Evolution and stoichiometry of heterogeneous processing in the Antarctic stratosphere


Abstract. Simultaneous in situ measurements of HCl and ClO have been made for the first time in the southern hemisphere, allowing a systematic study of the processes governing chlorine activation between 15 and 20 km in the 1994 Antarctic winter. Data for several other gases (O₃, NO, NOₓ, OH, HO₂, N₂O, CH₄, CO, H₂O, CFCs), particulates, and meteorological parameters were collected from the ER-2 aircraft out of New Zealand as part of the 1994 Airborne Southern Hemisphere Ozone Experiment/Measurements of Atmospheric Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign. Observations from the ER-2 in the fall (April-May), prior to polar night, show that chlorine activation begins with 60-75% of inorganic chlorine as HCl. By midwinter (July-August), near-total removal of HCl is observed. The wintertime loss of HCl in air recently exposed to extreme temperatures is found to be correlated with high levels of reactive chlorine (ClO and its dimer, Cl₂O₂) in the linear fashion expected from the stoichiometry of the heterogeneous reaction of hydrochloric acid with chlorine nitrate on polar stratospheric clouds (PSCs): HCl + ClONO₂ → Cl₂ + HNO₃. To constrain the role of different heterogeneous reactions and PSC types, we have used a photochemical trajectory model which includes heterogeneous sulfate and PSC chemistry. Model calculations of the evolution of reactive gases are compared with the in situ observations. In addition, simultaneous measurements of OH and HO₂ are used as a diagnostic for the occurrence of the heterogeneous reaction HOC₁ + HCl → Cl₂ + H₂O, which contributes to suppressed levels of HOₓ inside the vortex. It is shown that the amount of chlorine activation is not strongly dependent on the composition of PSCs. However, HOₓ levels exhibit different signatures depending on the type of heterogeneous surfaces that affected chlorine activation. Furthermore, this analysis implies that in the edge region of the Antarctic vortex, the observed near-total removal of HCl can result from latitudinal excursions of air parcels in and out of sunlight during the winter, which photochemically resupply HOC₁ and ClONO₂ as oxidation partners for HCl.

1. Introduction

Stratospheric inorganic chlorine (Clₓ = HCl + ClONO₂ + HOCI + ClO + 2 Cl₂O₂ + OCIO + 2 Cl₂ + Cl) is produced primarily from the emission of man-made chlorofluorocarbons (CFCs) and hydrofluorocarbons (HCFCs) at the surface of the Earth followed by transport to the stratosphere where their photochemical breakdown releases chlorine atoms [Molina and Rowland, 1974]. At middle and low latitudes, inorganic chlorine is mainly composed of the stable inactive reservoir forms HCl and ClONO₂. During the Antarctic winter, abrupt and sustained shifts in the partitioning of chlorine from HCl and ClONO₂ to photochemically reactive chlorine forms (or Clₓ = ClO + Cl + 2 Cl₂O₂ + 2 Cl₂ + OCIO) occur as a result of heterogeneous conversion on the surfaces of polar stratospheric cloud particles [Solomon et al., 1986; Crutzen and Arnold, 1986]. The high levels of reactive chlorine throughout the polar winter initiate massive ozone loss in the Antarctic polar spring [Farman et al., 1985; Hofmann et al., 1994]. Many observational studies [Tuck et al., 1989; Anderson et al., 1991; Toohey et al., 1993; Webster et al., 1993; Waters et al., 1993; Pyle et al., 1994] as well as gas phase and heterogeneous laboratory studies [Molina and Molina, 1987; Tolbert et al., 1987; Leu, 1988] have helped elucidate the mechanisms for heterogeneous processing and for the gas phase catalytic cycles ultimately responsible for the springtime ozone loss. The integration of this accumulated set of data has allowed modeling studies of these processes [Crutzen et al., 1992; Salawitch et al., 1993; Lefèvre et al., 1994; Chipperfield et al., 1995].
In our current understanding of the polar stratosphere, three principal heterogeneous reactions are believed to convert inorganic chlorine reservoirs to Cl$_x$ [Solomon, 1990]:

$$\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3 \quad (1)$$
$$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCI} + \text{HNO}_3 \quad (2)$$
$$\text{HCl} + \text{HOCI} \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \quad (3)$$

