Relationships between aerosol and snow chemistry at King Col, Mt. Logan Massif, Yukon, Canada

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Abstract

Simultaneous samples of aerosol (n = 48) and recent snow (n = 193) chemistry were collected at King Col (4135 m) in the St. Elias Mountains, Yukon, between 17 May and 11 June 2001. Major ion concentrations in aerosol samples were low with the total ionic burden averaging 5.52 neq m⁻³ at standard temperature and pressure (STP). Interspecies aerosol relationships indicate the presence of (NH₄)₂SO₄ aerosol at King Col. An aerosol Cl⁻ deficiency relative to seawater suggests volatilization of HCl by reaction with unneutralized SO₂⁴⁻ that is present in half of the samples. Backwards trajectories for select aerosol concentration peaks document the transport of Asian dust and anthropogenic emissions, the eruption plume from the 22 May eruption of Sheveluch, Kamchatka, and sea salt from the marine boundary layer over the Gulf of Alaska to King Col during the sampling period. Fresh snow chemistry generally mimics aerosol chemistry with similar relative abundances and interspecies relationships except for large enrichments in snow Cl⁻ and NO₃⁻ relative to aerosol due to snow scavenging of gas-phase HCl and HNO₃. Although relatively strong correlations between aerosol and snow concentrations were observed for species associated with accumulation mode aerosols, e.g. NH₄⁺ (r = 0.56) and SO₂⁴⁻ (r = 0.43), only weak correlations were observed for dust and sea-salt species. These results are influenced by greater variability in concentrations between replicate snow samples for species associated with coarse mode dust and sea-salt particles and by snow scavenging of gas-phase HCl and HNO₃.

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1. Introduction

Ice cores retrieved from the polar ice sheets and suitably located mountain glaciers arguably provide the highest resolution and most direct view of Earth’s paleoatmosphere (e.g., Legrand and Mayewski, 1997). Recently, the St. Elias Mountains in northwest North America have become the focus of an international ice coring effort (Fig. 1). Prior work on St. Elias ice cores recovered from the Northwest Col (5430 m) of Mt. Logan in 1980 and Eclipse Icefield (3017 m) in 1996 demonstrated that differences in elevation allow the sites to sample different layers of the atmosphere, resulting in
complementary and distinct records (Holdsworth et al., 1988; Yalcin and Wake, 2001; Wake et al., 2002; Yalcin et al., 2003). During the 2001 and 2002 field seasons, a suite of new ice cores were recovered from the St. Elias Mountains spanning an elevation range from 3017 to 5340 m. Ice cores were drilled at both Prospector-Russell Col (5340 m) and King Col (4135) on Mt. Logan (Goto-Azuma et al., 2003; Fisher et al., in press). Additional cores were drilled at the saddle (4400 m) between Mt. Bona and Mt. Churchill (Thompson et al., 2004) and the summit ice cap 4100 m) of Mt. Wrangell (Kanamori et al., 2004), and two new ice cores were collected from Eclipse Icefield (3017 m) (Yalcin et al., 2006a, b). Together, these records offer a unique opportunity to construct a three-dimensional view of the paleoatmosphere.

However, interpreting the chemical records contained in ice cores requires knowledge of the site-specific relationships between snow chemistry and that of the precipitating air mass that can be obtained by simultaneous collection of aerosol and snow samples (e.g., Dibb and Jaffrezo, 1997). Such investigations are important given the wealth of paleoenvironmental information potentially available from ice cores and the uncertainty in relating glaciochemical to atmospheric concentrations. Programs such as the Dye 3 (Greenland) Gas and Aerosol Sampling Program and the Summit, Greenland atmospheric research program represent international collaborative efforts to better understand the processes influencing chemical species eventually preserved in Greenland ice cores (Jaffrezo and Davidson, 1993; Dibb and Jaffrezo, 1997). Sampling campaigns have also characterized the aerosol and investigated air–snow chemical relationships at mountain glacier sites in the European Alps (Baltensperger et al., 1992) and Central Asia (Wake et al., 1994; Sun et al., 1998; Shrestha et al., 2002).

In support of ice coring efforts on the summit plateau of Mt. Logan, an intermediate elevation climbing camp and research station was established at King Col (60.35°N, 140.36°W, 4135 m elevation) on the Mt. Logan massif during the 2001 field season (Fig. 1). From 17 May to 11 June, twice daily aerosol and three to five replicate fresh or surface snow samples were collected. The resulting database provides the information needed to characterize the late spring–early summer aerosol at King Col and examine the relationships between aerosol and snow chemistry on an event basis.

2. Methods

2.1. Sample collection

Twice-daily aerosol samples were collected at King Col from 17 May to 11 June using a 24 V high-volume pump with inline flow meter powered by a combination of photovoltaic cells and batteries. Care was taken to minimize contamination. Aerosol sampling was conducted on the south side of the Col, 120 m from camp in a direction perpendicular to the prevailing wind direction to minimize potential local contamination from the camp. A non-particulating suit, face mask, and polyethylene gloves were worn at all times during aerosol and
snow sample collection. Each filter was pre-loaded onto a polyethylene cassette in a class 100 clean room at the University of New Hampshire and sealed inside a clean polyethylene bag. Just prior to sample collection, the filter was removed from the sealed bag and mounted face down inside a 0.20-m diameter protective cylindrical Delrin housing 2 m above the snow surface. A polyethylene wind baffle housing the aerosol filter holder minimized the potential for collecting airborne snow and ice crystals.

