SULFUR DIOXIDE INCORPORATION INTO ICE DEPOSITING FROM THE VAPOR

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Abstract. An experimental study has been made of the incorporation of SO₂ into ice depositing from the vapor at -15°C. Surprisingly, SO₂ was captured in deposited ice at concentrations comparable to those given by SO₂/NO₃ aqueous equilibrium at 0°C. A consequence of this result is that, in the remote troposphere, unrimed snow scavenging ratios for SO₂ may be comparable to those for sulfate. In addition, ozone and HCHO appeared to inhibit, rather than enhance, SO₂ uptake. An aqueous-film model is developed to account for SO₂ capture. If SO₂ dissolves in a liquid-like layer on growing ice surfaces, the concentration of S(IV) species may become enhanced within the layer as a result of retarded diffusional transport away from the advancing ice-layer interface. Such a concentration increase can produce significant solute incorporation into the bulk ice, despite effective solute rejection from the ice.

Introduction

Previous investigators have felt that trace gas scavenging by falling snow could be significant because of the large surface area available for gas adsorption and dissolution [Junge, 1977; Slinn, 1983]. However, with the exception of highly water soluble gases such as HNO₃ [Huebert et al., 1983], such scavenging has been largely ignored, probably for two main reasons. First, solutes are excluded from the ice crystal structure in freezing aqueous solutions [Gross, 1968]; by reasonable extension, it might be assumed that the interaction of most gases with ice should be small. Second, the scavenging of supercooled droplets and their dissolved solutes by snow crystals upon riming appears efficient enough to explain much of the chemical burden found in snow [Junge, 1977; Scott and Lauferen, 1979; Barrie, 1985].

This investigation has dealt with the question of whether significant amounts of SO₂ might be incorporated into ice growing from the vapor. To the authors' knowledge, this is the first study of its kind; previous works have dealt with SO₂ incorporation into riming ice [Iribarne et al., 1983; Lamb and Blumenstein, 1987] or SO₂ adsorption onto ice surfaces [Lee and Kinsley, 1986; Sommerfeld and Lamb, 1986].

Experimental Procedure

The experimental setup is illustrated in Figure 1. The apparatus was located within the inner chamber of a walk-in cold room maintained at T = -15°C (41.5°F). A continuous flow of outside air was brought to ice saturation at the temperature of the inner chamber by warming the air below its frost-point temperature in two steps; condensation/deposition ceased in the air input line upon temperature equilibration. Traps permitted the removal of deposited ice between runs; nevertheless, fluctuations in airflow (and hence SO₂ concentration) occurred on a few occasions because of obstructing ice. After passing through a glass wool filter to remove any suspended ice crystals, the main airflow received a small side flow of dry SO₂ (Matheson, 24 parts per million by volume pptm) in N₂. The airflow (with SO₂), at near 100% ice saturation and free of suspended ice particles, then passed into the ice collector, where slight cooling permitted the deposition of ice from the vapor onto a prepared ice substrate.

To avoid riming or wet deposition, it was necessary to keep the temperature difference between the ice substrate (T₁) and the incoming air (T), ∆T = T₁ - T, well below theoretical water condensation. At T = -15°C, water condensation can occur if ∆T > 1.6°C [List, 1971]. It was not possible, however, to directly measure ∆T with great accuracy, since ∆T was not only very small, but also varied with position. Temperature gradients existed across and through the growing ice substrate, as a result of ventilation and heat exchange above and cooling from below. Rimming could be made highly unlikely by maintaining the measured ice-collection rate r₁ (g h⁻¹):

\[ r₁ = F \left[ \rho_r(T₁) - \rho_s(T₁) \right] \]  \hspace{1cm} (1)

well below the theoretical critical rate (g h⁻¹)

\[ r_c = F \left[ \rho_w(T₁) - \rho_s(T₁) \right] \]  \hspace{1cm} (2)

where \( \rho_w \) and \( \rho_s \) are the water and ice saturation vapor densities (g m⁻³), respectively, and F is the airflow rate (m³ h⁻¹), if collection is complete (see below) and not kinetically limited. In general, \( r₁ \) was maintained at half the value of \( r_c \), giving strong assurance that riming did not occur.