The surfaces on which these reactions take place are provided by the particles making up polar stratospheric clouds (PSCs) [McCormick et al., 1982], which are believed to be HNO$_3$/$\text{H}_2\text{SO}_4$/$\text{I}_2\text{O}_5$ systems of different compositions and phases [Carslaw et al., 1994; Tabazadeh et al., 1994], and form at the cold temperatures typical of the winter polar vortex. The gaseous products of reactions (1)-(3), Cl$_2$, and HOCI (which are seen to desorb from the PSC surfaces in laboratory observations) are rapidly converted to ClO and Cl$_2$O$_5$, the two dominant forms of Cl$_x$ in the polar winter stratosphere [Anderson et al., 1991].

The occurrence of reaction (1) is supported by the stoichiometry of HCl loss and ClO production from in situ observations in the Arctic [Webster et al., 1993]. After the eruption of Mount Pinatubo, high levels of OClO were observed in the Antarctic vortex and were attributed to chlorine activation via reaction (2) on volcanic sulfate aerosols [Solomon et al., 1993].

In addition to providing sites for heterogeneous chemical reactions, PSCs can sequester a significant fraction of stratospheric HNO$_3$ in condensed forms [Toon et al., 1986]. Growth and subsequent sedimentation of these particles lead to denitrification, further enhancing ozone loss [Fahhey et al., 1990]. Indeed, while chlorine radicals control the rate at which ozone is being destroyed, the duration of the destruction of O$_3$ is limited by the resupply of reactive nitrogen which sequesters Cl$_x$ in the form of ClONO$_2$ [Salawitch et al., 1988]. Given photochemical decomposition of HNO$_3$ to NO$_2$ under sufficient levels of sunlight, conversion of ClO back to ClONO$_2$ can take place via

$$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}. \quad (4)$$

HCl itself is reformed through the reaction

$$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3. \quad (5)$$

Thus understanding the factors controlling chlorine activation and deactivation is central to predicting ozone loss rates in the polar regions.

In this paper, we present simultaneous in situ measurements of HCl and ClO in the Antarctic lower stratosphere during the fall and winter 1994, which were carried out as part of the Airborne Southern Hemisphere Ozone Experiment /Measurements of Atmospheric Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign [Tuck et al., 1997]. Observations of HCl and ClO, in combination with the other reactive gases measured (OH, HO$_2$, NO) and complemented by aerosol measurements as well as observations of precursors and tracers, constitute a powerful set of indicators on the impact of chlorine chemistry in the perturbed environment of the polar vortex. The first simultaneous in situ measurements of HCl and ClO in the Antarctic provide additional insight into the heterogeneous processes taking place in a vortex generally colder and more extensive than that of the Arctic. While ClO by itself reflects largely the amount of recent processing that has taken place, HCl, on the other hand, keeps a much longer “memory” of the heterogeneous conversion because of its very slow recovery, and provides a useful measure of the accumulated effect of chlorine activation. Furthermore the simultaneous in situ measurements of HO$_x$ species during ASHOE/MAESA allow a unique assessment of the occurrence of reactions (2) and (3) in the stratosphere (D.W. Kohn et al., manuscript submitted to J. Geophys. Res.: “Constraints on sulfate aerosol reactions along back trajectories imposed by HO$_x$ and ClO$_x$ in situ measurements”, 1996) (hereinafter referred to as K96).

To interpret the chemical and dynamical factors affecting the chemical composition of the stratosphere during the Antarctic winter, this study uses a photochemical box model along trajectories. Because this approach takes into account the temperature history of an air parcel, it has already proved useful in studying stratospheric chemistry under polar conditions [Austin et al., 1989; Jones et al., 1989; Schoeberl et al., 1993; Lutman et al., 1994a, b]. In particular, trajectory models compared well with satellite and in situ observations of high ClO levels [Jones et al., 1989; Lutman et al., 1994a] and quantitatively predicted the relaxation of these enhanced ClO concentrations following encounters with PSCs [Schoeberl et al., 1993; Lutman et al., 1994b].

