had been depleted. This is not observed.

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The Seasonal Evolution of Reactive Chlorine in the Northern Hemisphere Stratosphere

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In situ measurements of chlorine monoxide (ClO) at mid- and high northern latitudes are reported for the period October 1991 to February 1992. As early as mid-December and throughout the winter, significant enhancements of this ozone-destroying radical were observed within the polar vortex shortly after temperatures dropped below 195 k. Decreases in ClO observed in February were consistent with the rapid formation of chlorine nitrate ($ClONO_2$) by recombination of ClO with nitrogen dioxide (NO_2) released photochemically from nitric acid (HNO_3). Outside the vortex, ClO abundances were higher than in previous years as a result of NO_x suppression by heterogeneous reactions on sulfate aerosols enhanced by the eruption of Mount Pinatubo.

Ozone destruction in the stratosphere by chlorine compounds occurs at a rate that is proportional to the abundance of ClO (*1, 2*). Large enhancements of this reactive form of inorganic chlorine were observed in the Arctic polar vortex in the winter of 1989 during the first Airborne Arctic Stratospheric Expedition (AASE I), but, because the measurements were limited to a 6-week period, one much shorter than the life cycle of the vortex, the total amount of ozone destroyed by chlorine was unknown. In this report we present in situ observations of ClO taken from the NASA ER-2 high-altitude aircraft from October 1991 through February 1992 during AASE II. These results, which were obtained before the appearance of perturbed chemistry in the vortex and during recovery in springtime, illustrate the main features of the seasonal variation of ClO inside and outside the Arctic polar vortex and provide the basis for numerical estimates of ozone loss (*2, 3*).

At mid-latitudes, below 20 km, ClO is normally present at abundances under 50 parts per trillion by volume (pptv) (*4*), representing less than 5% of the chlorine available (*5*). The relatively unreactive species HCl and $ClONO_2$ are the most abundant forms of inorganic chlorine and are produced by the reactions $ClO + NO \rightarrow Cl + NO_2$ followed by $Cl + CH_4 \rightarrow HCl + CH_3$, and the termolecular recombination reaction $ClO + NO_2 \rightarrow ClONO_2$. In daytime, photochemical production of ClO is limited by slow photolysis of $ClONO_2$, whereas at sunset ClO is tied up into $ClONO_2$ by a surplus of NO_2 present from photolysis of the more abundant NO_x-containing compounds HNO_3 and N_2O_5. Observations in October 1991 illustrate this normal photochemical exchange between ClO and NO_x in sunlight and between ClO and $ClONO_2$ in darkness (Fig. 1A). Within air masses that were ultimately entrained within the vortex ClO was present at less than 100 pptv. In sunlight, NO (and consequently NO_x) was in excess of ClO, such that the disappearance of ClO at latitudes poleward of 82°N was due to its recombination with NO_2 to form $ClONO_2$, because this region was in total darkness. The dominant forms of inorganic chlorine were HCl and $ClONO_2$ from 40°N to the pole before winter (*6*).

By 12 December (Fig. 1B), temperatures within the polar vortex had decreased below 195 K, the threshold for co-condensation of HNO_3 and water at 20 km (*3*). The abundance of ClO had risen abruptly in the vortex, while that of NO had dropped to near the detection threshold. On the basis of back trajectory analyses, the air masses with high ClO abundances had been below 195 K, whereas air masses that had remained above this temperature for the previous 2 weeks appeared "normal." Although NO_2 was not observed directly, had it been present to any great extent at the northernmost portion of the flight track ClO would have been nearly undetectable because photolysis of $ClONO_2$ is slow at these high solar zenith angles (*7*). Therefore, a significantly different type of chemistry, one dominated by reactive chlorine rather than by NO_x, occurred in the cold vortex air. As corroborated by observations of HCl loss, reactive chlorine formed at the expense of both HCl and $ClONO_2$ (*6*).

