crystals were measured from the snow crystal replicas using the image analysis system.

Accreted drops present on the surface of rimed ice crystals may have been collected anywhere along the trajectory of the ice crystal prior to its arrival at SPL. Although we have good information about drop sizeresolved cloud chemistry at SPL, we have no observations about how it

varied in space. Nor do we know what trajectory each ice crystal followed or where it captured cloud drops. To estimate the uncertainty introduced by using cloud drop compositions at SPL in estimating snow chemistry, we have examined vertical variations of cloud liquid water content (LWC) and the ion concentrations in cloud drop populations by considering a simplified vertically lifting cloud parcel model, as described below. Using the observed LWC, drop size-resolved ion concentrations in cloudwater, cloud drop size spectrum (FSSP) and meteorological data at Storm Peak Laboratory, we have estimated the altitude-dependent variations of cloud drop size spectrum and drop size-resolved ion concentrations in cloudwater. Then we averaged the cloud drop ion concentrations for each size fraction to obtain the C_i (j=S, M or L), needed for the snow chemistry computation (Equation 8). Cloud drop ion concentrations will decrease with height due to dilution resulting from condensational drop growth during parcel ascents. Consequently, ion concentrations in rimed snow will be higher if accreted drops are captured near cloud base and will be lower if the drops are captured high in the cloud. We can estimate the possible range of snow concentrations by computing the result for capture of all drops at cloud base or at the cloud top.

(2) Estimation of cloud base:
Cloud base was estimated by lifting an air parcel dry adiabatically until it reaches its lifting condensation level (LCL), where water vapor starts to condense. The temperature, T_L , at LCL is given by (Bolton, 1980):

$$T_L = \frac{1}{\frac{1}{T_K - 55} - \frac{\ln(U/100)}{2840}} + 55$$
(11)

or

$$T_{L} = \frac{1}{\frac{1}{T_{D} - 56} - \frac{\ln(T_{K} / T_{D})}{800}} + 56$$
(12)

where T_K is the initial temperature, T_D is the initial dew point temperature, and U is the initial relative humidity of the air parcel. All temperatures are specified in degrees K. In the calculation we used atmospheric sounding data collected 12 hours prior to our sampling period at the Grand Junction station, located southwest of SPL.

Using temperature data measured on the mountain for three different levels (2407 m, 2758 m and 3208 m (SPL) mean sea level (MSL)) in case 1, we regressed temperature against height to obtain a linear in-cloud lapse rate $\Gamma_m = \Delta T / \Delta Z$ and intercept T_0 . T_0 represents a temperature at Z=0 (MSL). Using these two regression constants, Γ_m and T_0 , the relationship of in-cloud temperature (T) and height (Z) can be written as $T = \Gamma_m * Z + T_0$. Since the cloud base temperature, T_L , has been determined from equation 11 or 12, the cloud base height Z_L is therefore calculated by:

$$Z_L = \frac{T_L - T_0}{\Gamma_m} \tag{13}$$

(3) Top limit of the cloud range:

At first we attempted to use satellite infra-red image data to estimate the cloud top temperature near SPL during the sampling periods. We found that most infra-red temperature data were significantly higher than air temperatures at SPL during sampling periods. This could result from the presence of some regions near SPL where gaps in cloud coverage occurred, so that ground temperature contaminated the signal.

Consequently, another method was used to estimate cloud top. As described above, almost all snowflakes collected at the site were planar types in case 1. The formation of planar ice crystals is only favored under a specific range of ambient temperature (approximately -10 to -20 °C) (see, e.g., Pruppacher and Klett, 1997, page 44). Previous experimental work conducted at SPL (Rauber and Grant, 1986) also revealed a cloud top temperature between -15 to -20 °C for most wintertime clouds. So we chose T_T =-20 °C to estimate cloud top temperature. The cloud top height was estimated by:

$$Z_T = \frac{T_T - T_0}{\Gamma_m} \tag{14}$$

where Γ_m and T_0 are in-cloud lapse rate and intercept temperature at Z=0, derived from a linear fit for observed in-cloud temperature versus height, as described above.

(4) Vertical variations of cloud liquid water content (LWC), cloud drop size spectrum and drop size-resolved cloud chemistry:

As a cloud parcel is lifted above cloud base, water vapor in the cloud parcel condenses and cloud drops grow. This results in a simultaneous shift of the cloud drop size spectrum to larger sizes and a dilution of the solute content in cloud drops.

Since the clouds we are examining are mixed-phase (ice plus supercooled water), the variation of LWC is significantly influenced by inertial capture of cloud drops by falling ice crystals and by diffusion of water molecules from supercooled cloud drop surfaces to ice crystal surfaces, due to the fact that the equilibrium vapor pressure of water over ice is lower than the equilibrium vapor pressure over supercooled water at the same temperature. Consequently it is inappropriate to calculate a LWC vertical profile from expansion and condensation alone.

To estimate the vertical profile of LWC in these mixed-phase clouds, we used the observed LWC at Storm Peak laboratory during sampling periods and assumed a linear LWC profile given by:

$$LWC(Z) = \left(\frac{dL}{dZ}\right)_0 \times (Z - Z_L) \tag{15}$$

where $\left(\frac{dL}{dZ}\right)_0$ is a constant calculated by:

$$\left(\frac{dL}{dZ}\right)_0 = \frac{LWC|_{SPL}}{Z_{SPL} - Z_L} \tag{16}$$

 Z_{SPL} and Z_L are the heights of SPL and the cloud base, respectively. $LWC|_{SPL}$ is the measured LWC at Storm Peak Lab. In essence we are assuming that the vertical gradient in LWC observed between cloud base and SPL is maintained throughout the upper part of the cloud as well.

Using the measured cloud drop size spectrum (FSSP) at Storm Peak lab and the calculated LWC profile, we can therefore determine the cloud drop size spectrum and ion concentration spectrum at all levels in clouds. It is known that the rate at which a single water droplet changes its diameter, D, due to diffusional growth is inversely proportional to D and may be expressed by (see, e.g., Pruppacher and Klett, 1997):

$$\frac{dD}{dt} = \chi \times \frac{1}{D} \tag{17}$$

or

$$dD \propto \frac{1}{D}$$
 (for drops in a single cloud parcel) (18)

where χ is a function of the ambient temperature. We used equation (17) or (18) to distribute the increase in LWC predicted for each height across the

drop size bins and calculated a new cloud drop size spectrum. Using this approach we can determine the water mass change for individual cloud drops and subsequently compute new ion concentrations in individual drops of each size bin. The calibrated bin midpoints for the FSSP were used in this computation. The calculated cloud drop concentration data were binned to match the size cuts for the three-stage (FROSTY) cloud chemistry measurements.