We begin in section 2 by briefly describing the data collected by instruments aboard the ER-2 during ASHOE/MAESA. Sections 3 and 4 will present observations of the conversion of chlorine reservoirs to reactive chlorine and how these can be analyzed to gain quantitative information on the stoichiometry of the processes responsible for chlorine activation. We describe the Lagrangian photochemical model in section 5. In sections 6 and 7, model simulation results are presented and compared with observations. We conclude by presenting in section 8 a summary of the results obtained in this investigation.

2. Observations and Instruments

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument is a scanning tunable diode laser spectrometer [Webster et al., 1994] which measures HCl [Webster et al., 1993], CO, N$_2$O, and CH$_4$ using high-resolution laser absorption at wavelengths from 3 to 8 pm in an 80-m multipass cell. The measurement uncertainty depends on signal size as well as on uncertainties in spectral parameters. The total uncertainty ($\sigma$) for 30 s averages of HCl is typically 10% at 1 ppbv and 30% for the mixing ratios below 0.3 ppbv. The minimum detectable HCl amount is about 0.1 ppbv, although in some flights, this can be as low as 0.05 ppbv. Table 1 briefly summarizes information on the other instruments onboard the ER-2. In addition, temperature and pressure are measured by the meteorological measurement system instrument [Scott et al., 1990] with accuracies of +0.3 mbar and ±0.3 K.

The series of flights discussed here were part of the ASHOE/MAESA mission, between the months of April and October of 1994. In southern flights out of Christchurch, New Zealand (44°S, 172°E), the ER-2 aircraft typically sampled air from 15 km (~120 mbar) to 20 km (~55 mbar). The length of the flights is limited to 8 hours, and therefore from Christchurch, the ER-2 predominantly sampled the edge region of the Antarctic vortex. Southern flights generally penetrated ~1°-3° of latitude inside the vortex up to ~70°S.

3. Chlorine Activation and Recovery

In this section, we first describe observations of the chlorine partitioning prior to polar night (April-May), deriving empirical relations for reference levels that will allow us to assess the amount of change in HCl and ClONO$_2$ when heterogeneous processing takes place during the winter. We then present HCl
Table 1. Instruments Onboard the ER-2

<table>
<thead>
<tr>
<th>Observed Quantities</th>
<th>Techniques</th>
<th>Accuracy (1σ, %)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl, N₂O, CH₄, CO</td>
<td>tunable diode-laser absorption</td>
<td>10, 5, 5, 10</td>
<td>Webster et al. [1994]</td>
</tr>
<tr>
<td>ClO</td>
<td>resonance fluorescence</td>
<td>15</td>
<td>Brune et al. [1989]</td>
</tr>
<tr>
<td>NO, NO₂</td>
<td>NO₂, chemiluminescence</td>
<td>15, 15</td>
<td>Fulch et al. [1989]</td>
</tr>
<tr>
<td>OH, HO₂</td>
<td>laser-induced fluorescence</td>
<td>30, 40</td>
<td>Wernberg et al. [1994]</td>
</tr>
<tr>
<td>CFCs</td>
<td>gas chromatograph</td>
<td>3</td>
<td>Likius et al. [1996]</td>
</tr>
<tr>
<td>O₁</td>
<td>differential UV absorption</td>
<td>5</td>
<td>Profitt et al. [1989]</td>
</tr>
<tr>
<td>H₂O</td>
<td>hygrometer</td>
<td>10</td>
<td>Kelly et al. [1989]</td>
</tr>
<tr>
<td>Aerosols (0.06-0.2 μm)</td>
<td>focused cavity spectrometer</td>
<td>100</td>
<td>Jourou et al. [1995]</td>
</tr>
<tr>
<td>Aerosols (0.2-20 μm)</td>
<td>multi angle spectrometer</td>
<td>100</td>
<td>Raungkircher et al. [1992]</td>
</tr>
<tr>
<td>Aerosol composition</td>
<td>impactor</td>
<td>100</td>
<td>Pueschel et al. [1989]</td>
</tr>
</tbody>
</table>

and ClO measurements during the flight of August 6, 1994, during which processed air was encountered. Finally, we summarize the evolution of the HCl and ClO observations spanning the four ASHOE/MAESA phases from April to October 1994.