The design of the ice collector had to satisfy several criteria. First, the amount of water frozen to prepare an initial ice substrate had to be minimized, in order to limit the extent of S(IV) dilution after melting. Second, the ice-substrate surface area had to be maximized, to
ensure that complete temperature equilibration between the ice and incoming air had occurred. Third, the surface-area ratio of wettable (but SO_2 exposed) collector wall to ice substrate had to be minimized, in order to reduce the contribution of wall-adsorbed SO_2 to the melt. Fourth, the ice collector had to be light in weight, in order to permit an accurate measurement of the small weight of ice deposited from the vapor. Lastly, the ice collector had to permit uniform cooling of the ice substrate to promote ice deposition.

A lightweight flat-bottomed, polystyrene petri dish (8.7 cm diameter, 1.2 cm deep, approximately 9 g in weight) was chosen as the preferred ice collector. The inside surface of the petri dish was scored by sandpaper and pretreated with concentrated H_2SO_4 to create a sulfonated surface that would wet easily. Only 2 mL of water were required to coat the flat interior of the dish. This water was then frozen to create the initial ice substrate. Sixteen evenly spaced holes in the rim of the petri dish permitted easy escape for the air introduced at the center of the dish. The dilute SO_2/airflow entered the lid of the ice collector via a tube (L = 6.7 cm, ID = 3.0 cm) small enough to allow the flow to impinge on the ice surface and to cause appreciable vapor deposition.

Ice collection generally ceased at about half the radius of the ice collector, indicating that incoming air and ice surface temperature equilibration had occurred.

Experiments showed that, at low SO_2 concentrations (<20 parts per billion by volume (ppbv)), the total amount of sulfur adsorbed in an empty dish was comparable to the total amount incorporated by depositing ice when an ice substrate was present. This result suggested that for experiments where ice was depositing on an ice substrate, the proportion of the sulfur found in the melt as a result of adsorption on the ice collector walls should be roughly equivalent to the surface area ratio of exposed, wettable, ice substrate wall to ice substrate. This surface area ratio was reasonably low (0.1). Therefore the deposition data given in this paper may overestimate actual deposition to ice by up to 10% at low SO_2 concentrations. At higher SO_2 concentrations, experiments showed that the proportion of total sulfur found in the melt due to adsorption was much less.

The ice collector sat upon and was cooled by downward heat transfer through a portable aluminum plate, which sat, in turn, on a copper chamber through which refrigerant, chilled with respect to the cold room, was pumped. Good heat transfer between dish and plate was maintained by clamping the two together during a run.

To begin an experiment 7 mL of deionized water were placed in the lower half of the petri dish and mixed. Five milliliters of the water were withdrawn to serve as a blank, and the remaining 2 mL were frozen by putting the petri dish on the precooled aluminum plate and placing the dish and plate in a freezing environment (the walk-in cold room). While the water was freezing, a plastic shell was placed over the dish to exclude stray SO_2.

The weight of collected ice was determined by weighing the ice collector immediately before and after each run on a balance at room temperature (and humidity). The balance was capable of determining weights to 30,000 g. Changes in weight due to uptake of condensation on the cold dish could not be avoided, but, since the weighing conditions (dish temperature, ambient humidity) and procedure were similar for both weight determinations, error in the weight of collected ice could generally be held to ±0.009 g.

After runs, the ice was melted at room temperature. Roughly 12 min passed from the initiation of warming to sample analysis. Anion concentrations in the melt were determined by ion chromatography (Dionex). Total SO_3 deposited was the sum of aqueous sulfate and bisulfite; oxidation during analysis was not inhibited but was small. Melt pH was not measured.

SO_2 in the feed gas (prior to dilution with air) was provided at 1-35 mL min^-1 and determined by trapping in a bubbler containing 15 mL of NaOH, to which a few drops of 3% H_2O_2 had been added. Sulfate was determined by ion chromatography (Dionex) after heating the solution to boiling to destroy remaining H_2O_2. SO_2 concentrations in the main airflow after dilution ranged from close to common urban values (10 ppbv) to much higher levels (400 ppbv).

Ozone could be produced by passing dry compressed air at 10 mL min^-1 through an ultraviolet ozone generator into the main airflow just upstream of the SO_2 entrance. Ozone concentrations in the main airflow were monitored with calibrated Desibi 1003-AH analyzer. Radical production was taken to be negligible.
Low concentrations of formaldehyde could be generated (at T = -15°C) by passing dry compressed air at 10 ml min⁻¹ past a diffusion tube containing Formalin solution; high concentrations were generated by passing the compressed air directly through an impinger containing Formalin solution. The HCHO-laden air was then passed into the main airflow. As will be seen below, SO₂ uptake was relatively insensitive to HCHO concentrations; therefore, only approximate HCHO concentrations were determined (in the compressed airflow by the chromotropic acid method [Brieger and Johnson, 1945]).