Uncertainty analysis of calculated snow chemistry

Several uncertainties associated with our approach and data may reduce the accuracy and precision of the calculated snow chemistry. These include errors in ion concentration measurement, uncertainties of riming masses, uncertainties of ice crystal masses, and uncertainties associated with vertical variations in cloud physical and chemical properties. The magnitudes of these uncertainties are discussed in Appendix F.

Results

The calculated ion (nitrate, sulfate and ammonium) concentrations in snow samples are compared with observed data in Figure 15. Calculations

are included for the first 7 periods in case 1; snow crystal data were not available in the 8th period. Because the FSSP data were not available for the 1st sampling period, the FSSP data during the 2nd period were applied for periods 1 and 2. We see that generally the predicted data in the first 3 periods are much higher than the observations. The predicted ion concentrations in snow significantly decrease with time early in the event and stabilize in later periods, while the observed concentrations in snow samples are fairly constant during all periods. The predicted snow ion concentration decreases result from decreases in observed cloud concentrations of nitrate, sulfate and ammonium at Storm Peak Laboratory in early periods (see Table 1 and Figure 3b).

The observed snow ion concentrations all fall within the uncertainties included in our simple model. These uncertainties are quite large, however, due mainly to our lack of information concerning the altitude range over which most of the rimed mass is accumulated. This conclusion was not unexpected. The vertical measurements needed to predicted snow chemistry were beyond the scope of the current field experiment which was designed to focus primarily on effects of size-dependent cloud drop chemistry on rates of aqueous sulfur oxidation and efficiencies of wet scavenging of individual aerosol solutes.

It is worthwhile to mention that there are several limitations in the calculation of snow chemistry from the above model. We only considered vertical variations of LWC in the model, while it is likely that horizontal variations of LWC over the SPL region also exist as documented in previous field measurements (Rauber and Grant, 1986). Another limitation in the model calculation is that we assumed a closed cloud parcel model, in which no entrainment is allowed. The occurrence of entrainment can significantly alter the physical and chemical properties of the cloud drops and, therefore, can significantly influence the calculated snow chemistry. We also assumed that changes in LWC associated with vertical parcel displacement from SPL were distributed across the entire cloud drop distribution measured at SPL. In reality droplet number must also change with height in the cloud due to drop-ice crystal interactions.



Figure 15. Observed and predicted concentrations of (a) sulfate, (b) nitrate, (c) ammonium in snow samples during the first seven consecutive periods in case 1. Error bars represent total uncertainties for predicted data.

3.5.4 Relationship between the rimed mass fraction and the degree of riming

The rimed mass fraction (f) is defined as the ratio of the mass of accreted cloud drops (m_c) to the mass of the entire rimed ice crystal (M_r) . The latter can be expressed as the sum of the mass of unrimed crystal (m_u) and the mass of accreted cloud drops, namely,

$$f = \frac{m_c}{M_r} = \frac{m_c}{m_u + m_c} \tag{19}$$

Therefore, the rimed mass fraction can be calculated for each ice crystal using our observations of rime drop size distributions and ice crystal size and habit. A single snow crystal's mass can be calculated by the massdimensional relationship of equation 10. We used the following relationships to calculate single snow crystal masses (Heymsfield and Kajikawa, 1987; Mitchell et al., 1990; Mosimann et al., 1994):

$m_u = 0.00247 L^{2.59}$	for stellar crystals
$m_u = 0.00664 L^{2.81}$	for plates with simple extension
$m_u = 0.00314 L^{2.29}$	for dendrites
$m_u = 0.00623L^{2.53}$	for stellar crystals with end plate
$m_u = 0.0061 L^{2.79}$	for broad-branched crystals
$m_u = 0.0094 L^{2.83}$	for sector-branched crystals
$m_u = 0.028 L^{2.5}$	for hexagonal plates

where the mass, m, is specified in milligrams and L is the diameter (or maximum dimension) of a single snow crystal in millimeters.

The rimed mass fraction of the 70 planar ice crystals versus their visually determined degree of riming is depicted in Figure 16, which reveals a strong increase of rimed mass fraction with the degree of riming. The data were fit using a curve of the form (Mosimann et al., 1994)

$$f = \frac{b(a^{R} - 1)}{[1 + b(a^{R} - 1)]}$$
(20)

where f is the rimed mass fraction, a and b are fit parameters, and r represents the degree of riming. A nonlinear least square fit yields values of a=1.88 and b=0.159. This results compares with Mosimann's (1994) relation for planar crystals with a=3.1 and b=0.020, also shown in Figure 16. The present relationship is generally consistent with Mosimann's results, except that our data revealed higher rimed mass fraction at lower (~1.0) degrees of riming. The difference is not surprising since there are several uncertainties in the calculation of the rimed mass fraction. These uncertainties come from errors in rime masses, ice crystal masses, and visually determined degrees of riming. The visually determined degree of riming possesses an uncertainty of approximately 0.5 to 1.0 riming degree units (Mosimann et al., 1994). This is nearly enough by itself to explain the

difference between our curve and the curve presented by Mosimann et al. (1994).



Figure 16. Rimed mass fraction (f) versus the degree of riming for planar ice crystals. The scattered points are data measured from image analysis of 70 planar ice crystal replicas sampled during periods of case 1. Curves are empirical relations between f and the degree of riming from a nonlinear least-square fit. The thick curve is the result from the work of Mosimann et al. (1994). The thin curve is derived from data of the present study.

4. Conclusions

Field measurements of chemical compositions of snow and cloud samples were made among the winter mixed-phase clouds in the Rocky mountains of northern Colorado. Four cases were examined in this project. Both snow and cloudwater composition were dominated by sulfate, nitrate, ammonium, calcium, and hydrogen ion.