3.1. Initial Partitioning

At midlatitudes away from polar processing, most of inorganic chlorine is in the form of its reservoirs, HCl and ClONO₂, with small contributions from ClO and HOCl. In order to identify chemical changes in either the chlorine reservoirs (HCl and ClONO₂) or the radical (ClO) in an air parcel, we need to establish the expected amounts of these species relative to a dynamical tracer such as N₂O or CFC-11. Figure 1 shows the HCl mixing ratios as a function of CFC-11 for four ER-2 flights between April and early June. The observed correlation of HCl with CFC-11 is due to the direct relationship between the source gas and the main inorganic chlorine reservoir, as well as to the fact that HCl mixing ratios are mostly controlled at these altitudes by O₁ and CH₄ which themselves have tight correlations with CFC-11 [Plumb and Ko, 1992; Chan et al., 1996].

We will assume ER-2 observations in the fall to be representative of the unperturbed atmosphere. A potential problem with this approach is that the air sampled by the ER-2 later during the winter (in July-August) most likely originated from higher altitudes as a result of descent within the vortex [Schoeberl et al., 1995]. Current estimates of descent rates inside the Antarctic vortex range between 0.02 and 0.07 cm s⁻¹ [World Meteorological Organization (WMO), 1995], suggesting that air could have descended by 2 km to a maximum of 7 km between April and August. To assess the impact of descent on HCl/tracer relationships, we have examined HCl and CH₄ profiles obtained by the Halogen Occultation Experiment (HALOE) [Russell et al., 1993] aboard the Upper Atmospheric Research Satellite (UARS) in March 1994 (70°-74°S). The correlation between HCl and CH₄ obtained with these HALOE observations between 20 and 28 km is about 10% lower than the ER-2 correlation, well within the respective uncertainties of these instruments (J. Russell, personal communication, 1996). These satellite observations thus show that descent within the Antarctic vortex does not greatly affect the initial chlorine partitioning illustrated by the correlations in Figure 1.

The total inorganic chlorine, Clᵣ, expected in an air parcel is based on organic chlorine measurements aboard the ER-2 and is calculated for each CFC-11 value (or N₂O, when no CFC-11 observations are available) using SF₆ to calculate the mean age of...
the air mass [Elkins et al., 1996]. The estimated uncertainty on the derived Cl$_y$ is 20% [Woodbridge et al., 1992]. Flights north of Christchurch (45°-20° S) have slightly higher values of HCI (dashed line in Figure 1), because of stronger CINO$_2$ photolysis at these latitudes, combined with lower CH$_4$ (which increase formation of HCl via Cl + CH$_4$) and lower O$_3$ (which decreases the loss of Cl via Cl + O$_3$ and decreases the conversion of NO to NO$_2$ through NO + O$_3$). At these lower latitudes the relationships among CFC-11, N$_2$O, O$_3$, and CH$_4$ are different than at midlatitudes [Plumb and Ko, 1992], thus generating different tracer-tracer relationships, and through the indirect chemical effects outlined above, the HCl(CFC-11) relationship has also a different slope.