The main airflow (1.5-3.0 L min⁻¹) was generated by a stainless steel bellows pump. Flows were regulated by constrictions and checked periodically by water volume displacement; they remained constant to within about 5% during any set of runs (in the absence of ice blockage).

### Results

A total of 132 experiments on SO₂ uptake by depositing ice were done. These data fell into nine sets: three preliminary, five regular, and one in the presence of O₃ or HCHO. Sets were distinguished from each other primarily by SO₂ concentration. Regular data sets were distinguished from preliminary data sets by several procedural differences that made the determination of collected ice mass more accurate. The data for the first and second sets (preliminary) were collected at -7°C (±2°C), as opposed to -15°C (±1°C) for the others, but not enough data were collected to permit conclusions to be made about the temperature dependence of SO₂ incorporation. Data from two of the better sets are given in Tables 1 and 2, and the results are plotted in Figure 2.

It is apparent from Figure 2 that the amount of total sulfur [S(IV) + S(VI)] incorporated into the ice increased linearly with the amount of ice deposited. The slope of the regression line through the data gives the concentration of total sulfur incorporated into the deposited ice.

The regression line slopes (i.e., total sulfur concentrations) for the five regular sets of data

| Amount of Ice Collected, SO₂ Collected, Time, Percent Run | Amount of | Run | Time, Percent
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Run g</td>
<td>10⁻² g</td>
<td>hour Oxidized</td>
<td></td>
</tr>
<tr>
<td>IB 103</td>
<td>0.159</td>
<td>5.53</td>
<td>11.86</td>
</tr>
<tr>
<td>IB 104</td>
<td>0.181</td>
<td>7.39</td>
<td>12.69</td>
</tr>
<tr>
<td>IB 105</td>
<td>0.075</td>
<td>3.49</td>
<td>5.95</td>
</tr>
<tr>
<td>IB 106</td>
<td>0.287</td>
<td>9.19</td>
<td>22.70</td>
</tr>
<tr>
<td>IB 107</td>
<td>0.163</td>
<td>4.85</td>
<td>11.58</td>
</tr>
<tr>
<td>IB 108</td>
<td>0.109</td>
<td>3.73</td>
<td>7.41</td>
</tr>
<tr>
<td>IB 109</td>
<td>0.194</td>
<td>7.15</td>
<td>14.21</td>
</tr>
<tr>
<td>IB 110</td>
<td>0.049</td>
<td>2.12</td>
<td>4.07</td>
</tr>
<tr>
<td>IB 111</td>
<td>0.220</td>
<td>7.61</td>
<td>18.29</td>
</tr>
<tr>
<td>IB 112</td>
<td>0.040</td>
<td>1.84</td>
<td>3.82</td>
</tr>
<tr>
<td>IB 113</td>
<td>0.177</td>
<td>5.41</td>
<td>14.85</td>
</tr>
</tbody>
</table>

SO₂ concentration was 47 ppbv.

a Upon analysis.

### Table 2. Seventy Data Set

<table>
<thead>
<tr>
<th>Amount of Ice Collected, SO₂ Collected, Time, Percent Run</th>
<th>Amount of</th>
<th>Run</th>
<th>Time, Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run g</td>
<td>10⁻² g</td>
<td>hour Oxidized</td>
<td></td>
</tr>
<tr>
<td>IB 97</td>
<td>0.199</td>
<td>18.70</td>
<td>12.44</td>
</tr>
<tr>
<td>IB 98</td>
<td>0.015</td>
<td>3.76</td>
<td>3.78</td>
</tr>
<tr>
<td>IB 99</td>
<td>0.217</td>
<td>19.10</td>
<td>15.51</td>
</tr>
<tr>
<td>IB 100</td>
<td>0.069</td>
<td>4.92</td>
<td>4.99</td>
</tr>
<tr>
<td>IB 101</td>
<td>0.156</td>
<td>12.20</td>
<td>13.13</td>
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<tr>
<td>IB 102</td>
<td>0.106</td>
<td>9.10</td>
<td>6.56</td>
</tr>
<tr>
<td>IB 103</td>
<td>0.228</td>
<td>18.94</td>
<td>12.61</td>
</tr>
<tr>
<td>IB 104</td>
<td>0.111</td>
<td>8.20</td>
<td>6.90</td>
</tr>
<tr>
<td>IB 105</td>
<td>0.273</td>
<td>23.69</td>
<td>15.37</td>
</tr>
<tr>
<td>IB 96</td>
<td>0.301</td>
<td>20.49</td>
<td>17.10</td>
</tr>
<tr>
<td>IB 97</td>
<td>0.055</td>
<td>4.43</td>
<td>3.55</td>
</tr>
<tr>
<td>IB 98</td>
<td>0.239</td>
<td>16.58</td>
<td>13.55</td>
</tr>
<tr>
<td>IB 99b</td>
<td>0.360</td>
<td>14.89</td>
<td>12.59</td>
</tr>
<tr>
<td>IB 100b</td>
<td>0.207</td>
<td>9.63</td>
<td>6.83</td>
</tr>
</tbody>
</table>