The measurements of cloud drop chemical composition in three separate size fractions (4-10 μ m, 10-17 μ m, and >17 μ m diameter) revealed significant variations of cloud drop pH and ion (SO₄²⁻, NO₃⁻, NH₄⁺, Ca²⁺, Fe, and Mn) concentrations with drop size. During most sampling periods smaller cloud drops contain higher concentrations of SO₄²⁻, NO₃⁻, and NH₄⁺ than found in larger cloud drops. Ca²⁺ concentration distributions across the drop size spectrum are generally more variable than other species. Cloud pH generally increases with increasing drop size, although this is not always true.

The observed chemical heterogeneity across the drop size spectrum is expected to affect the average S(IV) oxidation rate in cloud drops. The existence of this chemical heterogeneity tends to enhance in-cloud aqueous phase sulfate production rates by the ozone pathway and by the metal catalyzed autooxidation pathway. The chemical heterogeneity had no effect on S(IV) oxidation by hydrogen peroxide since S(IV) oxidation by hydrogen peroxide is not dependent on cloud acidity and is a linear function of aqueous H_2O_2 concentrations. At the relatively high cloud pH values and low hydrogen peroxide concentrations observed, the ozone pathway is an important contributor to the total rate of sulfur oxidation. The effect of chemical heterogeneity on overall in-cloud S(IV) oxidation rates will largely depend on relative contributions of the different paths to S(IV) oxidation. In the present work we found that S(IV) oxidation was dominated either by hydrogen peroxide or by ozone in most samples; and nearly 40% of all samples experienced enhancement of S(IV) oxidation rates larger than 20%.

Inertial collection of cloud drops by falling ice crystals (riming) can be an important route for precipitation scavenging of atmospheric aerosols. In cases 1 and 3 examined here we found significant positive correlations between ion concentrations in snow and the extent of ice crystal riming. In the other two cases the variations of ion concentrations in snow were significantly correlated with air mass changes.

The observed chemical heterogeneity across the drop size spectrum was examined to assess its influence on scavenging of individual species by

falling snow crystals through the riming process. Non-uniform distributions of individual solutes across the cloud drop size spectrum result in less efficient incorporation of accumulation mode species (sulfate, nitrate, and ammonium) into precipitation than expected from the average cloud drop composition. The magnitude of this bias, however, was usually predicted to be less than 15% in our study.

Measurements of the size spectra of cloud drops attached on the surface of snow crystals showed that 10-17 μ m and >17 μ m cloud drop size fractions contributed significantly to accreted drop mass; little accreted mass was associated with drops smaller than 10 μ m, although accreted drops in this size range were observed on some crystals.

The calculated rimed mass fraction was regressed nonlinearly against the degree of riming observed. The relationship obtained was similar to the relation between ice crystal riming degree and rimed mass fraction reported by Mosimann, et al. (1994) for rimed snow collected in the Swiss Alps.

5. Recommendations for future work

In the present study we found that S(IV) oxidation rates by ozone and autooxidation pathways were often enhanced significantly compared to rates estimated from the average cloud composition, due to chemical heterogeneity across the drop size spectrum. Results revealed that the total S(IV) oxidation was dominated either by O₃ or H₂O₂. The autooxidation pathway was not predicted to be an important contributor to S(IV) oxidation in these winter clouds. However, these conclusions were drawn only from a limited number of case studies. The present study was also limited to one sampling site. It is recommended that future similar work should extend to more cases of winter clouds and more environments. Because of the apparent importance of the ozone pathway for S(IV) oxidation, it would also be desirable to have simultaneous ozone measurements in future work.

Observations in the present study also indicate that the size-dependent chemical composition of clouds tends to result in decreases in the efficiency with which accumulation mode aerosol species are scavenged by falling snow crystals. Although the magnitude of this bias was usually less than 15%, this result is based on only one case study. Further case studies are

needed to test whether this result is typical, since the lifetimes of accumulation mode aerosol species are strongly dependent on the efficiency of their removal by precipitation.

The calculated collection efficiencies of cloud drops by small ice crystals (~100 μ m) using Hall's (1980) formulation are not consistent with observations of small drop collection as discussed in section 3.5.2. It would be useful to use other methods (see, e.g., Böhm, 1998 and references therein) to calculate the collision efficiencies between cloud drops and falling crystals and compare them with results from the present or future studies.

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Appendix A. Procedures for ice crystal replica collection

Introduction:

A glass microscope slide is coated with a solution of formvar and ethylene dichloride. The solution hardens upon contact with water/ice. Thus impaction of an ice crystal on a microscope slide yields a plastic replica (a mold) of the ice crystal.

Materials needed:

-formvar	-ethylene dichloride
-glass bottles	-glassware
-stirrer, stir plate	-scoop
-gloves, safety glasses	-glass slides (with frosted end)
-glass slide vases (staining vase)	-slide box
-drier with drierite	-falling snow crystals
-big box to work in/from	-watch/stopwatch
-kimwipes	

Making the formvar solution:

Depending on the conditions during sampling, different concentrations of formvar solution may be desired. Light/smaller ice crystals may preserve better in a more dilute solution (e.g., less than 2%) while aggregates and more heavily rimed crystals may be better preserved in a more concentrated solution (e.g., more than 4%). Table A-1 gives proportions of formvar and ethylene dichloride for different percent solutions.

% solution	formvar mass (g)	ethylene dichloride volume (ml)
1%	3.76	300
2%	7.56	300
4%	15.12	300

Table A-1

Use a magnetic stirrer to mix completely and get rid of formvar lump.

Ice crystal collection:

Store all the materials outside in the big box, equilibrated at outdoor temperature. Fill the slide vases with formvar solution and put the slides into the vase (frosted side up, out of the solution). Wearing gloves, remove one slide from slide vase and use a tissue to wipe excess solution off edges and one side of the slide. Wave slide in the falling snow to catch a few ice crystals on surface. When finished collecting crystals on slide, place slide in drier with drierite so water and formvar dry quickly. Repeat process with additional slides at appropriate time intervals. The slides in the drier can be moved after 10-15 minutes and placed in the slide box.

Appendix B. Analysis of ice crystal replica images

An image analysis system is used to analyze the size distribution of accreted droplets on rimed ice crystal replicas created using the Formvar method described elsewhere (Appendix A; Van der Hage, 1969). Many parameters can influence the results of image analysis and these parameters have been controlled, adjusted and tested until a satisfactory result was obtained. In this way we determined the best combination of these parameters for routine processing of ice crystal replica images. The following discussion is divided into four sections. In section 1 we give a general description of the equipment and software in our image analysis system. The parameters that are important to the image processing are also listed and explained in section 1. Section 2 details the procedures to perform the image processing and analysis, the limitations in these procedures and how we dealt with these limitations. In section 3 we have discussed the issues associated with the spreading and shape deformation effect of cloud drops accreted on the ice crystal surface, which makes the diameter presented in the crystal replica images different from the original ambient cloud drop diameter. Summary of discussions is presented in section 4.