Samples were collected on 1 μm pore size; 90 mm diameter Teflon filters (Fluropore filters, Millipore, Bedford, MA). Sample collection times ranged from 8 to 15 h and averaged 12 h. Corrections for ambient temperature and pressure allowed conversion of the measured air volumes to cubic meters at standard temperature and pressure (m³ STP); Sampled volumes ranged from 17.19 to 42.63 m³ STP and averaged 29.89 m³ STP. The mean flow rate was 2.4 m³ STP h⁻¹ yielding a velocity at the face of the filter of 10.5 cm s⁻¹. This velocity is high enough for this kind of filter to have collection efficiency greater than 90% for aerosol particles larger than 0.3 μm (Hinds, 1999). The cutoff for large particles, as given by their sedimentation velocity, is estimated at about 20 μm (Hinds, 1999).

After sampling, the filters, still in their cassettes, were returned to their original clean polyethylene bags, double sealed in plastic bags, and stored in a snow cave. Ten procedural blanks were collected in the course of the sampling campaign by placing a loaded filter cassette in the housing and immediately removing and re-sealing. Filter blanks were analyzed with the samples to quantify blank levels and check for contamination. Concurrent with aerosol sample collection, three to five replicate fresh or aged surface snow samples were collected about 20 m away from the aerosol sampling site by scraping the surface snow layer directly into pre-cleaned polypropylene cups. If measurable snow fell during the sample collection time for a particular aerosol sample, then the surface snow layer concurrently sampled was considered fresh snow.

A total of 48 aerosol samples and 193 fresh and aged surface snow samples were collected during the sampling period.

2.2. Analysis by ion chromatography, detection limits, and precision

All samples were returned frozen to the Climate Change Research Center at the University of New Hampshire for processing and analysis. Filters were saturated with 0.5 ml high purity methanol and the soluble components extracted with three successive 5 ml aliquots of deionized Milli-Q water, and preserved with chloroform. Filter extracts as well as fresh and aged surface snow samples were analyzed by suppressed ion chromatography for eight inorganic ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻) and one organic ion (C₂O₄²⁻) in a dedicated laboratory at the University of New Hampshire Climate Change Research Center. The cation system used a CS12A column with CSRS-ultra suppressor in auto suppression recyle mode with 20 mM MSA eluent. The anion system used an AS11 column with an ASRS-ultra suppressor in auto suppression recycle mode with 6 mM NaOH eluent. Precision of the results was monitored by running 10% of the samples in duplicate and found to be 10% for aerosol Mg²⁺, less then 5% for other aerosol cations, and less than 2% for aerosol anions. For snow samples, precision was 7% for K⁺, 4% for NH₄⁺, 3% for Ca²⁺, and less then 2% for other species. Detection limits for snow samples were less than 2 ng g⁻¹ for NO₃⁻, SO₄²⁻, and C₂O₄²⁻, and less than 1 ng g⁻¹ for all other species.

Aerosol detection limits were defined as two standard deviations of the blank values divided by the mean sample volume (Shrestha et al., 2000). The detection limits for aerosol species were (in neq m⁻³ STP): Na⁺ (0.281), NH₄⁺ (0.008), K⁺ (0.034), Mg²⁺ (0.023), Ca²⁺ (0.025), Cl⁻ (0.236), NO₃⁻ (0.004), SO₄²⁻ (0.049), C₂O₄²⁻ (0.002). The mean concentration of the ten aerosol procedural blanks were subtracted from the sample concentrations, which occasionally resulted in below detection limit values for Na⁺ (6 samples), NH₄⁺ (2 samples), K⁺ (5 samples), Mg²⁺ (11 samples), Ca²⁺ (6 samples), and Cl⁻ (12 samples). Sea-salt (ss) and non-sea-salt (nss) fractions for aerosol and snow samples were estimated by determining the limiting sea-salt species (the species present in the lowest proportion relative to seawater ratios) in each sample and using that species as the sea-salt indicator (Keene et al., 1986).

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3. Results and discussion

3.1. Characterization of King Col aerosol

Summary statistics of King Col aerosol chemical composition measured between 17 May and 11 June 2001 are presented in Table 1 and time series of aerosol concentrations for major inorganic ions are presented in Fig. 2. Aerosol concentrations are very low, reflecting the remote location of the King Col site relative to source regions. The total ionic burden (total cations plus total anions) ranged from 1.30 to 13.21 neq m\(^{-3}\) STP and averaged 5.52 neq m\(^{-3}\) STP. There is an excess of cations in all but three samples; with the charge balance (sum of measured cations minus sum of measured anions) averaging 0.71 neq m\(^{-3}\) STP. This cation excess could be balanced by carbonate ions (\(\text{HCO}_3^-/\text{CO}_2^->\)) that were not measured in this study. In fact, if the observed concentrations of