SO₂ concentration was 124 ppbv.

a Upon analysis.

b Collected under rising or near-rising conditions.

As well as the others are listed in Table 3. In general, as the SO₂ concentration increased, the total incorporated sulfur concentration increased, though not linearly. The y intercepts of the regression lines, indicative of SO₂ incorporation in the absence of ice deposition, do not appear to be related to SO₂ concentration, though, in general, they are positive. High y intercepts do seem to correspond with data sets with low r² values, however.

The concentrations of total sulfur incorporated into depositing ice as a function of SO₂ concentration, determined from Table 3 and expressed as equivalent S(IV) concentrations, are plotted as points in Figure 3. Also included in Figure 3 are curves indicating the concentration of aqueous S(IV) in equilibrium with SO₂ and atmospheric CO₂ at two temperatures, -15°C and 0°C. The curves were calculated using reactions, equilibrium constants, and NH₄⁺ values tabulated by Bales et al. 1987. Remarkably, depositing ice incorporated total sulfur in roughly the same proportion as if the depositing ice were liquid water in equilibrium with SO₂ at 0°C in the absence of sulfate acidification. Since most of the total sulfur was recorded as S(IV) (see Tables 1 and 2), it is plausible that SO₂ was incorporated as S(IV) and oxidized upon melting to S(VI). The striking parallel between SO₂ uptake by liquid water and ice is highly suggestive of a role for liquid water (bulk or quasi-liquid) in the uptake of SO₂ into ice.

It does not seem likely that adsorption alone is responsible for SO₂ incorporation into depositing ice; the amounts of SO₂ trapped were too large. In a typical run at -15°C, 3 x 10⁻⁷ g SO₂ were deposited on 59 cm² of ice at 50 ppbv SO₂. This corresponds to a surface density of 5 x 10¹² molecules SO₂ cm⁻², some 200 times higher than typical amounts adsorbed at much higher SO₂ concentrations (2.5 x 10¹¹ molecules SO₂ cm⁻² at 2 ppmv SO₂ near T = -15°C; Sommerfeld and Lamb, 1986).
Partial $SO_2$ exclusion from riming ice (compared to aqueous $SO_2/S^{(IV)}$ equilibrium) is evident for the two open-squares data points in Figure 2b. The ice collection rate for both runs approached the critical ice collection rate for the onset of riming. $SO_2$ exclusion was also evident for the first set of data (preliminary), where ice collection rates were several times higher than those necessary to initiate riming. $SO_2$ exclusion from riming ice has been noted before by Irigares et al. [1983]; Lamb and Blumenstein [1987] have linked the amount of exclusion to the extent of supercooling.

The percentage of oxidized sulfur in the melt varied unsystematically: 25-55% for runs through the fourth data set, 5-25% thereafter. The cause of the drop was never clarified. Standard S(IV) solutions typically underwent 3-5% oxidation during chromatography. Oxidation was elevated among samples exposed to ozone and not diminished among samples exposed to HCHO. Formaldehyde was not detected in measurable concentrations in the ice.

The amounts of total sulfur incorporated into the ice in runs where conditions led to net sublimation were low and roughly constant. This result indicated that most of the total sulfur observed in these cases resulted from dissolution of wall-adsorbed $SO_2$ into the melt or from the coexistence of regions of deposition and sublimation in the same run (due to ventilation-caused radial temperature gradients). Data collected under conditions of net ice sublimation were not used in determining regression line slopes (Table 3).