B.1 Description of equipment and software

B.1.1 Equipment and software in image analysis system (Figure B-1)

- Microscope: A Nikon SMZ-U stereo zoom microscope is used with a total magnification range from 30 to 300. A Javelin JE-7442 video camera is attached to the microscope.
- 2. Image Grabber Board: The video camera's output is connected by cable to an Oculus-TCX frame grabber board. The grabber's output connector is directly connected with an auxiliary monitor's cable. The grabbing board occupies one slot in the computer.
- Computer: A Dell Dimension Pentium 133c/xps with a #9 Tri Graphics Accelerator PCI (2MB DRAM) and a 17" color monitor is used. The computer operating system is Windows '95.
- 4. Software: The software used for image-analysis is Image-Pro Plus (Version 1.2) for windows, which is developed by Media Cybernetics Inc. Image-Pro Plus has the capability of acquiring, enhancing and analyzing images. This includes the ability to:
 - Acquire image data from a camera, microscope, VCR, scanner or photo CD.
 - Read and write image data in several standard image file formats including TIFF, JPEG, BPM, GIF, TGA and many others.

• Perform image enhancement using powerful color and contrast filters (including Fast Fourier Transforms), morphology, field flattening, background subtraction and other spatial and geometric options.

- Trace and count objects manually and automatically. Measure object attributes such as area, perimeter, diameter, roundness, and aspect ratio. Calibrate a spatial scale to any unit of measure.
- View collected data numerically, statistically or in graphic form (histogram or scattergram). Save the measurement data to disk.

• Create organized collections of image thumbnails, from which images can be located and loaded.

• Automate repetitive tasks and customize *Image-Pro* to a particular need using *Auto-Pro*, a macro language that lets you call *Image-Pro* functions.



Figure B-1. The ice crystal replica image analysis system.

B.1.2 Parameters that influence the analysis of ice crystal replica images:

1. Microscope Adjustment:

* Brightness Control Dial: This should be set to maximum position.

* Zoom and Focus: Zoom is set to the maximum value (300x) and the microscope is focused.

* Illumination Selector Lever: To select the image viewing mode as brightfield or darkfield. We chose the viewing mode as brightfield; this often needs adjustment for getting the clearest images. * Diaphragm Control Knob: Adjustment of diaphragm can change brightness and depth of focus as follows:

	open close
Brightness:	bright dark
Depth of focus:	shallow deep

This is often adjusted to get the clearest image.

2. Picture Grabbing:

Two factors can influence image quality.

* Physical Signal's Stability: Due to the communicating signal's tiny fluctuation, a slight difference may be expected among grabbed images. This variability was assumed not to be very large.

* Adjustable Configurations for Picture Grab: Some configurations have been matched with the hardware and do not require any changes. Others are software options, such as brightness, contrast, etc. These parameters can be adjusted to get the clearest image.

3. Pre-processing:

There are many pre-processing tools in Image-Pro Plus that can influence image analysis results. These include:

* Basic ones: Brightness, Contrast, Gamma Correction (another kind of contrast correction)

* Filtering tools: The most useful for our purpose are spatial filtering tools. These include: low-pass, median, hi-pass and sharpen. Many options are available with each of these tools.

4. Other Parameters:

In Count/Measurement options, we can set ranges for selected parameters to help confine image selection to the desired drops:

- * Aspect ratio: major axis/minor axis (set to be 1-1.8)
- * Average diameter (set to be 3-95 µm)
- * Roundness: Perimeter²/($4\pi \times \text{Area}$) ≥ 1 (=1 for circle) (set to be 1-2.5)

B.2 The analysis procedures

We use the "count/measurement" option in "Image-Pro Plus" to do the analysis. Two things are important when we perform the image analysis. First, we want only accreted cloud drops to be counted and sized. Second, we want counted droplets to be accurately sized. In this section we shall discuss these issues in detail.

In the crystal replica images being analyzed, a rime droplet appears like a light hole with a round dark edge. The droplets are often so close to each other that the dark edges merge. The image analysis software provides two ways to define objects: bright objects or dark objects. The only way for us to define the desired droplets is as bright objects.

Object counting and measurement by the software can be better restricted to the desired drops by defining appropriate ranges for several image object parameters. Only the objects within the set ranges will be selected. Three parameters have been used in our work, which are: aspect, average diameter and roundness. Ranges set for these parameters have been:

- Aspect: from 1 to 1.8
- Average diameter: from 3 to 95 μm
- Roundness: from 1 to 2.5

Even with these restrictions the complex nature of the replica images being analyzed prevent us from completely and correctly counting and sizing all of the desired droplets.

A further limitation is that the average diameters of the drops are measured from the inside edges of the dark droplet edges. These edges, which are an optical artifact of the transmission of light through the crystal replicas, usually possess a considerable thickness. A portion of the edge is actually part of the droplet. By not including the edge, the image processing procedure results in an undersizing of the accreted droplet diameters. To evaluate the significance of this problem, we have compared manual measurements of drop size (with the actual droplet edge defined at the center of the dark edge present in the image) with the drop sizes determined by automated image analysis. The results reveal a good linear correlation between the inside (automatically sized) and true (manually sized) diameter. The existence of this correlation allows the diameters of droplets sized automatically to be corrected by applying a simple linear transformation. However, preliminary testing revealed that applying this simple linear transformation sometimes resulted in significant errors in evaluating volume distributions/total volumes of accreted cloud drops. To deal with this problem, further we applied a Monte Carlo method by adding a small random number to each linearly corrected diameter. The random number possesses a distribution generated in the following way. First, we evaluated the difference between the manually-determined diameter and the linearly corrected diameter. Then we calculated a frequency distribution of these differences in various ranges. Further testing showed that this Monte Carlo improved the result; however, we chose to manually measure diameters of accreted cloud drops in this project.