In the late fall of 1994 the measured HCI represents 60-75% of Cl$_y$ at 20 km. The remaining 20-25% of inorganic chlorine is present as CINO$_2$, ClO, and HOCI. ClO is observed at levels typically less than 5% of Cl$_y$. The concentration of HOCI can be calculated from its steady state relationship with observed concentrations of ClO and HO$_2$:

$$[\text{HOCl}^*] = k_{\text{ClO-HO}_2}[\text{ClO}][\text{HO}_2]/J_{\text{HOCl}} \tag{6}$$

The photolysis rate of HOCI ($J_{\text{HOCl}}$) and the reaction rate for ClO-HO$_2$ ($k_{\text{ClO-HO}_2}$) are calculated based on recommendations by DeMote et al. [1994]. Using equation (6), we calculated HOCl$^+$ to be less than 1% of the budget for the ER-2 altitude range. Because we do not have measurements of chlorine nitrate, we infer it from

$$[\text{CINO}_2^*] = [\text{Cl}_y] - [\text{HCl}] - [\text{ClO}] - [\text{HOCl}^*] \tag{7}$$

for which we then derive a relation as a function of CFC-11 (see Figure 1 caption). Throughout this paper we will denote chemical species that are inferred from other in situ observations by an asterisk *. Total uncertainties of 70% and 80% are estimated for CINO$_2$* and HOCl$, respectively, based on uncertainties in measurements and rate constants. The CINO$_2$ calculated from its steady state relation with ClO and NO$_2$ is very close to CINO$_2^*$ [C. R. Webster et al., manuscript submitted to Geophys. Res. Lett., "Evolution of HCl concentrations in the lower stratosphere from 1991 to 1996 following the eruption of Mt. Pinatubo", 1996](hereinafter referred to as W96a).

These 1994 southern hemisphere measurements, where HCl is seen to be the dominant chlorine reservoir, are to be contrasted with those taken by the same instrument in the northern hemisphere between 1991 and 1993 [Webster et al., 1994], which showed that HCl was measured to represent less than 40% of Cl$_y$. This change in chlorine partitioning could reflect the return of the lower stratosphere to low levels of aerosols 3 years after the eruption of Mount Pinatubo [W96a].

### 3.2. PSC Processing in Winter

By late fall, the vortex is well established [Manney and Zurek, 1993; Schoeberl and Hartmann, 1991] and minimum temperatures fall below 190 K. During the flight of August 6, 1994, the ER-2 attained a maximum latitude of 67.7° S before descending down to 15 km, climbing back to its cruise altitude of 19 km and returning to New Zealand. Observations of N$_2$O, wind speed, HCl, and ClO are shown in Plate 1, as a function of the latitude of the ER-2 aircraft. At most latitudes the observations of HCl closely follow the expected reference HCl (Plate 1 b). Poleward of 64° S, HCl abruptly decreases to very low values, while ClO increases to reach a maximum of about 0.9 ppbv. Comparing the HCl observations to the predicted reference levels clearly shows that this decrease (by 90%) cannot be due to dynamical descent in the vortex. We therefore identify the observed loss of HCl and associated high values of ClO with recent chemical conversion.

At low temperatures and high ClO levels, a significant fraction of active chlorine can be present as Cl$_2$O$_3$, the ClO dimer [Molina and Molina, 1987; Sander et al., 1989]. Assuming that Cl$_2$O$_3$ is in photochemical steady state equilibrium with the observed ClO, we can calculate it from the expression

$$[\text{Cl}_2\text{O}_3^*] = (k_{\text{ClO-ClO}}[\text{ClO}]^2[M] + J_{\text{Cl}_2\text{O}_3}) \tag{8}$$