<table>
<thead>
<tr>
<th>(\text{Na}^+)</th>
<th>(\text{NH}_4^+)</th>
<th>(\text{K}^+)</th>
<th>(\text{Mg}^{2+})</th>
<th>(\text{Ca}^{2+})</th>
<th>(\text{Cl}^-)</th>
<th>(\text{NO}_3^-)</th>
<th>(\text{SO}_4^{2-})</th>
<th>(\text{C}_2\text{O}_3^{2-})</th>
<th>(\Delta C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1.26</td>
<td>1.34</td>
<td>0.17</td>
<td>0.15</td>
<td>0.52</td>
<td>0.94</td>
<td>0.24</td>
<td>1.38</td>
<td>0.07</td>
</tr>
<tr>
<td>Median</td>
<td>0.86</td>
<td>1.22</td>
<td>0.15</td>
<td>0.10</td>
<td>0.40</td>
<td>0.64</td>
<td>0.18</td>
<td>1.12</td>
<td>0.06</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.86</td>
<td>0.92</td>
<td>0.11</td>
<td>0.12</td>
<td>0.45</td>
<td>0.83</td>
<td>0.20</td>
<td>0.96</td>
<td>0.05</td>
</tr>
<tr>
<td>Max</td>
<td>4.13</td>
<td>4.12</td>
<td>0.47</td>
<td>0.57</td>
<td>2.36</td>
<td>3.29</td>
<td>1.08</td>
<td>4.59</td>
<td>0.19</td>
</tr>
<tr>
<td>Min</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>0.05</td>
<td>0.17</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(\Delta C\): charge balance (sum of measured cations minus sum of measured anions); DL: detection limit.

Fig. 2. Concentrations of soluble ionic species in aerosol samples (solid line) and concurrent fresh (solid circles) and aged surface (open circles) snow samples collected at King Col between 17 May and 11 June 2001.
Ca\(^{2+}\) and Mg\(^{2+}\) are assumed to be accompanied by an equal amount of carbonate ions (Toom-Sauntry and Barrie, 2002), the calculated charge balance is excellent (averaging 0.14 neq m\(^{-3}\) STP). The remaining cation excess is likely balanced by small amounts of methanosulfonate (MSA) or organic acids (e.g., formate, acetate) (Toom-Sauntry and Barrie, 2002).

Linear regression on all water-soluble species in the aerosol (Table 2) showed that the sea-salt species Na\(^{+}\) and Cl\(^{-}\) are highly correlated (r = 0.89) and the dust indicators Ca\(^{2+}\) and Mg\(^{2+}\) are well correlated (r = 0.76). Ammonium is highly correlated with SO\(_2\)^{4−} (r = 0.90) and also correlates well with NO\(_3\)^{−} (r = 0.73), suggesting that these species are present in the same air masses. The higher correlation between NH\(_4\)^{+} and SO\(_2\)^{4−} than between NH\(_4\)^{+} and NO\(_3\)^{−} reflects the preferential reaction of ammonia with sulfuric rather than nitric acid (Bassett and Seinfeld, 1983). The mean NH\(_4\)^{+}/SO\(_2\)^{4−} molar ratio is 2.16, suggesting the principal form of ammonium sulfate particles at King Col is (NH\(_4\))\(_2\)SO\(_4\) and not NH\(_4\)HSO\(_4\). This result differs from Barrie and Barrie (1990) and Shrestha et al. (1997) who demonstrated that NH\(_4\)HSO\(_4\) was the principal sulfate aerosol species in the high Arctic and Himalayas, respectively. Because sufficient NH\(_4\)^{+} exists in King Col aerosols to fully neutralize SO\(_2\)^{4−} more than half the time, ammonium nitrate aerosol (NH\(_4\)NO\(_3\)) may be present at King Col, as implied by the good correlation between NH\(_4\)^{+} and NO\(_3\)^{−}. The collection of particulate nitrate as ammonium nitrate may lead to a possible negative sampling artifact through individual evaporation as HNO\(_3\). However, nitrate loss from the filters by reaction with sulfate is expected to be important only when the NH\(_4\)^{+}/SO\(_2\)^{4−} ratio is less than 1.5 (Pathak and Chan, 2005).

Dust species, for example Ca\(^{2+}\), are highly correlated with NO\(_3\)^{−} (r = 0.91) and well correlated with SO\(_2\)^{4−} (r = 0.75), which suggests uptake of sulfate and nitrate by dust particles (Jordan et al., 2003). However, we do not observe a strong relationship between the equivalence ratios of NH\(_4\)^{+}/SO\(_2\)^{4−} and Ca\(^{2+}\)/SO\(_2\)^{4−} (r = 0.20) as has been reported from high elevations sites in central Asia (Sun et al., 1998). This is probably due to lower dust loadings in the King Col aerosol relative to Central Asian aerosols, making (NH\(_4\))\(_2\)SO\(_4\) a far more important sulfate-bearing aerosol species than CaSO\(_4\) at King Col. King Col aerosol Ca\(^{2+}\) averages 0.52 neq m\(^{-3}\) STP, while at a 5000 m site in the Himalaya aerosol Ca\(^{2+}\) averages 1.24 neq m\(^{-3}\) STP during the monsoon season, when dust loadings are at their annual minimum, while concentrations are even higher at other times of the year (Shrestha et al., 1997).