The experiments were conducted in the presence of other trace gases ($O_3$ and HCHO) to see if chemical interactions could fix $SO_2$ more readily into the ice and lead to enhanced collection. Though the data were relatively few, it appeared that the uptake of $SO_2$ into the ice was certainly not enhanced and may have been inhibited by as much as 50% by the presence of these trace gases, as determined by the slope of the regression line (ninth data set; Table 3). The inhibitory effect appeared to be insensitive to trace gas concentrations. Despite the different experimental conditions and the variable trace gas concentrations, the regression line has a fairly high $r^2$ value (0.93).

Model

It has been surmised that there exists on the surface of ice a liquid-like interfacial layer; it has been equated to surface roughening of a crystal as its melting temperature is approached. Reviews on the topic are available [Jellinek, 1967; Kenow, 1984]. It is plausible that $SO_2$ dissolves in this interfacial layer in amounts close to $SO_2/S^{(IV)}$ aqueous equilibrium. What seems remarkable is that as this layer advances, by deposition ahead and ordering (freezing) behind, the dissolved $SO_2$ is apparently included in, rather than excluded from, the growing ice.

The phenomenon of inorganic ion exclusion from ice has been investigated by Gross [1968] and by Gross et al. [1987]. The distribution coefficient $k_d$ (defined as the equilibrium ratio of solute concentration by mass in ice to that in water) for chloride is reported to be $3 \times 10^{-3}$ [Gross et al., 1987]. Distribution coefficients for nitrate and sulfate are apparently small ($<10^{-3}$) [Cobb and Gross, 1969]. A $k_d$ for bisulfite has apparently not been measured, though it is undoubtedly $<<1$, since $SO_2$ is excluded from rimed ice. The model below suggests a means whereby the amount of S(IV) incorporated into ice can be comparable to aqueous S(IV) in equilibrium with $SO_2$, despite low $k_d$.

There is a considerable body of work [see Gross, 1968] indicating that as a solid (in this case, ice) advances rapidly into a semi-infinite column of liquid (water), the solute concentration in the ice at steady state may rise to approach the initial solute concentration in the
### Table 3. SO₂ Concentration and Regression Line Information for the Experimental Data

<table>
<thead>
<tr>
<th>SO₂ Concentration, Data, ppbv</th>
<th>Deposited SO₂ B Concentration, μM S(IV)</th>
<th>Intercept, 10⁻⁶ g SO₂</th>
<th>r²</th>
<th>Number of Data Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular Runs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>52</td>
<td>1.0</td>
<td>0.62</td>
</tr>
<tr>
<td>8</td>
<td>47</td>
<td>46</td>
<td>0.7</td>
<td>0.94</td>
</tr>
<tr>
<td>5</td>
<td>77</td>
<td>57</td>
<td>2.9</td>
<td>0.48</td>
</tr>
<tr>
<td>7</td>
<td>124</td>
<td>115</td>
<td>1.2</td>
<td>0.93</td>
</tr>
<tr>
<td>6</td>
<td>409</td>
<td>211</td>
<td>-1.9</td>
<td>0.84</td>
</tr>
<tr>
<td>Runs With O₃ and HCHO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>65</td>
<td>35</td>
<td>0.2</td>
<td>0.93</td>
</tr>
</tbody>
</table>

**Notes:**

- **SO₂ concentration in the deposited ice is given as μM S(IV) in the melt, and represents the slope of the regression line.**
- **The intercept of the regression line is indicative of SO₂ uptake in the absence of ice deposition.**
- **Regular runs are ordered by SO₂ concentration.**

**Figure 3.** Data points are the total sulfur uptake into deposited ice, in equivalent S(IV) units, as given in Table 3. The curves are the calculated dissolved S(IV) in equilibrium with the gas phase, at 0 °C and -15 °C.