During January 1992, the abundance of

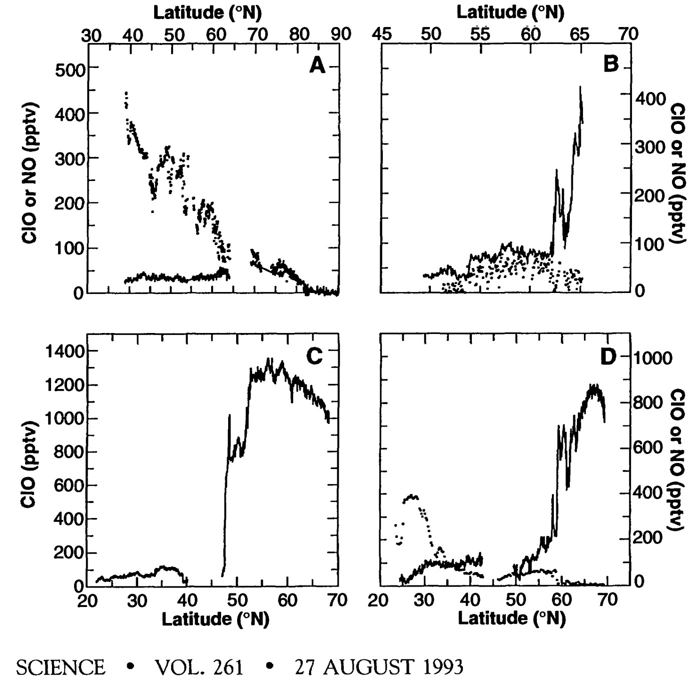

Fig. 1. Mixing ratios of ClO and NO (in parts per trillion by volume) plotted versus latitude for selected flights of the NASA ER-2 aircraft during the AASE II mission: (**A**) 12 and 14 October 1991; (**B**) 12 December 1991; (**C**) 12 and 20 January 1992; (**D**) 13 and 22 February 1992. For each panel ClO data are represented as a solid line and NO data as discrete points.

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ClO was above 1000 pptv in a large fraction of the vortex sampled by the ER-2 (Fig. 1C), as in 1989 (*8*), whereas HCl and NO were nearly unmeasurable (*6*). The removal of HCl was coincident with a nearly equivalent inferred loss of $ClONO_2$, such that a large fraction of the available inorganic chlorine (greater than 70%) was converted into reactive forms, ClO and Cl_2O_2 (*6*). It was at this time that O_3 destruction by catalytic reactions involving ClO and BrO was most rapid (*2*).

To investigate the possible mechanisms for the initiation of perturbed chlorine chemistry, we examined individual air masses sampled by the ER-2. Because conditions at the time of the measurement were significantly different from those that prevailed days to weeks earlier, we used the back trajectory method described elsewhere (*3, 9*). The time scale for recovery of a perturbed air mass can be a month or longer in the polar region during wintertime (*10*). Therefore, although the chemical partitioning in the air mass retains the memory of a processing event that occurred at an earlier time and at a different location, the meteorological parameters do not. We plotted measured ClO concentrations versus the minimum temperatures experienced in the previous weeks as determined from the back trajectories (Fig. 2). With few exceptions, all parcels that had cooled to the nitric acid trihydrate (NAT) formation threshold of about 195 K (*3*) displayed significant enhancements of ClO. Inverse behavior for HCl was observed in the same air masses (*6*).

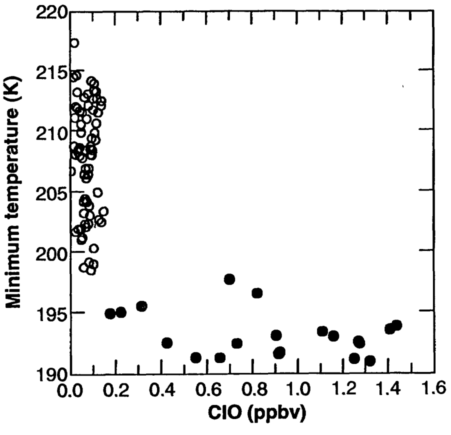

Fig. 2. Minimum temperature along back trajectories versus measured ClO for flights in December 1991 and January 1992. Open circles denote trajectories with temperatures that remained more than 3 K above the NAT condensation point (*3*) and filled circles denote trajectories that experienced temperatures less than 3 K above the NAT threshold. Trajectory lengths are 10 days, and all that occurred near the vortex edge have been excluded to avoid uncertainties in the meteorological parameters. See (*3, 10*) for a description of the trajectory method and (*6*) for a similar presentation for HCl.