The Cl\(^{−}/Na^{+}\) equivalent ratio on a per-sample basis averages 0.69, considerably less than the seawater ratio of 1.16 (Keene et al., 1986), indicating a Cl\(^{−}\) deficiency in the King Col aerosol relative to the Cl\(^{−}/Na^{+}\) seawater ratio despite the high correlation between the two. Differences in Cl\(^{−}/Na^{+}\) ratios relative to seawater may be attributable to acidification of sea-salt particles by reaction with H\(_2\)SO\(_4\) (Legrand and Delmas, 1988). This reaction volatilizes sea-salt chloride to produce gas phase and highly soluble HCl, resulting in depletion of aerosol Cl\(^{−}\) and enrichment of Cl\(^{−}\) in precipitation. Although the mean NH\(_4\)^{+}/SO\(_2\)^{4−} molar ratio in the King Col aerosols is 2.16, suggesting (NH\(_4\))\(_2\)SO\(_4\) is the principal ammonium sulfate aerosol species, there is an excess of SO\(_2\)^{4−} charge equivalents relative to NH\(_4\)^{+} in 49% of the samples. A good correlation between the Cl\(^{−}\) deficit and unneutralized SO\(_2\)^{4−} (SO\(_2\)^{4−} minus NH\(_4\)^{+}, in equivalence units) in our samples (r = 0.57) suggests this mechanism is indeed responsible for the Cl\(^{−}\) deficiency in the King Col aerosol. Acidification of sea-salt aerosol by nitric acid may be an additional volatilization mechanism contributing to the aerosol Cl\(^{−}\) deficiency relative to seawater.

Apportionment of the King Col aerosol into sea-salt and non-sea-salt fractions using Na\(^{+}\) and Mg\(^{2+}\) as the sea-salt indicators (K\(^{+}\), Ca\(^{2+}\), and SO\(_2\)^{4−} were not found to be limiting in any of the samples) suggests that nearly all (>90%) of the aerosol Na\(^{+}\) at King Col is from sea salt. Mean-
while, nearly all (>90%) of the aerosol $K^+$, $Ca^{2+}$, and $SO_2^{4-}$ is from non-sea-salt sources. Only $Mg^{2+}$ is found to have significant contributions from both sea-salt and non-sea-salt sources, with $1/3$ of the aerosol $Mg^{2+}$ at King Col from sea salt.

3.2. Temporal variations in aerosol chemical composition

Multi-day variations in aerosol concentrations at King Col (Fig. 2) can be related to changes in aerosol source regions and transport and to the timing of precipitation events. To investigate aerosol source regions and transport pathways, backward trajectories using King Col as the end point were calculated for elevations of 3500, 4200 and 5000 m above sea level using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1997) with the NCEP global reanalysis data and model vertical velocity (available online at http://www.arl.noaa.gov/ready/hysplit4.html). While the complex terrain of the St. Elias Mountains cannot be captured, the backward trajectories can indicate source regions and large-scale circulation patterns affecting the region during the sampling campaign (e.g., Carrico et al., 2004). Knowledge of aerosol source regions (arid regions for dust aerosols, urban centers for anthropogenic aerosols) can be used to infer where different aerosols were added to an air mass. Tightly coupled trajectory paths between 3500 and 5000 m elevation provide confidence in the model calculations for trajectory paths reaching King Col, while divergent trajectory paths over this elevation range suggest a degree of uncertainty in the trajectory paths. We discuss aerosol source regions as deduced using backward trajectories for four aerosol concentration peaks observed during the 17 May–11 June sampling period, as well as a “clean air” period free of local precipitation (Fig. 3).

Events 1 and 2 are characterized by high concentrations of $Ca^{2+}$, $Mg^{2+}$, $NO_3^-$, $NH_4^+$, and $SO_2^{4-}$ on 22 May and 26–27 May (Fig. 2). Modeled back trajectories for Event 1 diverge significantly after only 48 h. Consequently, we have less confidence in source region identification, although an Asian influence is suggested by the trajectories ending at 4200 and 5000 m. However, trajectory paths for Event 2 are tightly coupled back through time and suggest an Asian source region incorporating both crustal dust from Central Asia and anthropogenic pollution from northeast China and Korea (Fig. 3). Trajectories move around the base of a low-pressure trough from central Siberia and across the Gobi desert region, as would be expected during an outbreak of continental polar air concomitant with dust storm generation (Sun et al., 2001). Trajectories continue across industrialized regions of Korea and northeast China where an anthropogenic $SO_2^{4-}$ and $NO_3^-$ component could have been added to the air mass. The air then moves north around a high pressure ridge over the western Pacific where precipitation scavenging would be minimal before being entrained by the Aleutian Low and advected into the St. Elias Mountains.

Precipitation plays an important role in short-term reductions of aerosol concentrations because wet deposition is an important aerosol removal process (Shrestha et al., 2000). This is illustrated by abrupt decreases in aerosol concentrations at King Col that are closely tied to the timing of local snowfall events. For example, the King Col aerosol was cleansed by snowfall events on 22–23 May and 27 May, as reflected by abrupt decreases in aerosol concentrations, ending the aerosol concentration peaks associated with Events 1 and 2.