**Equation 3:**

\[
\text{SO}_2^{\text{aq}} + \text{H}_2\text{O} + \text{HSO}_3^+ + \text{SO}_3^{2-} \quad \text{at air-ice interface (C)}_1, \quad \text{is in equilibrium with the uniform atmospheric concentration (C)}_A
\]

**Equation 4:**

\[
C_1 = K_A C_A
\]

**Equation 5:**

\[
\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} + R \frac{\partial C_1}{\partial x}
\]

**Figures:**

- **Figure 4.** Conceptual model of concentration enhancement in an interfacial layer on the surface of ice. The reference frame is fixed with respect to the advancing film. An effective Henry's Law equilibrium for all S(IV) species is maintained at the upper interface; solute exclusion from the ice occurs at the lower interface. If Rd/D >> 1, C₁ = C₁ (see equation (8)).
for all $x > 0$, (2) $C = C_1$ as $x \to \infty$ for all $t$, and (3) $2C/\partial x = -q(R/\partial t)C$ at $x = 0$ for all $t$, where $q = 1 - k_d$. Boundary condition (3) is required by mass conservation at the ice-film interface. The solution is given by

$$C(x,t) = C_1 F(x,t)$$

where

$$F(x,t) = 1 + \left[ \frac{q}{2k_d} \exp(-Rx/D) \operatorname{erfc} \left[ \frac{1}{2} \left( \frac{1}{D} \frac{1}{x} \right)^{1/2} \right] \right]$$

- $\frac{1}{2} \operatorname{erfc} \left[ \frac{1}{2} \left( \frac{1}{D} \frac{1}{x} \right)^{1/2} \right]$

- $\left[ \frac{1}{2} \left( \frac{1}{D} \frac{1}{x} \right)^{1/2} \right]$

- $\exp \left[ -qR(x + k_d) \frac{1}{D} \right]$

- $\operatorname{erfc} \left[ \frac{1}{2} \left( \frac{1}{D} \frac{1}{x} \right)^{1/2} \right]$

(7)

[Smith et al., 1955; Eq. 26].

In the case of an interfacial layer, $SO_2 / S(IV)$ aqueous equilibrium at $x = d$ will cause replacement of boundary condition (2) to condition (4): $C = C_1$ at $x = d$ for all $t$.

The time-dependent solution to (5), subject to boundary conditions (1), (2), and (4), was not determined, because of problems in inverting the Laplace transform. The steady state solution to (5) for the liquid film is given by

$$C(x) = C_1 \left[ 1 + \frac{q \exp(-dx/D)}{k_d} \right]$$

(8)

If $Rd/D \gg 1$, $C(0) = C_1/k_d$ and $C_1 = C_1$. (Note that in the case of a "real" interfacial layer, where degree of order increases with depth, boundary condition (3) gives an upper limit to the concentration gradient.)

Diagrams of "acceptable" values of $R$ and $D$ for two values of $D$ (3 and 30 mm), given three values of $k_d$ ($10^{-2}$, $10^{-3}$, $10^{-4}$), are given in Figures 5a and 5b. Acceptability is determined by the ability of $C_1$ to reach or exceed $67\%$ of $C_1$ based on ($R$). The value of $67\%$ was chosen, since uptake of total sulfur into the ice was roughly two-thirds the value of aqueous $S(IV)$ equilibrium at $-15^\circ C$. In the experiments (Figure 3).

Discussion

There is considerable uncertainty about how large the film thickness ($d$) of the quasi-liquid layer might be. Many works suggest that $d$ is strongly dependent on temperature below $0^\circ C$ and not thicker than 5 nm below $-1^\circ C$ [Fletcher, 1962, 1968; Fukuta, 1987; Furukawa et al., 1987]. In the presence of impurities the layer may be somewhat thicker [Furukawa et al., 1987], perhaps as thick as 30 nm at $-15^\circ C$ [Golec, 1978]. The $SO_2$ adsorption data of Sommerfeld and Lamb [1986] have been shown to be consistent with equilibrium between $SO_2$ and an aqueous layer 17 nm thick at $-11^\circ C$ (D. Mitchell, personal communication, 1988, inter alia).

There are more data on growth rates. Plate-like habits are generally found for crystals grown from the vapor at $T = -15^\circ C$ [Hobbs, 1974]. The interface velocity of the prism face of an ice crystal falling through the atmosphere, growing at its limiting thickness of $2c = 40 \mu m$ (where $c$ is half the length of the crystal along its $c$ axis), can be calculated at $R = 10^{-25} cm s^{-1}$ in an environment at water saturation [Mason, 1957; pp. 186-189]. Somewhat higher interface velocities have been reported for the prism face at a lower excess vapor pressure over ice ($R = 4 \times 10^{-5} cm s^{-1}$ at $1.3 \times 10^{-2} mb$ excess vapor pressure at $T = -15^\circ C$; Hobbs and Lamb [1971]). Referring to Figure 5, it can be seen that these interface velocities place rather stringent limitations on the maximum acceptable size of the diffusional constant $D$.

