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ANTARCTIC OZONE: METEORIC CONTROL OF HNO_3

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Abstract. Atmospheric circulation leads to an accumulation of debris from meteors in the Antarctic stratosphere at the beginning of austral spring. The major component of meteoric material is alkaline, comprised predominantly of the oxides of magnesium and iron. These metals may neutralize the natural acidity of stratospheric aerosols, remove nitric acid from the gas phase, and bond it as metal nitrates in the aerosol phase. Removal of nitric acid vapor has been previously shown to be a critical link in the photochemical depletion of ozone in the Antarctic spring, by allowing for increased catalytic loss from chlorine and bromine.

Introduction

The rapid decline in stratospheric ozone over Antarctica in the spring [Farman et al., 1985; Stolarski et al., 1986; Hofmann et al., 1987] has led to a number of photochemical theories that relate the depletion of O_3 to the observed buildup of chlorine in the stratosphere [Solomon et al., 1986; McElroy et al., 1986a,b; Tung et al., 1986; Rodriguez et al., 1986a; Crutzen and Arnold, 1986; Molina and Molina, 1987]. These models require that a substantial fraction of the total chlorine liberated from halocarbons (Cl_x) is present in active forms (ClO, Cl_2O_2, $HOCl$) rather than in more photochemically passive reservoirs (HCl, $ClONO_2$). The active forms of Cl_x participate in rapid catalytic destruction of O_3 when sunlight returns to the polar vortex in spring.

For midlatitude conditions, when a substantial fraction of NO_x ($NO+NO_2$) and HNO_3 is removed from photochemical participation in the lower stratosphere, partitioning of the Cl_x family shifts radically from HCl to ClO, and photochemical ozone loss attributable to chlorine and bromine increases substantially [Prather et al., 1979; 1984]. For Antarctic conditions, heterogeneous reactions are likely needed to effect this partitioning. Low NO_x can be achieved either by fast heterogeneous chemistry throughout the early spring [Solomon et al., 1986; McElroy et al., 1986a; Rodriguez et al., 1986a] or by removal of NO_x and HNO_3 from the gas phase [McElroy et al., 1986b; Toon et al., 1986; Crutzen and Arnold, 1986]. In the latter case, reductions of about 90% in gaseous HNO_3 are needed to maintain high levels of active Cl_x throughout September and early October [see Figure 3 of McElroy et al., 1986b]. Formation of polar stratospheric clouds (PSCs) provides only a temporary reservoir for nitric acid; HNO_3 is released upon evaporation of the PSCs unless the cloud particles fall out of the stratosphere. We propose here that permanent removal of HNO_3 vapor is likely to occur when the acid is neutralized by metal oxides in the PSCs.

Ablation of meteoroids provides a source of alkalinity for stratospheric aerosols [Turco et al., 1981]. The dominant components of chondritic meteorites, and presumably meteors, are Si, O, and the metals Mg and Fe [Mason, 1971]. Formation of metal nitrates and sulfates is likely to occur in PSCs, and these neutralized salts remain in the aerosol phase after the clouds evaporate, irrevocably removing HNO_3 from the gas phase. On a global average, meteoric metals are expected to be present in the middle stratosphere at concentrations much less than a part per billion [Rodriguez et al., 1986b], insufficient to neutralize fully the acidity of the Junge sulfate layer [Junge et al., 1961; Rosen, 1971]. Over polar regions, however, meteoric debris accumulates in winter and early spring as a result of the pole-to-pole mesospheric circulation illustrated here in three-dimensional tracer simulations. Largest concentrations of meteoric material in the stratosphere occur in the Antarctic spring in amounts sufficient to neutralize parts per billion of acidic vapor.

The proposed sequence of chemical reactions assumes that, sometime during the polar winter, most of the lower stratosphere is processed through a PSC at least once and hence undergoes heterogeneous chemistry as outlined in Section 2. This process accomplishes two major chemical conversions: NO_x and HNO_3 into metal nitrates which bond to the aerosols, and HCl and $ClONO_2$ into active Cl_x. Depletion of O_3 in the spring thus depends on the amount of HNO_3 sequestered in the aerosols, and hence on the concentration of meteoric metals present in the Antarctic stratosphere, as described in Section 3. Abundances of nitric acid and NO_x in the gas phase will return to typical levels as the Antarctic vortex mixes with air from the midlatitude stratosphere, although photolysis of low levels of HNO_3 could produce the observed increases in column NO_2 before the breakdown of the vortex [Mount et al., 1987]. The observable features of this mechanism and its consequences for the Arctic are discussed in Section 4.