On the basis of recent laboratory investigations of heterogeneous reactions (*11, 12*), these results imply that polar stratospheric clouds (PSCs) composed of NAT form at temperatures near 195 K at ER-2 altitudes, subsequently shifting the normal partitioning of inorganic chlorine in favor of reactive forms quite rapidly. This result seems to be at odds with observations from the AASE I campaign, when thick PSCs formed predominantly when high degrees of supersaturation were achieved, typically at temperatures below 192 K (*13*). However, the behavior of ClO (and HCl) observed during AASE II can be reconciled with the AASE I observations if (i) small numbers of larger frozen particles, which may form at about 195 K [at supersaturation ratios near one, as suggested previously (*13*)], are sufficient to rapidly alter the balance of inorganic chlorine; or (ii) a PSC-like chemistry involving both $ClONO_2$ and HCl is occurring rapidly on dilute sulfate aerosols that contain trace amounts of HNO_3 (*14*), as suggested recently by laboratory studies (*15, 16*); or (iii) the temperatures determined by the trajectory analyses are uniformly high by about 4 K. The results shown here cannot be used to distinguish among these three possibilities. Clearly, further studies, especially in the laboratory and directly within PSCs, are warranted to resolve this critical issue. However, whatever process is responsible for the shift in the chlorine partitioning, the change that occurs is dramatic and unambiguous, initiating chemical reactions that rapidly destroy O_3. Therefore, because temperatures within the vortex throughout the winter of 1991–1992 were not abnormally low and the occurrence of PSCs was fairly typical (*3*), highly elevated abundances of ClO are likely to recur within the Arctic vortex in all but the warmest winters.

In February 1992, enhanced ClO no longer filled the vortex; rather, regions near the edge of the vortex showed marked recovery with significantly lower ClO abundances and higher NO_x abundances than observed in January (Fig. 1D). Unlike the late fall, however, when HCl and $ClONO_2$ were both dominant reservoirs of inorganic chlorine, in February $ClONO_2$ was the main form of inorganic chlorine in regions of recovery. This was most apparent on 13 February near 60°N, where ClO and NO at the outer vortex were closer to their prewinter abundances but the abundance of HCl still remained low [see figure 6 in (*6*)]. This recovery, as detailed by Schoeberl *et al.* (*10*), can be quantitatively explained as due to the rapid photochemical release of NO_2 from HNO_3 remaining within the air mass after the last processing event in late January when the vortex began to warm. Throughout February and into late March, the abundances of ClO within the recovered vortex air remained nearly twice as great as abundances outside the vortex at similar altitudes as a result of the enhanced $ClONO_2$ and reduced HCl abundances. Thus, vortex air remained clearly distinguishable from mid-latitude air by the relatively high ClO abundances for at least 2 months after the vortex warmed above PSC threshold temperatures (*17*).

Throughout the measurement period, especially in winter, midday ClO abundances outside the vortex were uniformly between 50 and 120 pptv at 20 km, greater than those observed under similar conditions in previous years (*18*). Comparable fractional decreases in NO_x were observed by Fahey and co-workers (*19*). The high ClO abundances at mid-latitudes were observed well before temperatures within the vortex dropped below 200 K; therefore, it is unlikely that they were primarily the result of mixing out of processed air from within the vortex. In fact, at no time during the AASE II mission were mid-latitude ClO abundances as low as values measured in summer. These observations are consistent with changes expected from heterogeneous chemistry on sulfate aerosols (in particular, the hydrolysis of N_2O_5 into HNO_3, a species that is photolyzed more slowly) (*4, 19, 20*), and they provide additional evidence that the role of chlorine species is greater, and that of NO_x is less, in catalytic O_3 destruction in the lower stratosphere than previously believed.

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17. After February, only the edge of the vortex was sampled by the ER-2, so details of the recovery of air deeper within the interior are unclear. However, on the basis of observations from February and the fact that temperatures remained well above those required for PSCs for the previous month (*3*), the abundance of ClO was probably no greater than observed in February and likely decreased to more normal abundances by early March with continued release of NO_x as the solar declination increased. A recent overview of satellite observations of ClO during this same time period by J. W. Waters *et al.* [*Nature* **362**, 597 (1993)] presents a complementary view.
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21. We are indebted to the pilots of the ER-2 and the Lockheed ground crew at the National Aeronautics and Space Administration (NASA) Ames Research Center, without whom this work would not have been possible. Special thanks are due to N. Allen, J. Demusz, N. Hazen, B. Heroux, T. Martin, E. Schomp, D. Spillane, E. Thompson, and E. Weinstock for logistical and engineering support throughout the mission. We are especially grateful for various forms of support provided by P. Hathaway, S. Gaines, S. Hipskind, J. Arvesen, E. Condon, V. Eliason, A. Roberts, and S. Wegener. L.M.A. acknowledges a NASA Global Change Research Graduate Fellowship. This work was supported by the NASA Upper Atmosphere Research Program, grant number NAG-1-1305, under the direction of M. Kurylo.