Event 3 is a peak in aerosol $SO_2^{4-}$ and $NH_4^+$ on 30–31 May without concurrent increases in aerosol species indicative of marine ($Na^+$, $Cl^-$) or crustal ($Ca^{2+}$, $Mg^{2+}$) sources (Fig. 2). A volcanic eruption is one possible source of the $SO_2^{4-}$ peak that would not be associated with concurrent enhancements in dust or sea-salt species. Three major eruptions of Sheveluch Volcano on the Kamchatka peninsula occurred between 19 and 22 May (Bulletin of the Global Volcanism Network, 2001). The eruption of 22 May was the largest and reached an altitude of 20 km. Back trajectories suggest the 22 May eruption plume did in fact reach the St. Elias on 31 May within a narrow elevation range centered on King Col. Trajectories arriving at lower (3500 m) or higher (5000 m) elevations between 30–31 May originated south of the Aleutians or near the Bering Strait, respectively, and may not have carried the signature of the Sheveluch eruption. Consequently, this moderately large eruption (VEI 4) may not be identifiable in glaciochemical records from lower (Eclipse Icefield) or higher (Mt. Logan) sites, illustrating that differences in transport patterns can result in distinct paleovolcanic records at nearby sites with different elevations.

The volcanic $SO_2^{4-}$ peak at King Col is associated with a concurrent enhancement in $NH_4^+$. This could be explained by oxidation of volcanic $SO_2$ in the
plume to produce sulfuric acid aerosols, which are then neutralized by reaction with ammonium from biological or combustive sources. If neutralization of volcanic \( \text{SO}_4^{2-} \) by \( \text{NH}_4^+ \) commonly occurs before preservation in glacial ice, then volcanic \( \text{SO}_4^{2-} \) deposition would be associated with concurrent enhancement in \( \text{NH}_4^+ \). Statistical techniques for extracting paleovolcanic signatures from multivariate glaciochemical records, such as EOF analysis, are based on the assumption that volcanic \( \text{SO}_4^{2-} \) deposition should be independent of other ion deposition (Zielinski et al., 1996; Yalcin et al., 2003). This may not be the case when volcanic \( \text{SO}_4^{2-} \) has reacted with \( \text{NH}_4^+ \) to produce ammonium.
Table 3
Summary of fresh and surface snow composition (n = 193) at King Col (ueq l⁻¹), 17 May–11 June 2001 (unit: ueq l⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₂⁻</th>
<th>C₂O₄²⁻</th>
<th>ΔC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.29</td>
<td>0.79</td>
<td>0.08</td>
<td>0.21</td>
<td>0.97</td>
<td>1.07</td>
<td>1.18</td>
<td>1.18</td>
<td>0.05</td>
<td>0.39</td>
</tr>
<tr>
<td>Median</td>
<td>0.19</td>
<td>0.78</td>
<td>0.05</td>
<td>0.17</td>
<td>0.82</td>
<td>0.96</td>
<td>1.06</td>
<td>1.06</td>
<td>0.04</td>
<td>0.21</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.34</td>
<td>0.34</td>
<td>0.09</td>
<td>0.15</td>
<td>0.65</td>
<td>0.38</td>
<td>0.78</td>
<td>0.75</td>
<td>0.05</td>
<td>0.90</td>
</tr>
<tr>
<td>Max</td>
<td>3.04</td>
<td>1.74</td>
<td>0.80</td>
<td>0.65</td>
<td>3.81</td>
<td>4.02</td>
<td>3.44</td>
<td>3.91</td>
<td>0.30</td>
<td>1.90</td>
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<tr>
<td>Min</td>
<td>0.01</td>
<td>0.13</td>
<td>0.00</td>
<td>0.03</td>
<td>0.09</td>
<td>0.06</td>
<td>0.17</td>
<td>0.13</td>
<td>0.01</td>
<td>-3.16</td>
</tr>
</tbody>
</table>

ΔC: charge balance (sum of measured cations minus sum of measured anions).

The average total ionic burden (total cations plus total anions) ranged from 1.88 to 11.79 ueq l⁻¹ and averaged 5.07 ueq l⁻¹. Ammonium and sulfate represent a smaller fraction of the total soluble ionic impurities in the snow (40%) than in the aerosol (49%). Meanwhile, both dust (Ca²⁺ and Mg²⁺; 23%) and NO₃⁻ (20%) represent greater fractions of the total ionic burden in snow relative to the aerosol (11% and 5%, respectively). The charge balance (sum of cations minus sum of anions) of King Col fresh and surface snow averages -0.39 ueq l⁻¹, with an anion excess in 62% of the samples that is presumably balanced by the hydrogen ion. Samples with a cation excess are presumably balanced by carbonate ions, in the case of samples with high dust concentrations, and/or organic acids (e.g., formate, acetate, methylsulfonate).