Heterogeneous Conversions and Metal Chemistry

The relevance of heterogeneous reactions in stratospheric chemistry has received increasing attention, see NASA/WMO [1986, pp. 46-48]. Considerable uncertainty exists regarding the rates for heterogeneous reactions in the stratosphere, and also the physical state of PSCs [Steele et al., 1983]. We review here one plausible sequence for the heterogeneous chemistry that involves a liquid phase for PSCs (see Figure 1). This reaction sequence can serve as a paradigm for similar reactions that may occur in the ice phase.

As winter approaches, the predominant forms of total odd-nitrogen in the Antarctic stratosphere are HNO_3, N_2O_5, NO_x and $ClONO_2$, and the major Cl_x reservoirs are HCl and $ClONO_2$. The NO_x will form N_2O_5 during the polar night by

[Fe^{++}]   [Mg^{++}]
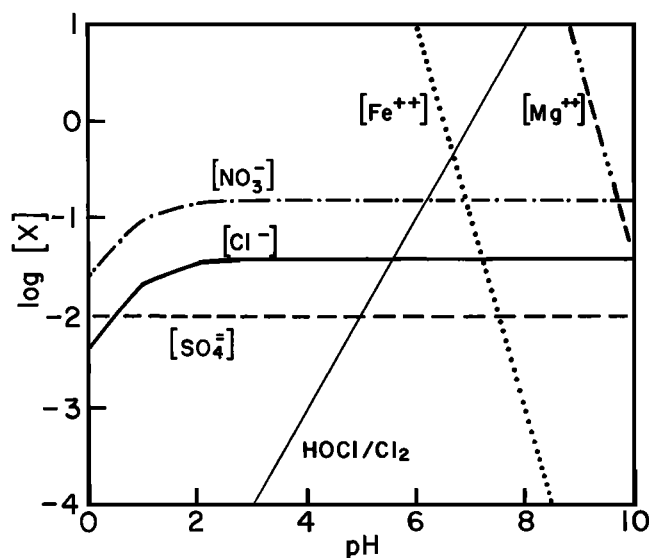
[NO$_3^-$]

[Cl$^-$]

[SO$_4^=$]

HOCl/Cl$_2$

Fig. 1. Chemical equilibrium concentrations [X] (moles/liter) as a function of pH. The model assumes that 3 ppm of H$_2$O condenses at 70 mbar in the presence of 0.5 ppb of H$_2$SO$_4$, 2 ppb of HCl and 8 ppb of HNO$_3$. The fractional volume of liquid is 1.7x10^{-10}. The abundances [SO$_4^-$], [Cl$^-$] and [NO$_3^-$] represent all forms of these gases which are in solution. HNO$_3$ and HCl are almost completely in the liquid phase for pH > 2. The abundances [Mg^{++}] and [Fe^{++}] are calculated with respect to Mg(OH)$_2$ (solid, brucite) and FeO (solid), respectively. Equilibrium constants are evaluated at 273 K [Stumm and Morgan, 1981; Chase et al., 1985]. The species HOCl and Cl$_2$ are mainly in the gas phase, and the value X = HOCl/Cl$_2$ is the relative abundance of these gases in equilibrium with the solution. The H$_2$O and H$_2$SO$_4$ alone would have a pH ~ 1.7, including HNO$_3$ and HCl would decrease this value below 1. The actual acidity of the solution may be controlled by FeO and MgO which, if present in sufficient abundance, could buffer the system to pH > 6.

gas-phase reactions; N$_2$O$_5$ in turn could react with water on surfaces to form HNO$_3$ [Wofsy, 1978].

Reaction sequences for the Cl$_x$ family are more varied but lead to heterogeneous conversion of the major Cl$_x$ reservoirs into Cl$_2$ and HOCl. One such sequence begins with hydrolysis of ClONO$_2$ in water or sulfuric acid [Rowland et al., 1986; Rossi et al., 1987],

$$ClONO_2(g) + H_2O(a) \leftrightarrow HOCl(a) + H^+(a) + NO_3^-(a) \quad (1)$$

where (a) denotes aqueous phase and (g) denotes gas phase. Under PSC conditions with liquid present, high acidities (pH ~ 1) will be maintained by dissolution of hydrochloric and nitric acid vapor, see Figure 1,

$$HCl(g) \leftrightarrow H^+(a) + Cl^-(a) \quad (2)$$

$$HNO_3(g) \leftrightarrow H^+(a) + NO_3^-(a). \quad (3)$$
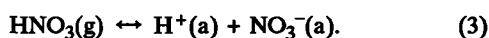
With Cl$^-$(a) present under moderate acidities, the standard chlorine redox equilibrium [e.g., Stumm and Morgan, 1981, p. 444] will favor Cl$_2$(a),