The image analysis process returns a list of identified objects which we termed the count result. The count result really refers to two things: how many objects have been counted in the image analysis and how many of them are the desired droplets. Due to the complex nature of the replicas and software limitations, all the droplets on a crystal replica are usually not counted nor are all objects identified actually real drops. Many identified objects are the result of optical effects which appear similar to drops. These objects had to be deleted manually.

B.3 Size correction for spreading and geometry deformation of accreted droplets

B.3.1 Experimental and observational results on the spreading of accreted water drops:

We can not directly observe the spreading of the accreted droplets on planar crystal replicas due to the difficulty obtaining side views of these ice crystal replicas. However, we can get some side-views of droplets on columnar ice crystal replicas, which can provide spreading information for accreted droplets on columnar ice crystals. The spreading character of water droplets freezing on a planar surface has been experimentally investigated by Brownscombe and Hallett (1967); and Dong and Hallett (1988; 1989). These studies disclosed that the spreading is a very common character when a water droplet impacts and freezes on an ice surface and that the spreading observed can come about as a result of the drop's impacting and the reduction of its kinetic energy to surface energy or come about as a result of the ice surface nature and the reduction of energy of the system. In this section we summarize and analyze their experimental results in detail. Combining these results with the analysis of some observations for field sampling, we estimate an upper limit of the spreading ratio, defined as the ratio of the radius of a spread droplet "cap" to its height, of drops accreted on planar ice crystals.

1. Experimental observations of spreading of droplets accreted on planar ice crystals:

In the work by Brownscombe and Hallett (1967), the experiment was arranged in such a way that drops of radius $9\pm1\mu$ m, $19\pm2\mu$ m, $40\pm7\mu$ m were produced by ultrasonic generators and the drops fell about 1 m in the cold air before entering a wind tunnel where they were deposited on the ice-coated edge of a microscope slide. The temperature in the cold room could be varied down to -20 °C. The variations of spreading ratio with impact velocity are summarized in Figure B-2. In addition, a best fit curve for the data of each drop size at temperature of -10 °C is presented in Figure B-3. Equations for these best fit curves are given by:

$y = 0.021x^2 - 0.010x + 1.00$	(for drop radius =10 μ m)	(B-1a)
$y = 0.041x^2 - 0.017x + 1.00$	(for drop radius =18 μ m)	(B-1b)

 $y = 0.031x^2 + 0.342x + 0.937$ (for drop radius =40 µm) (B-1c)

where y represents spreading ratio and x represents impact velocity in m s⁻¹.

From these best fit curves, we can evaluate the spreading ratios of drops with radius 10 μ m, 18 μ m and 40 μ m for any given impact velocity at temperature of -10 °C. These results revealed that the spreading ratio of accreted drops increases with drop size, impact velocity and ambient temperature.

As discussed previously, following Mitchell's (1996) approach we can determine the terminal velocity of ice crystal particles using the mass- and area-dimensional power laws. For ice crystals in the size range of 0.5-1.0

mm (typical crystal sizes observed at SPL), the typical fallspeed of ice particles is estimated from a few tenths to 1.0 m s⁻¹. The temperature at Storm Peak Laboratory in a typical winter storm is usually below -5 °C, we therefore used the best fit curves for spreading ratio versus impact velocity at temperature of -10 °C to evaluate the spreading ratios of accreted water drops with radius of 10 μ m, 18 μ m and 40 μ m. The calculated spreading ratios for an impact velocity of 1.0 m s⁻¹ are summarized in Figure B-4. We can see from Figure B-4 that for drops of radius 10 μ m and 18 μ m, the spreading ratio is very close to 1.0, increasing very slowly with droplet size. Since the observed mode diameter of cloud droplets at SPL ranges from approximately 10 to 20 μ m, the above result implies that the spreading ratio of accreted cloud drops should be close to 1.0 under typical cloud conditions at Storm Peak Laboratory.

We can further analyze the influence of temperature and other factors on spreading of accreted water drops using additional experimental data from the work of Dong and Hallett (1988; 1989). The experimental arrangement is similar to that of Brownscombe and Hallett (1967), but the impaction characteristics and temperature range are quite different. The impaction characteristics are represented by the characteristic splash index L, defined as the ratio of drop kinetic energy to the drop surface energy:

$$L = \frac{E_{\kappa}}{E_{s}} \tag{B-2}$$

We can rewrite this parameter as (Brownscombe and Hallett, 1967):

$$L = \frac{E_{\kappa}}{E_{s}} = \frac{1}{2} \frac{\frac{4}{3} \pi r^{3} \rho_{W} V_{0}^{2}}{4 \pi r^{2} \sigma_{Wal}} \cong \frac{r V_{0}^{2}}{480}$$
(B-3)

Where *r* is the drop radius (cm), ρ_w the density of water, V_0 the impact velocity of the drop (cm s⁻¹) and σ_{Wat} the interfacial energy of water-vapor (80 ergs cm⁻²).



Figure B-2. Observed variations of spreading ratio versus impact velocity for water drops accreted on ice surface with radius of 10 μ m, 18 μ m and 40 μ m. Experimental data were from Brownscombe and Hallett's paper (1967). The ambient temperatures are: (a) -10 °C; (b) -20 °C.



Figure B-3. The best fit curves of spreading ratio versus impact velocity for the experimental data in Figure B-2 (a)T=-10 °C. The thinnest curve is for droplets of radius 10 μ m. The thickest curve is for droplets of radius 40 μ m.



Figure B-4. The calculated variation of spreading ratio versus the size of accreted droplets for the impact velocity of 1.0 m s^{-1} and the ambient temperature of $-10 \degree$ C.

In the work of Brownscombe and Hallett, experiments were performed at temperatures of -10 $^{\circ}$ C and -20 $^{\circ}$ C while the value of L was varied from 0.0007 to 15, depending on the drop radius and impact velocity. In the work of Dong and Hallett, L is of the order of 0.01 with droplet radius of 11 μ m while the ambient temperature varies from -20 °C to approximately 0 °C. The spreading observed in the latter case comes about only as a result of the nature of the ice surface and results in a reduction of energy of the system. Some important conclusions in Dong and Hallett's work can be summarized as follows:

(1) The spreading ratio is insensitive to temperature below -4 $^{\circ}$ C (with a value slightly above 1.0), but increases dramatically when temperature is above -3 $^{\circ}$ C.

(2) Even at very low temperatures, below -18 °C, the droplets still spread significantly on the ice surface with a spreading ratio close to 1.0.