These limitations can be relaxed somewhat by recognizing that ice crystals generally do not grow by the propagation of a rough interface normal to the macroscopic interface plane (at rate $R$). Instead, ice crystals usually grow by the propagation of steps (at rate $R'$) from emergent screw dislocations. For a 25-μm-tall step, velocities $R'$ of the order of $5 \times 10^{-4} cm s^{-1}$ are suggested by Hallett [1961] and Kobayashi [1967]; velocities $R'$ of the order $10^{-4} cm s^{-1}$ can be inferred from the calculations of Kuroda [1982].

Data on diffusion constants of the (presumably ionic) solutes in the interfacial film are apparently nonexistent; values would be
expected to lie between those for bulk water ($D = 10^{-5} \text{ cm}^2 \text{s}^{-1}$) and those for bulk solids, e.g., minerals ($D = 10^{-15} \text{ cm}^2 \text{s}^{-1}$). High diffusion constants have been deduced by Barnaal and Slottfeldt-Ellingsen [1983] for 
HNO$_3$, HCl and NaCl in ice stored at -30°C ($D = 4 \times 10^{-9} \text{ cm}^2 \text{s}^{-1}$). The equality of the values for these three solutes is hard to reconcile, however. HF has been reported to diffuse rapidly in ice ($D = 10^{-7} \text{ cm}^2 \text{s}^{-1}$) [Haltenerth and Klinger, 1969]. None of these solutes may have been ionic, however; no data for ionic diffusion in ice have been found, though because of charge interaction they may be much smaller than the constants for self-diffusion (i.e., of H$_2$O) in ice, which are available.

Near -15°C, Dengel and Nieh [1963] obtained a self-diffusion constant of $2 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}$; Itagaki [1967] and Ramsayer [1967] obtained $10^{-11} \text{ cm}^2 \text{s}^{-1}$. Recently, Mizuno and Hansfusue [1987] reported the self-diffusion constant in the quasi-liquid layer on ice ($1.8 \times 10^{-9} \text{ cm}^2 \text{s}^{-1}$ at -15°C). This can be regarded as an upper limit for the solute diffusion constant D in the quasi-liquid layer. On the basis of this prior work, solute diffusion constants in the layer will probably fall in the range $10^{-13} \leq D < 10^{-9} \text{ cm}^2 \text{s}^{-1}$. Referring back to (8) and Figure 5, the model is consistent with observed sulfur concentrations in ice, provided $R' \Rightarrow D$. If $5 \times 10^{-6} \text{ cm}^2 \text{s}^{-1} > R' > 10^{-4} \text{ cm}^2 \text{s}^{-1}$ and $d = 30 \text{ mm}$ or $3 \text{ m}$, D cannot exceed $2 \times 10^{-10}$ or $4 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}$. The possibility that diffusion can be delayed by the formation of an SO$_2$ hydrate cannot be dis- missed [Fezza and Calo, 1982], though clathrate hydrate formation seems unlikely, because of the extremely low pressure of SO$_2$ [Berezcz and Balilla-Acha, 1983].

Equation (7) suggests that the incorporation of SO$_2$ into depositing ice can be strongly dependent on the interface velocity rate $R$ and therefore on the ice collection rate, but only over certain ranges of $R$. The data from this experiment are examined, no dependence on the collection rate can be distinguished; however, the experiment was not designed to observe such a dependence.

It should be noted that enhanced uptake of SO$_2$ could result from preferential adsorption at grain boundaries of polycrystalline ice. The density of grain boundaries in the ice surface given in this study is unknown. This phenomenon is thought to be partly responsible for the large and rapid uptake of HCl at -10°C noted by Molina et al. [1987].

Applications

The scavenging ratio $W$, a dimensionless ratio linking contaminant concentrations in precipitation and in air, is defined by

$$W = \frac{X_p}{X_a} \rho$$

(9)

where $X_p$ ($\mu g \text{ g}^{-1}$) is the contaminant concentration in precipitation, $X_a$ ($\mu g \text{ m}^{-3}$) is the contaminant concentration in air, and $\rho$ ($g \text{ m}^{-3}$) is the average air density. Figure 6 gives the scavenging ratio to be expected for SO$_2$ by liquid water at 0°C; it is based on equilibrium calculations in the absence of acidifying sulfate. From the experimental data given here, the scavenging ratios of SO$_2$ by unrimed snow should be approximately the same.