$$Cl^-(a) + H^+(a) + HOCl(a) \leftrightarrow Cl_2(a) + H_2O(a), \quad (4)$$
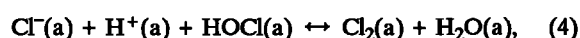
which is relatively insoluble and will be partitioned mostly in the gas phase,

$$Cl_2(a) \leftrightarrow Cl_2(g). \quad (5)$$

Equilibrium balance between Cl$_2$(g) and HOCl(g) is shown in Figure 1; Cl$_2$ is greatly favored for all acidic environments, pH < 7.

The chlorine redox reaction has a stoichiometric ratio of 1:1 and thus the HCl in excess of ClONO$_2$ + HOCl will not be converted to Cl$_2$. Nevertheless, recycling of Cl$_2$(g) by photolysis is possible in the twilight conditions for much of the polar winter. Subsequent oxidation of Cl to ClONO$_2$ or HOCl can lead to further conversion of HCl to active Cl$_x$.

The atmospheric chemistry of sodium has been studied recently [Rodriguez et al., 1986b, and references therein]. Magnesium and iron, however, are predicted to be the dominant metals deposited in the upper atmosphere by meteors, with sodium and other metals present in much lesser abundances. The oxides MgO and FeO are the more likely form of these metals due to their greater stability, and these compounds will be present as dissolved Fe^{++} and Mg^{++} in the acidic environment of PSCs as shown in Figure 1.

$$Mg(OH)_2(s) + 2H^+(a) \leftrightarrow Mg^{++}(a) + 2H_2O(a) \quad (6)$$

$$FeO(s) + 2H^+(a) \leftrightarrow Fe^{++}(a) + H_2O(a) \quad (7)$$
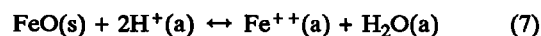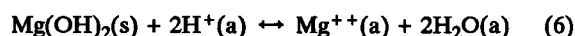
Metal oxides buffer the solution, reducing the concentration of H$^+$. When water evaporates and pH levels fall, not all NO$_3^-$ is released as HNO$_3$(g), but the metal salts, Mg(NO$_3$)$_2$ and Fe(NO$_3$)$_2$, will remain with the aerosol nucleus of the PSC. If metal concentrations are insufficient to neutralize fully the H$_2$SO$_4$, then the aerosols will remain acidic and not retain NO$_3^-$. This latter condition is expected for the lower stratosphere on a global average, but not for the Antarctic spring as shown below.

Global Distribution of Meteoric Material

The distribution of meteoric metals was simulated with a 3-D global tracer model based on a stratospheric general circulation model (GCM) [Rind et al., 1988]. The tracer model is similar to the tropospheric chemical transport model described in Prather et al. [1987] with adaptions for the stratosphere: 7.8° latitude by 10° longitude by 21 vertical layers, with 12 layers between 100 mbar and 0.01 mbar. The second-order moments scheme was used for advection. No explicit stratospheric diffusion was applied in the tracer model although the GCM employed vertical mixing by breaking gravity waves. A globally uniform flux was applied to the upper boundary (0.01 mbar), and tracer reaching the lower troposphere (below 720 mbar) was removed every time step (4 hr). The simulation was initialized with zero concentrations of tracer and run for 7 years until a near steady-state was achieved between the amount removed annually from the boundary layer and the integrated flux in the top.

Meteoric material builds up in the Antarctic stratosphere during the months of May, July and September as shown in Figure 2, and then disperses by November. The pole-to-pole mesospheric circulation produces a substantially different distribution of meteoric gases than that predicted from 1-D models; concentrations below 30 km vary by more than a factor of 15 from equator to pole. The lines in Figure 2
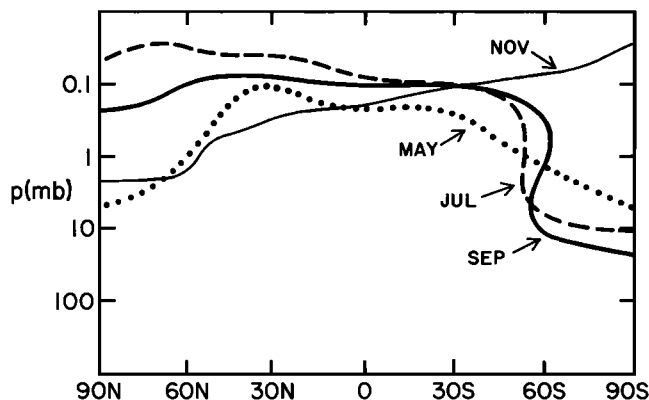
Fig. 2. Zonally averaged, monthly mean extent of meteoritic material. The region above each line represents that portion of the atmosphere with a great enough concentration of metals to neutralize 1 ppb of HNO_3 (i.e., volume mixing ratios in excess of 10 ppt Na, 0.25 ppb Mg, and 0.20 ppb Fe). Results for the months of May, July, September and November show the buildup of high concentrations in the vernal Antarctic stratosphere. The 3-D tracer calculations are based on a stratospheric general circulation model (see text) and assumed a globally uniform flux of 10^4, 2.5×10^5, 2×10^5 atoms cm^{-2} s^{-1} of Na, Mg and Fe, respectively.