As with aerosol samples, linear regression of species measured in snow samples (Table 4) showed that the sea-salt species Na⁺ and Cl⁻ are highly correlated (r = 0.90), as are the dust species Ca²⁺ and Mg²⁺ (r = 0.89). Calcium and magnesium are also highly correlated with SO₄²⁻ (r = 0.87 and 0.83, respectively), but not as well correlated with NO₃⁻ in snow samples (r = 0.63 and 0.58, respectively) compared to aerosol samples (r = 0.90 and 0.80, respectively). The equivalence ratios NO₃⁻/NH₄⁺ and NO₃⁻/SO₄²⁻ suggest enrichment of NO₃⁻ in snow (1.36 and 1.09, respectively) relative to the aerosol (0.20 and 0.19, respectively). This could reflect dry deposition or snow scavenging of gas-phase HNO₃ (Baltensperger et al., 1992; Shrestha et al., 1997; Toom-Sauntry and Barrie, 2002). Furthermore, NH₄⁺ is highly correlated with SO₄²⁻ (r = 0.70) in snow, as with the aerosol, but not as well correlated with NO₃⁻ (r = 0.55), again suggesting snow scavenging of gas-phase HNO₃. Although enrichment of

Table 4
Correlation coefficients (n = 193) between soluble species in fresh and surface snow collected at King Col, 17 May–11 June 2001

<table>
<thead>
<tr>
<th></th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>C₂O₄²⁻</th>
</tr>
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<tbody>
<tr>
<td>NH₄⁺</td>
<td>0.43</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
<td>0.90</td>
<td>0.57</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.09</td>
<td>0.63</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.08</td>
<td>0.67</td>
<td>0.23</td>
<td>0.94</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.81</td>
<td>0.61</td>
<td>0.90</td>
<td>0.32</td>
<td>0.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.06</td>
<td>0.64</td>
<td>0.37</td>
<td>0.60</td>
<td>0.67</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.16</td>
<td>0.75</td>
<td>0.37</td>
<td>0.87</td>
<td>0.91</td>
<td>0.44</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂O₄²⁻</td>
<td>0.16</td>
<td>0.54</td>
<td>0.51</td>
<td>0.33</td>
<td>0.33</td>
<td>0.50</td>
<td>0.72</td>
<td>0.50</td>
<td></td>
</tr>
</tbody>
</table>

Bold entries denote correlations significant at the 99% confidence level. Italicized entries are significant at the 90% confidence level.
\( \text{SO}_4^{2-} \) relative to \( \text{NH}_4^+ \) is often observed in precipitation due to heterogeneous \( \text{SO}_2 \) oxidation in clouds (Calvert et al., 1985). \( \text{SO}_4^{2-}/\text{NH}_4^+ \) ratios at King Col suggest only slight \( \text{SO}_4^{2-} \) enrichment in snow (1.06) relative to aerosol (0.93). This result implies that much of the sulfur reaching King Col has already been oxidized to \( \text{SO}_4^{2-} \) aerosol. Interestingly, all correlations are positive for the snow data while the aerosol data show negative correlations between sea-salt (\( \text{Na}^+, \text{Cl}^- \)) and some non-sea-salt (\( \text{Ca}^{2+}, \text{NH}_4^+, \text{NO}_3^- \)) species (Table 2). This reflects the greater importance of removal processes (wet and dry deposition, riming) in controlling concentrations in snow, while air mass source region and transport processes are of greater importance in controlling aerosol concentrations.

In addition to snow scavenging of gas-phase HNO\(_3\), there is also evidence for snow scavenging of gas-phase HCl at King Col. While the Cl\(^-\)/Na\(^+\) ratio in aerosol samples showed a chloride deficit relative to the seawater ratio, snow samples show a chloride excess. The Cl\(^-\)/Na\(^+\) equivalent ratio in our samples averages 2.12, greater than both the seawater ratio of 1.16 (Keene et al., 1986) and the ratio of 0.69 observed in aerosol samples. Excess chloride in snow could be attributable to precipitation scavenging of HCl produced by acidification of sea-salt particles (Legrand and Delmas, 1988; Toom-Saunter and Barrie, 2002). With respect to the snow, Na\(^+\) was the limiting sea-salt species in 90% of the samples, Mg\(^{2+}\) in 8%, K\(^+\) in 1%, and \( \text{SO}_4^{2-} \) in 1%. As was the case for aerosols, nearly all of the Ca\(^{2+}\) (99%), SO\(_4^{2-}\) (96%), and K\(^+\) (90%) are from non-sea-salt sources while nearly all of the Na\(^+\) (96%) is from sea salt. Only Mg\(^{2+}\) has both significant sea-salt (35%) and non-sea-salt (65%) sources.

### 3.4. Relationships between aerosol and snow chemistry

To quantify the relationship between concentrations of soluble ionic impurities in King Col snow and aerosols, scavenging ratios \( W \) were calculated according to

\[
W = \frac{p_{\text{air}} C_{\text{snow}}}{C_{\text{air}}},
\]

where \( C_{\text{snow}} \) is the concentration in snow (ng g\(^{-1}\)); \( C_{\text{air}} \) the concentration of aerosol (ng m\(^{-3}\) STP), and \( p_{\text{air}} \) the density of air (1225 g m\(^{-3}\) at STP) (Davidson et al., 1993). Large values of \( W \) indicate efficient scavenging of that species by precipitation. Scavenging ratios were calculated from those aerosol samples with concurrent fresh snow samples (21 of 48 aerosol samples) and limited to aerosol measurements above detection limits.