High SO$_2$ scavenging ratios by snow will be most significant in those regions where unrimed snow is common, and where SO$_2$ concentrations are low (<1 ppbv) yet equal or exceed sulfate concentrations. For typical SO$_2$ concentrations near 0.3 ppbv over Greenland [Flyger et al., 1976a], Figure 6 suggests that scavenging ratios by unrimed snow in the range 300-500 could be expected, easily dominating sulfate scavenging ratios of 100-200 reported for unrimed snow by Davidson et al. [1987]. Since mean SO$_2$ concentrations typically exceed sulfate concentrations by 250% over Greenland [Flyger et al., 1976], it can be calculated that close to 50% of the sulfate in unrimed snow may be due to SO$_2$ uptake, not particulate sulfate capture. This percentage is probably an upper limit for polar snows, since sulfate concentrations will exceed SO$_2$ concentrations in many other remote areas (e.g., Antarctica). Nevertheless, it is clear that under certain cold conditions, SO$_2$ scavenging can rival particulate sulfate scavenging as a source for sulfate in unrimed snow.

The reason SO$_2$ is more completely excluded from riming water droplets than from depositing ice may be because an effective transport mechanism (diffusion in bulk liquid water) exists for the removal of SO$_2$ from freezing water, provided contact with the surrounding air is maintained. The warming of freezing water droplets towards 0°C by latent-heat release and delayed solidification promotes SO$_2$ escape. Pronounced supercooling aids SO$_2$ capture, since droplets will freeze more rapidly and form more traps for dissolved SO$_2$ at colder temperatures [Lamb and Blumenstein, 1987].
In rimed snow, SO$_2$ scavenging is negligible compared to sulfate scavenging, because of the exclusion of SO$_2$ from freezing droplets [Iribarne et al., 1983; Lamb and Blumenstein, 1987], and enhanced particulate sulfate capture [Scott, 1981; Murakami et al., 1981].

Rahn and McCaffrey [1979] and Borys [1983], among others, have suggested that there will be a pronounced fractionation between Arctic snow and aerosol sulfate concentrations, because of the inability of unrimed snow to scavenge sulfate efficiently. If SO$_2$ at concentrations below 1 ppbv represents much of the atmospheric sulfur present, Figure 6 suggests that the fractionation effect might be obscured or erased. The sulfur in the snow would result from SO$_2$, not particulate sulfate scavenging. After oxidation, the original source of the sulfate would be obscured.

Conclusions

SO$_2$ is incorporated into depositing ice in amounts comparable to SO$_2$/S(IV) aqueous equilibrium. This conclusion is based on arguments made at several SO$_2$ concentrations primarily at $-15^\circ$C, and at ice collection rates that ensured the absence of riming.

The presence of ozone and formaldehyde did not enhance SO$_2$ uptake into the ice and they have inhibited it, probably for two reasons: (1) the dramatically lower diffusion constants for S(IV) and other reactants in the surface film would inhibit reaction, and (2) the reactions that did occur (oxidation or adduct formation) may simply serve to destroy the film (with sulfuric acid or H$_2$SO$_4$), lowering the reaction rates yet further and restricting the ability of the surface layer to dissolve S(IV).

Riming leads to decreases in the concentrations of sulfur in the collected ice, as previously reported by Iribarne et al. [1983] and Lamb and Blumenstein [1987].

Not enough data were gathered at temperatures other than $-15^\circ$C to permit conclusions to be drawn about the temperature dependence of SO$_2$ incorporation into depositing ice.

The incorporation of SO$_2$ into depositing ice or growing by vapor deposition at amounts comparable to SO$_2$/S(IV) aqueous equilibrium, despite a low distribution coefficient, may be due to solute concentration enhancement in the liquid-like film present on advancing ice surfaces. The extent of solute enhancement is critically dependent on the diffusion constant (D) of the solute in the film and the interface advance rate (R), as well as the thickness of the film (d). Very low SO$_2$ diffusion constants ($< 10^{-5}$ cm$^2$ s$^{-1}$) are indicated.

The experimental results suggest that unrimed snow SO$_2$ scavenging ratios should approximate those for SO$_2$ by liquid water at 0°C (200-500) at tropospheric background SO$_2$ concentrations (<1 ppbv), comparable to or larger than scavenging ratios for particulate sulfate (100-200, Davidson et al., [1987]).

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