denote zonally and monthly averaged mixing ratios of metals such that concentrations above the lines are sufficient to neutralize 1 ppb of HNO_3. These calculations are based on a Na flux of 1×10^4 atoms cm^{-2} s^{-1} and on scale factors for Mg (25×) and Fe (20×) from chondrites [Mason, 1971].

Our calculation predicts that buffering of nitric acid in the polar stratosphere would be greatest in the late winter and early spring. The mechanism proposed here would need greater concentrations of metals than indicated in Figure 2, approximately 2-5 ppb of bivalent metals to neutralize 4-10 ppb of HNO_3 expected in the Antarctic lower stratosphere [NASA/WMO, 1986, pp. 555-562]. Such concentrations are achieved in the present calculations near 3 mbar and above.

Uncertainty in our knowledge of the total meteoric flux is large, see discussion by Wasson and Kyte [1987]. In particular, their value for the average infall, based on accumulation of iridium, is 6 times larger than that used here. If this flux were in the form of small particles rather than crater-producing bodies, then the contours in Figure 2 would correspond to 6 ppb. A further factor that may amplify concentrations within the vortex would be gravitational settling of the larger meteoric aerosols [Junge et al., 1961; Turco et al., 1981], an effect not included in these calculations.

Some uncertainty in this model is associated with the details of GCM's climatology for Antarctica. Meteoric material builds up a large vertical gradient in the middle stratosphere near 30 mbar and has difficulty penetrating to 100 mbar; however, the single year of model winds used for these simulations may not be a representative climatology. Further, the tracer model did not incorporate the vertical mixing associated with the GCM's treatment of gravity waves, which would lead to dilution of concentrations above 30 mbar but enhancement in the lower stratosphere.

Conclusions

We propose that infall of meteoric material is the source of alkalinity that controls nitric acid vapor in the Antarctic

stratosphere, providing one link in the chain of photochemical and heterogeneous processes that are responsible for the current decline in Antarctic ozone. If this mechanism is valid for Antarctica, what are the consequences? For one, the composition of aerosols in the springtime Antarctic stratosphere should have large abundances of the metals Mg and Fe plus NO_3^-, unlike the trace detections of iron and nitrates found in the corresponding aerosols at midlatitudes [Junge et al., 1961; Rosen, 1971]. For another, this phenomenon-the formation of metal nitrates-may occur also in the Arctic where meteoric material is predicted to accumulate in the middle and upper stratosphere during spring.

Furthermore, meteoritic particles and meteoric smoke may play a more direct role in the formation of stratospheric aerosols [Turco et al., 1981], especially PSCs [Aikin and McPeters, 1986] in view of their polar concentration in late winter and early spring. They are likely to dissolve in the acidic environment of PSCs and to contribute to the alkalinity of stratospheric aerosols.

Removal of nitric acid from the gas phase controls the rate of depletion of ozone in the Antarctic spring. Interannual changes in the amount of nitric acid bound in Antarctic aerosols could add further variability to the polar ozone minimum. Volcanic eruptions have great potential to alter the natural acid-base balance in stratospheric aerosols. It is not clear whether volcanic emissions (i.e., El Chichón in 1982) contain an excess of sulfur gases to increase the acidity of polar stratospheric aerosols, or whether they release sufficient metals to neutralize them. The major, annually recurring meteor showers exhibit large fluctuations in strength from year to year which could affect the annual average of meteoritic influx. A major source of year-to-year variability is certainly due to changes in the atmospheric circulation and temperature structure [Mahlman and Fels, 1986; Newman and Schoeberl, 1986]. All of these factors may be expected to modulate the monotonic decline expected from chlorine alone.

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