Calculated scavenging ratios (Table 5) are consistent with values reported in the literature for sites in Greenland (Davidson et al., 1985, 1993; Silvente and Legrand, 1993) and Central Asia (Sun et al., 1998; Shrestha et al., 2002), except for Ca\(^{2+}\), which is found to be a factor of 2 higher at King Col. Meanwhile, scavenging ratios at King Col are a factor of two to four higher than those reported for Jungfraujoch (3450 m) in the Swiss Alps, except for Na\(^+\) and Cl\(^-\) which show lower scavenging ratios at King Col (Schwikowski et al., 1995). The higher scavenging ratios at King Col and other sites relative to Jungfraujoch might be explained by the fact that Jungfraujoch was in the cloud during all observed precipitation events, hence the reported scavenging ratios include only in-cloud processes, whereas below-cloud scavenging processes may also be important elsewhere. Event-based studies such as that presented here report scavenging ratios as much as an order of magnitude higher than scavenging ratios calculated from annual average concentrations because event-based studies reflect only the conditions during precipitation events (Schwikowski et al., 1999).

Scavenging ratios are highly variable at King Col for all species as seen by their standard deviations. This variability could be due to differences in precipitation formation, particularly the extent of snowflake riming, but may also be influenced by spatial variability in snow chemistry, wind redistribution and mixing of fresh snow with older snow, and differences in aerosol compositions between precipitating air masses. Higher scavenging ratios are observed for species associated with coarse dust particles (e.g., Ca\(^{2+}\) and Mg\(^{2+}\)) compared to species associated with accumulation mode aerosols (e.g., NH\(_4^+\) and SO\(_4^{2-}\)), reflecting more efficient precipitation scavenging of coarse dust particles.

### Table 5

<table>
<thead>
<tr>
<th>( \text{Na}^+ )</th>
<th>( \text{NH}_4^+ )</th>
<th>( \text{K}^+ )</th>
<th>( \text{Mg}^{2+} )</th>
<th>( \text{Ca}^{2+} )</th>
<th>( \text{Cl}^- )</th>
<th>( \text{NO}_3^- )</th>
<th>( \text{SO}_4^{2-} )</th>
<th>( \text{C}_2\text{O}_4^{2-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>462</td>
<td>1559</td>
<td>700</td>
<td>2697</td>
<td>4540</td>
<td>872</td>
<td>8253</td>
<td>1708</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>361</td>
<td>1504</td>
<td>479</td>
<td>1893</td>
<td>2972</td>
<td>779</td>
<td>5744</td>
<td>1072</td>
</tr>
</tbody>
</table>

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Accumulation mode aerosols (0.1–1.0 μm diameter) represent coagulation of ultra-fine nuclei mode particles produced by gas-to-particle conversions, such as SO$_2^-$ from SO$_2$ and NH$_4^+$ from NH$_3$ (Hinds, 1999). The highest scavenging ratios are observed for NO$_3^-$, reflecting enrichment of NO$_3^-$ in snow relative to aerosol by precipitation scavenging of gas-phase HNO$_3$ (e.g., Davidson et al., 1985; Shrestha et al., 2002). Scavenging ratios for Cl$^-$ are twice those observed for Na$^+$, indicating snow scavenging of gaseous HCl, leading to enrichment of Cl$^-$ in snow relative to aerosol and relative to seawater ratios. It is possible that the high scavenging ratios for NO$_3^-$ and Cl$^-$ could partly result from negative sampling artifacts through evaporation of HNO$_3$ and HCl from the filters. However, molar ratios suggest full neutralization of sulfate by the ammonium-rich King Col aerosol observed during the sampling period, suggesting volatilization on the filters by reaction with sulfate acidity may be negligible. Furthermore, the dissociation constant for ammonium nitrate decreases with decreasing temperature and increasing relative humidity (Chang et al., 2000). Since the ambient temperature at King Col did not exceed 0 °C during the sampling period and relative humidity is likely to approach saturation during precipitation events, the calculated scavenging ratios may not significantly affect evaporative nitrate losses.

As evident from the time series of aerosol and fresh/surface snow chemical concentrations measured at King Col (Fig. 2), increased concentrations in the aerosol are generally reflected by increased concentrations in the snow, and vice versa. To further investigate the relationship between aerosol concentrations and concentrations in snow, linear regressions were performed between aerosol and fresh snow concentrations for each of the nine species measured. Aerosol samples were paired with concurrent fresh snow samples collected immediately after the aerosol sample was collected. We used the mean concentration of the three to five replicate snow samples collected. Correlation coefficients ($r$ values) are low for species associated with sea salt (Na$^+$ and Cl$^-$) and dust particles (Ca$^{2+}$, Mg$^{2+}$, K$^+$), ranging from 0.12 to 0.26. Correlations between aerosol and snow concentrations are also low for NO$_3^-$ ($r = 0.20$). Stronger correlations between aerosol and snow concentrations are observed for species present primarily as accumulation mode aerosols, such as NH$_4^+$ ($r = 0.56$) and SO$_4^{2-}$ ($0.43$). The correlation between aerosol and snow concentrations is also high for C$_2$O$_4^{2-}$ ($r = 0.63$). The high correlation for C$_2$O$_4^{2-}$ could reflect the consistently low concentrations and lack of variability in both the aerosol and snow data.