(3) No significant effect of impurity on spreading ratio was found for concentrations below 10⁻³ M (mole l⁻¹). Concentrations below these levels are typical of cloud drops.

(4) Supercooled water droplets tend to freeze as individual spheres when they land on a curved ice surface, i.e., their spreading ratio tends to be smaller under this situation.

For a terminal rimed ice crystal velocity of 1 m s⁻¹ (approximated as the impact velocity of accreted cloud drops) and a typical drop radius of 5-10 μ m, the estimated L is of the order of 0.01, which suggests that the impaction characteristics at SPL are very similar to experimental conditions in Dong and Hallett's work. Since the typical ambient temperature at SPL in a winter storm is usually below -5 °C, we conclude that the spreading ratio of cloud drops accreted on the planar ice surface is close to 1.0 (hemispheric freezing). This result is in good agreement with the above estimation from the best fit curves.

However, as discussed above, the spreading ratio of accreted drops relies on observe cloud drop sizes and we can safely draw the above conclusions only for accreted cloud drops with radius smaller than 18 µm.

As shown in previous work conducted at SPL (Rauber and Grant, 1986; Hindman et al., 1994; Mitchell, 1995), the observed mode diameter of cloud drops near the SPL region falls between 10 to 20 μ m, or smaller than 10 μ m, depending on the air parcel trajectory that forms clouds. These observations are consistent with observed cloud drop size spectra in the current study, where the peak concentration drop diameter varied from 8 to 16 μ m (see Figure 5 in section 3.1.1).

We calculated the mass/volume size spectra of accreted cloud drops for case 1. The results are presented in Figure B-5, in which we have applied the correction factors for individual drop sizes to account for the spreading. The accreted cloud drops with diameter larger than 36 μ m contribute little to the total riming mass, so we can apply the above corrections in the current study without introducing much inaccuracy.



Figure B-5. Observed total mass size spectrum of accreted cloud droplets in case 1. The size correction factor of 0.9 was applied to individual droplets to account for drop spreading on the crystal surface.

2. Observed spreading of droplets accreted on rimed ice crystal replicas:

The analysis in this section is based on some observational results from previous studies (Mosimann et al., 1994) and from ice crystal formvar replicas collected at SPL in April, 1996. In the Storm Peak case, the ice crystal habit was dominated by columns with occasional round plates observed. Because we can obtain some side views of drops on columnar ice crystal replicas, we have manually determined these drops' radius and height and calculated their spreading ratios. The observed characters of spreading for the Storm Peak case (April, 1996) can be summarized as follows:

(1). for most accreted droplets observed (90%), the spreading ratio is less than 1.0. The spreading ratio for drops accreted on the ice crystal surface tends to increase with drop size (refer to Figures B-6 and B-7).

(2). for droplets accreted on top of other drops, we have observed that they are more likely to spherically freeze and the spreading ratio is therefore small (see Figure B-8, most spreading ratios are less than 0.6). This result is consistent with previous experimental results (Dong and Hallett, 1988; 1989).

As discussed in the above section, supercooled water droplets tend to freeze as individual spheres when they land on a curved ice surface. Since the columnar crystal's surface is highly curved, we therefore expect that the spreading ratio of drops accreted on the columnar crystals will be smaller than accreted on the ice plane if all other conditions are similar. This results is again consistent with the above observations for the Storm Peak case (April, 1996).


Figure B-6. The spreading ratio distribution for accreted droplets (< 25 μ m diameter) in the Storm Peak case (April, 1996). Data are presented as a drop number distribution with various ranges of spreading ratio. Diameters of all droplets considered here are smaller than 25 μ m.



Figure B-7. The spreading ratio distribution for accreted droplets (> 25 μ m diameter) in the Storm Peak case (April, 1996). Data are presented as a drop number distribution with various ranges of spreading ratio. Diameters of all droplets considered here are larger than 25 μ m.



Figure B-8. The observed spreading ratios for 10 droplets accreted on top of other drops in the Storm Peak case (April, 1996). All values presented here are close to 0.5 (spherical freezing).

Now we turn to consider drop freezing on planar ice crystals. An important character for planar ice crystal's riming is that the droplets tend to freeze at the edge of crystal plate. For heavily rimed cases, as observed, there are many droplets accreted on top of other drops. These situations are very similar to curvature or tip freezing, so we expect that the actual spreading ratio for drops accreted on planar ice crystals should be smaller than observed in experiments where conditions were well controlled. The observational results by Mosimann et al., (1994) are consistent with this viewpoint. As shown therein, for all three types of planar ice crystals (Plate, Broad-branched, Dendrite), the biggest spreading ratio observed is 1.0. The mean spreading ratios for them are: Plate 0.90, Broad-branched 0.93, Dendrite 0.75. As described in that paper, the average temperature is - 5 °C and the peak concentration diameter (without correction) of accreted drops is approximately 20 μ m.

3. Assumption for upper limit of the spreading ratio of accreted droplets:

Based on the above discussions, we propose 1.0 as an upper limit of the spreading ratio of accreted cloud drops, provided that the drop radius is not larger than 18 μ m, the splash index L is far below 1.0 and the ambient temperature is below -4 °C.

B.3.2 Theoretical investigation of spreading errors by including the geometrical deformation:

Due to spreading accreted cloud drops may deform to a spherical cap. In our observations we found that the top-viewed profile of the cap is roughly elliptical instead of circular. The elliptical profile may result from the heterogeneous nature in different directions on the ice surface.

In this section we consider errors caused by all these deformations and evaluate the validity of a simple factor correction to the measured drop size. We define the true diameter D as that of a sphere which has the same volume as the deformed elliptical drop. The measured diameter D_m is defined as the average diameter present on the crystal surface, as reported by image analysis. For top-viewed drops, it is the average diameter of the elliptical profile.

We define S as the relative error between the measured (D_m) and true diameter (D):

$$S = \frac{D_m - D}{D} \tag{B-4}$$

As shown in Figure B-9, we have assumed an ideal elliptical body for a single accreted droplet. In this figure we define the major axis as 'a' and

minor axis as 'b', with aspect ratio $\frac{a}{b}$. The shadowed plane in Figure B-9 is assumed to represent the ice base. Generally, the drop may deform with an arbitrary aspect ratio, however, the assumption of 1.0 for an upper limit of the spreading ratio allows us to restrict our study within two extreme situations: the whole elliptical body and the truncated elliptical body with spreading ratio of 1.0. The aspect ratio's upper limit is 2.0 when the spreading ratio for the whole elliptical body reaches $\frac{r}{h} = \frac{a}{2b} = 1.0$. From our observations in the Storm Peak case (April, 1996) and in the Bondville case (Devulapalli and Collett, 1994), we found that the typical aspect ratio lies strictly between 1.0 and 2.0 (see Figure B-10).