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Heterogeneous Reaction Probabilities, Solubilities, and the Physical State of Cold Volcanic Aerosols

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On 19 January 1992, heterogeneous loss of HNO_3, $ClNO_3$, and HCl was observed in part of the Mount Pinatubo volcanic cloud that had cooled as a result of forced ascent. Portions of the volcanic cloud froze near 191 kelvin. The reaction probability of $ClNO_3$ and the solubility of HNO_3 were close to laboratory measurements on liquid sulfuric acid. The magnitude of the observed loss of HCl suggests that it underwent a heterogeneous reaction. Such reactions could lead to substantial loss of HCl on background sulfuric acid particles and so be important for polar ozone loss.

Chemical reactions occurring on particles set the stage for O_3 loss in the global stratosphere. At most latitudes, sulfuric acid aerosols drive heterogeneous chemistry. At high latitudes, polar stratospheric clouds (PSCs) dominate heterogeneous chemistry because of their large surface areas. Sulfuric acid aerosols may also be important in the polar regions because chlorine-containing gases react on them at temperatures higher than those at which PSCs form (*1, 2*). However, there are several difficulties in assessing the role of sulfuric acid aerosols in polar chemistry.

Laboratory studies have shown that some heterogeneous reaction rates are greatly reduced on frozen sulfuric acid (*3*). Opposing theories suggest that sulfuric acid aerosols freeze either near 205 K (*4*), before significant heterogeneous conversion of chlorine into ozone reactive forms, or at about 190 K (*5*), allowing conversions to occur in the polar stratosphere. Reaction rates and solubilities also vary significantly with particle composition (*3, 6–8*). Because the minor components of stratospheric particulates are not known, reaction rates measured on laboratory analogs have uncertain applicability to the stratosphere. Unfortunately, background sulfuric acid aerosols have a limited abundance so that heterogeneous reactions involving chlorine-containing gases occur too slowly to be observed easily in the atmosphere.

Aerosols from the Mount Pinatubo eruption have the same composition as the background sulfuric acid aerosols, which may originate from smaller volcanic eruptions. However, the Pinatubo aerosols have enough mass to impact clearly the chlorine and nitrogen chemistry of the stratosphere. Observations from the National Aeronautics and Space Administration's (NASA's) DC-8 aircraft allow us to infer the physical state, heterogeneous reaction probabilities, and solubilities of cold volcanic aerosols.

The heterogeneous reaction probability γ is the fraction of molecules hitting a particle that irreversibly react either on the surface of or within the particle. The temporally and vertically averaged γ_a equals

$$4\ln(C_o/C)/(svt) \qquad (1)$$

where C_o is the initial column concentration of the gas in the altitude region of the volcanic cloud, C is the concentration after exposure to the particle surface for a time t, and v is the thermal velocity of the gas molecules. The particle surface area per unit volume is found from $s = S/\ell$, where S is the total surface area of particles per unit area of vertical column and ℓ is the vertical thickness of the cloud. For soluble gases, the vertically averaged effective Henry's

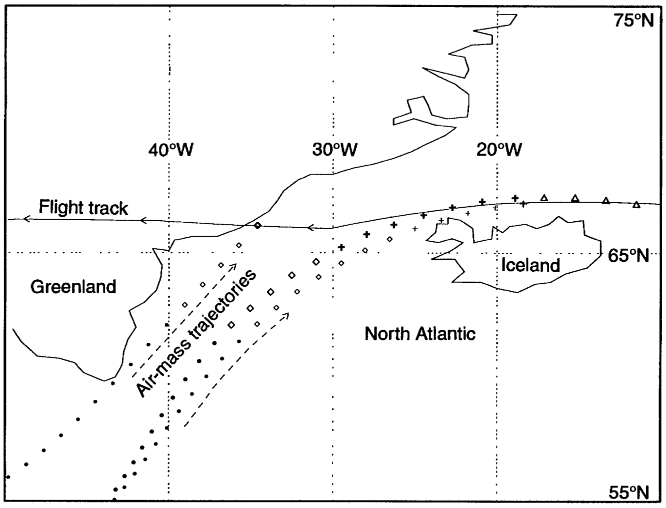

Fig. 1. Details of selected air mass trajectories ending at longitudes of 34.6°W, 18.4°W, and 11.5°W on the DC-8 flight track of 19 January 1992. The trajectories, which are on the 440 K potential temperature surface, reach a pressure of 60 mbar and a pressure altitude of 19.5 km near Iceland. Symbols show the hourly progression of the calculated *W* of the sulfuric acid in the volcanic cloud, which declined because of dropping temperatures: triangles, $W < 50\%$ and $T < 195$ K; crosses, $50\% < W < 55\%$ and $195\ K < T < 198.5$ K; diamonds, $55\% < W < 60\%$ and $198.5\ K < T < 203$ K; circles, $W > 60\%$ and $T > 203$ K.

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