A significant contribution from gas-phase HNO$_3$ to snow NO$_3^-$ concentrations has already been demonstrated; hence the weak correlation between aerosol NO$_3^-$ and snow NO$_3^-$ is expected. Snow scavenging of gaseous HCl could also explain the weak correlation between aerosol Cl$^-$ and snow Cl$^-$. Greater spatial variability in fresh snow concentrations for species associated with dust and sea-salt particles may contribute to weak correlations between aerosol and snow concentrations. The coefficient of variation (standard deviation divided by mean) for replicate snow samples is considerably higher for species present as coarse mode dust (Ca$^{2+}$, Mg$^{2+}$) and sea-salt (Na$^+$, Cl$^-$) particles (0.46–0.73) than for species associated with accumulation mode aerosols such as NH$_4^+$ (0.23) and SO$_4^{2-}$ (0.12). The greater spatial variability in fresh snow concentrations for coarse mode particles could weaken the relationship between aerosol and snow concentrations for Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, and Cl$^-$.

Interestingly, the coefficient of variation is significantly lower for Cl$^-$ (0.46) compared to Na$^+$ (0.73) since scavenging of gaseous HCl is an important contributor to snow chloride concentrations. Likewise, a low coefficient of variation for replicate snow samples was also observed for NO$_3^-$ (0.17) since scavenging of gas-phase nitrate is an important control on snow NO$_3^-$ concentrations. Greater spatial variability for species present as coarse mode particles relative to species found primarily in the accumulation mode or gas phase is a consistent result of snow chemistry surveys (Dibb and Jaffrezo, 1997; Yalcin et al., 2006a, b).

Differences between the observed aerosol and snow concentrations could also be a result of compositional differences between the aerosol sampled at ground level and aerosol concentrations at the heights where snow is forming (e.g., Dibb and Jaffrezo, 1997), as well as differences in the time integrated by aerosol and snow samples. However, the high elevation of King Col often results in orographic precipitation due to upslope flow, and hence snowflakes are forming at altitudes similar to King Col during such episodes. The degree of snowflake riming could also affect the relationship between aerosol and snow concentrations because of different scavenging efficiencies for rimed snow, unrimed snow, and fog (Bergin et al., 1995). This
idea is supported by two observations. First, fog was a common occurrence at King Col during the sampling period. Second, replicate fresh snow and rime samples collected concurrently from a clean surface on 4 June showed consistently higher concentrations in rime relative to snow samples. Enrichment in rime relative to snow ranged from 21% for NH$_4^+$ and 46% for SO$_4^{2-}$ to as much as 80–95% for dust and sea-salt species and 102% for NO$_3^-$. Hence, the extent of riming may affect the relationships between aerosol and snow chemistry to a greater degree for dust, sea salt, and NO$_3^-$. However, because rime samples were collected on just a single day, more work is needed to quantify the relative importance of riming for air–snow relationships at King Col.

4. Conclusions

King Col, a remote high elevation site in the St. Elias Mountains, provides a unique platform to sample the aerosol chemistry in the remote free troposphere. Ammonium and sulfate are highly correlated in the King Col aerosol ($r = 0.90$) with a mean NH$_4^+/SO_4^{2-}$ molar ratio of 2.16 indicating their presence as (NH$_4$)$_2$SO$_4$. Dust species (e.g., Ca$^{2+}$) are well correlated with SO$_4^{2-}$ ($r = 0.75$) and NO$_3^- (r = 0.91$), implying uptake by dust particles. Nitrate is also well correlated with NH$_4^+$ ($r = 0.73$), which together with the high NH$_4^+/SO_4^{2-}$ ratio suggests NH$_4$NO$_3$ aerosol may also be present. However, there is an excess of SO$_4^{2-}$ charge equivalents relative to NH$_4^+$ in 49% of the samples. Volatilization of HCl by reaction with unneutralized SO$_4^{2-}$ may explain the Cl$^-$ deficiency in King Col aerosol relative to seawater.

An understanding of the relationships between aerosol and snow chemistry in the St. Elias Mountains is also needed because a suite of ice cores have recently been collected from this region, including one from King Col Fresh snow chemistry generally mimics aerosol chemistry with similar relative abundances and interspecies relationships except for large enrichments in snow Cl$^-$ and NO$_3^-$. Relative to aerosol due to snow scavenging of gas-phase HCl and HNO$_3$. Although relatively strong correlations between aerosol and snow concentrations were observed for species associated with accumulation mode aerosols, such as NH$_4^+$ ($r = 0.56$) and SO$_4^{2-}$ ($r = 0.43$), only weak correlations were observed for dust and sea-salt species. These results may be influenced by greater variability in replicate snow samples for species associated with coarse mode dust and sea-salt particles. Snow scavenging of gas-phase HCl and HNO$_3$ influences relationships between aerosol and snow chemistry at King Col. Snowflake riming and fog deposition may also influence these relationships, although more work is needed to quantify the importance at King Col.

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