We calculated the relative error S as a function of the aspect ratio for the elliptical body under two extreme situations: the whole elliptical body and the truncated elliptical body with spreading ratio of 1.0. The calculated results are summarized in Figure B-11. The upper curve represents the result for the truncated elliptical body with a spreading ratio of 1.0. The relative error S decreases as the aspect ratio increases since part of the spreading error is canceled by geometrical deformation for this situation. The lower curve represents the result for the whole elliptical body with a According to our upper limit assumption of a specific aspect ratio. spreading ratio of 1.0, the relative diameter error S due to spreading and geometrical deformation falls between these two curves. From Figure B-11 we can see that, by applying a simple factor correction (approximately 0.9), the uncertainty in the diameter estimation remains below approximately 10%. To address this problem in more detail, we first apply a correction factor f to the measured diameter D_m , for a specific aspect ratio, and recalculate the relative errors $(S = \frac{f \times D_m - D}{D})$ for two extreme situations:

the whole elliptical body and the truncated elliptical body with spreading ratio of 1.0. We then take the larger value, termed maximum uncertainty (S_{max}) , out of these two errors. Subsequently, by comparing this maximum uncertainty S_{max} to an observed drop number frequency (as shown in Figure B-10) with the same aspect ratio, we can construct a drop number distribution with various maximum uncertainty (S_{max}) values. We further construct a cumulative drop number frequency distribution versus S_{max} to summarize our results, as presented in Figure B-12. Figure B-12 depicts the fraction of total droplets sized and corrected by applying a factor fpossessing an error below the maximum uncertainty S_{max} . It is worthwhile to notice that, from Figure B-11, the spherical droplet (aspect ratio 1.0) yields the most error since the deformation on aspect ratio may partly cancel the errors in diameter measurement and estimation. From Figure B-12, we can see that by applying a simple factor correction of 0.9, the uncertainty in the diameter estimation remains below 10% for approximately 80% of the total droplets. 100% of the droplets have size errors below 15% for the correction factor of 0.9.



Figure B-9. Illustration of an accreted droplet. The shadowed plane is the assumed ice base. The truncated elliptical body above the ice base is the accreted droplet.



Figure B-10. Observed distribution of aspect ratio of accreted cloud drops. The dashed lines are for a Bondville, Illinois snow case (Devulapalli and Collett, 1994). The solid lines are for the Storm Peak case (April, 1996).



Figure B-11. Variations of relative error S between the measured (D_m) and true diameter (D) with aspect ratio. The upper (thick) curve is for the truncated elliptical droplet with a spreading ratio of 1.0. The lower (thin) curve is for the whole elliptical body.



Figure B-12. The calculated maximum relative error S_{max} between the corrected (f^*D_m) and true diameter (D) versus the cumulative fraction of total droplets that possesses an error below S_{max} . The dashed curve with diamond markers represents the data for correction factor f = 0.85. The thin solid curve with square markers represents the data for correction factor f = 0.90. The thick solid curve with triangle markers represents the data for correction factor f = 0.95.

B.4 Summary

An image analysis system for analyzing ice crystal replicas was tested and applied in the current project. The system can aid us to automate routine procedures of analyzing the crystal habit and sizing the crystal and accreted cloud drops. Some limitations in image analysis procedures were also discussed in this appendix.

Combining experimental results and theoretical methods, we have further studied the characteristics of spreading and geometric deformation of accreted drops on rimed ice crystals and the validity of applying a simple correction factor to the observed drop sizes. By applying this correction factor (0.9), we can relate the measured diameter of accreted drops presented in the crystal replica images to the original diameter of ambient cloud drops with an estimated error below 10% for approximately 80% of droplets measured, under typical cloud conditions at SPL (splash index L<<1.0, T<-4 °C and characteristic diameter of accreted cloud drops \leq 36 µm).



Appendix C. Meteorological data during study periods

Figure C-1. Temporal profiles of observed liquid water content (LWC) during three consecutive days (1/8/-1/10/1997) at SPL. Time is specified in day of year.



Figure C-2. Temporal profiles of observed liquid water content (LWC) during two days (1/11/1997 and 1/14/1997) of study periods at SPL. Time is specified in day of year.



Figure C-3. Temporal profiles of meteorological data during study periods of cases 1, 2, and 3.



Figure C-4. Temporal profiles of meteorological data during study periods of case 4.

TUESDAY, JANUARY 7, 1997



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SATURDAY, JANUARY 11, 1997









WEDNESDAY, JANUARY 15,1997



12 UT DAY km hPa C 0 3.5 656 -16 1 2.7 734 -8 2 1.5 849 4 3 1.0 898 8

00 UT DAY km hPa C 0 3.5 658 -13 2.8 722 -6 1 2.2 772 -1 2 3 1.8 812 3

TRAJECTORIES TO SPK (40.45N,106.74W) 97008 - 1/ 8/97



 12 UT

 DAY km hPa
 C

 0
 3.5
 655
 -14

 1
 2.9
 714
 -7

 2
 2.4
 757
 -3

 3
 2.0
 797
 1

 4
 1.5
 851
 7

 5
 2.1
 791
 1

 6
 2.8
 720
 -6

00 UT DAY km hPa C 0 3.5 653 -15 1 3.1 697 -10 2 2.1 784 -1 3 1.7 819 3

TRAJECTORIES TO SPK (40.45N,106.74W) 97009 - 1/ 9/97



00 UT DAY km hPa C 0 3.5 653 -12 1 3.1 695 -8 2 2.3 773 1 3 1.9 811 4 4 2.0 809 4 5 3.3 679 -9 6 4.5 570 -22 7 4.8 542 -26

12 UT

DAY km hPa C 0 3.5 650 -14 1 2.7 734 -4 2 1.4 856 8 3 1.3 879 10 1.3 883 10 4 2.0 807 3 5 3.9 629 -16 6 7 4.4 578 -22 4.3 581 -22 8 4.3 577 -22 9 10 4.2 571 -23



З	1.8	825	8
4	1.6	847	11
5	1.6	848	11
6	1.8	829	9
7	2.9	722	-2
8	4.1	610	-15
9	3.2	678	-7
	. 1	2 UT	
DAY	í kn	h Pa	С
0	3.5	652	-12
1	2.6	737	-3
2	1.4	859	10
З	1.3	871	11
4	1.4	870	11
5	1.6	849	9
6	1.3	880	12
7	1.3	872	11
8	4.4	589	-19
9	6.6	424	-42
10	6.6	402	-46

00 UT DAY km hPa C 0 3.5 654 -10 1 2.3 761 2 2 2.0 799 6



Appendix D. Size-resolved cloud drop ion concentration data





Figure D-2. Drop size-resolved spectra of (a) NH_4^+ concentration; (b) NO_3^- concentration; (c) Cl⁻ concentration during the consecutive cloud sampling periods in each of four cases. The eight consecutive periods in case 1, the five consecutive periods in case 2, and the ten consecutive periods in case 3 correspond to those listed in Table 1. The six consecutive periods in case 4 correspond to the first six periods of case 4 listed in Table 1. For each period the data are presented as a three-stage ion concentration spectrum.



Appendix E. Diagrams

Figure E-1. Ion (sulfate, nitrate, and ammonium) concentrations in snow samples are regressed against riming degree in: (a) case 2; (b) case 4. The scattered points are sample data. The solid lines are regression fits for nitrate. The long dashed lines are regression fits for sulfate. The short dashed lines are regression fits for ammonium. Both cases yielded a poor correlation: (a) R-squared=0.00, 0.00, and 0.08 for sulfate, nitrate, and ammonium, respectively; (b) R-squared=0.11, 0.18, and 0.02 for sulfate, nitrate, and ammonium, respectively.



Figure E-2. Ion (sulfate, nitrate, and ammonium) concentrations in snow samples are regressed against equivalent potential temperature in: (a) case 1; (b) case 3. The scattered points are sample data. The solid lines are regression fits for nitrate. The long dashed lines are regression fits for sulfate. The short dashed lines are regression fits for ammonium. Both cases yielded a poor correlation (for most species): (a) R-squared=0.14, 0.01, and 0.01 for sulfate, nitrate, and ammonium, respectively; (b) R-squared=0.10, 0.43, and 0.14 for sulfate, nitrate, and ammonium, respectively.

Appendix F. Uncertainty analysis of calculated snow chemistry

F.1 Errors in ion concentration measurement:

The ion $(Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-})$ concentrations in the cloud and snow samples were measured using standard techniques of ion chromatography. The errors determined through replicate sample analysis for all these species were a few percent relative standard deviation, which is negligible.

F.2 Uncertainties of riming masses:

As described in former sections and in appendix B, the accreted cloud drops on the ice crystal replicas were sized using the image analysis system. The drop masses can be calculated from the mass-dimensional relationship for a single spherical drop. Uncertainty is associated with two aspects of this analysis: the number of rime drops on the crystal surface and the correction factor of 0.9 applied to account for drop spreading.

The major source of the uncertainty regarding the number of rime drops stems from the existence of some "dark regions" in the ice crystal replica images, resulting from stacking of many rime droplets. Because drops could not be visually counted in these dark areas, the drop number in "dark regions" was determined by assuming two or more layers (depending on the extent of rime) of drops with an area population the same as the most densely rimed area of the crystal, where individual drops could be clearly recognized and counted. The uncertainty for the estimated droplet number in these "dark regions" is assumed to be $\pm 100\%$.

In appendix B we argue that a correction factor of 0.9 should be applied to correct for effects of drop deformation on the ice crystal surface. This correction is shown to provide an error generally less than 10% of equivalent spherical drop diameter. The error in the estimated drop mass is therefore 30%.

To further estimate errors in the calculated snow chemistry, we used the error translation approach. In this approach, if a general quantity, Q, is a function of several variants, X_1 , X_2 , and X_3 , namely,

$$Q = Q(X_1, X_2, X_3)$$
(F-1)

the overall error in Q, δ Q, can be expressed in terms of errors in X₁, X₂, and X₃, δ X₁, δ X₂, and δ X₃, given by:

$$\delta Q = \sqrt{\left(\frac{dQ}{dX_1}\delta X_1\right)^2 + \left(\frac{dQ}{dX_2}\delta X_2\right)^2 + \left(\frac{dQ}{dX_3}\delta X_3\right)^2} \tag{F-2}$$

In our analysis we replaced Q with the calculated ion concentration in snow, and X_1 , X_2 , and X_3 with rime masses in small (4-10 µm), medium (10-17 µm), and large (>17 µm) drop size ranges.

By performing this error analysis on the calculated snow chemistry from the uncertainty of riming masses, we found that this error source introduced uncertainties of approximately 10%–30% in the calculated snow chemistry.

F.3 Uncertainties of ice crystal masses:

The image system was used to analyze the habit and size of ice crystal replicas. Masses of individual ice crystals were calculated from the massdimensional relationships of equation 10 (Mitchell, 1996). Since these relationships are based on statistical fits to observational data, uncertainties in the fits affect the calculated mass of each single ice crystal.

We used the raw data, provided through the courtesy of Dr. David L. Mitchell, to analyze this error. The errors in the predicted ice crystal masses ranged from a few percent to 130% with an average of 40%. We applied the average uncertainty of 40% to our snow chemistry model analysis and found that this uncertainty translated into 30%–40% error in the calculated snow chemistry.

F.4 Uncertainties associated with vertical variations in cloud physical and chemical properties.

As discussed above, ion concentrations in accreted cloudwater were not available from observations. Consequently, the range of cloud compositions in each drop size range was estimated by considering vertical displacement of cloud parcels characterized at SPL. The composition determined at cloud base and at cloud top define an uncertain range for the composition of drops captured by the ice crystals colleted at SPL (assuming the rime drops were collected inside the same cloud presented at SPL). This range of cloud concentrations is at times quite large, resulting in uncertainties in predicted snow chemistry as high as several hundred percent. We conclude, therefore, that accurate modeling of snow chemistry relies strongly on accurate knowledge about snow crystal trajectories and altitudes at which riming occurs. Snow chemistry is also strongly influenced, of course, by the particles and soluble gases present, which determined the cloud chemistry.