where $M$ is a third body, N$_2$ or O$_3$, and [M] thus represents the atmospheric density. The reaction rate constants for the ClO self-reaction ($k_{\text{ClO-ClO}}$) and the dimer thermal decomposition ($k_{\text{Cl}_2\text{O}_3(M)}$) are taken from DeMote et al. [1994]. The dimer absorption cross sections are taken from the recent laboratory measurements by Huder and DeMore [1995]. The corresponding photolysis rate ($J_{\text{Cl}_2\text{O}_3}$) is calculated taking into account the albedo and overhead ozone variations along the ER-2 flight track [Sabolich et al., 1994]. Cl$_2$O$_3^*$ determined in this manner has an
uncertainty of about 80% [Kawa et al., 1992]. At high solar
zenith angles (> 83°) the steady state assumption no longer holds,
and we have corrected ClO₂⁺ by the expected departure we
derived from comparison with our time-dependent model. A
similar approach is used to correct the steady state HOCl (for
solar zenith angles > 85°). On the flight of August 6, 1994, ClO₂
constitutes up to 0.5 ppbv, or 50% of the active chlorine (ClO + 2
ClO₂ = 1.9 ppbv) at the peak ClO value.
Huder et al.'s determination of the dimer cross sections
yields a photolysis rate 40% lower than values calculated using
currently recommended cross-sections [DeMore et al., 1994].
Previous measurements seem to overestimate the cross section of
Cl₂O₂ due to improperly accounted for contamination by Cl₂O.
This has a large impact on our predicted steady state abundances
of Cl₂O₂. As illustrated in Plate 1d, Cl₂O₂ would be 40% lower
if we used the cross sections by DeMore et al. Throughout this
paper, we have adopted the recent absorption cross sections
reported by Huder and DeMore [1995].

3.3. Evolution of HCl and ClO through the Vortex Lifetime

From measurements of HCl and ClO between April and
October 1994, a picture of the evolution of inorganic chlorine
partitioning at the inner edge of the vortex is built up before,
during, and after the period when temperatures are cold enough
for PSC formation. Figure 2 shows the observed time evolution
of HCl/Cl₂, and (ClO + 2 Cl₂O₂)⁻/Cl₂, inside the vortex during the
ASHOE/MAESA campaign. We have selected observations
obtained over 2°-3° latitude inside the vortex, the edge of which
we define by the polar jet wind maximum as measured aboard the
ER-2 [Tuck et al., 1995, Table 1]. The release of active chlorine,
ClO + 2 Cl₂O₂, mirrors the evolution of cold temperatures in the
vortex. During the period between June and late August the
temperatures are cold enough to promote the growth of PSCs
whose surfaces provide sites for the heterogeneous reactions (1)-(3). The levels of HCl were first seen to decrease in early June
1994. By early August, HCl was extensively processed, and high
levels of active chlorine were present inside the vortex. By
October, photochemical recovery of HCl, through reaction (5), is
nearly complete. On two occasions, October 10 and 13, the ER-2
sampled air where recovery of HCl to extremely high levels
(HCl/Cl₂~1) had taken place in a low ozone environment (C.R.
Webster et al., manuscript in preparation, "Total conversion of
inorganic chlorine in polar stratospheric air severely depleted in
O₃", 1996) (hereinafter referred to as W96b).

4. Stoichiometry of Chlorine Processing

Because of the 8-hour flight range of the ER-2, based in New
Zealand, and the location of the PSCs well over Antarctica,
flights during ASHOE/MAESA were confined mostly to the edge
region of the Antarctic vortex. During two flights (July 28 and
30, 1994), however, the ER-2 flew through PSCs, and on several
other occasions, it encountered air that had previously been
exposed to temperatures below PSC formation thresholds
(August 6, 8, and 10), as indicated by back trajectory
calculations.

From observations obtained in the vortex prior to PSC
processing, as shown in Figure 1, we have a knowledge of the
expected unperturbed levels of HCl and ClO₂. The difference
between a measured mixing ratio for HCl and a reference value
calculated from the simultaneously measured CFC-11 (or N₂O)
represents the chemical loss, defined as follows:

$$\Delta \text{HCl} = \text{HCl}^- \text{(CFC-11)} - \text{HCl}^+.$$  (9)

We can use the same approach for ClO₂⁻⁻, as inferred from the
inorganic chlorine budget residual:

$$\Delta \text{ClO}_2^- = \text{ClO}_2^- \text{(CFC-11)} - \text{ClO}_2^-.$$  (10)

Figure 2. Time evolution of chlorine species inside the vortex between April and October 1994. The medians of
observations are represented by the symbols (triangles, HCl/Cl₂; circles, (ClO + 2 Cl₂O₂)⁻/Cl₂) with their minimum
and maximum, as the vertical bars. The points are selected for latitudes poleward of the maximum horizontal wind
speed (typically south of ~ 64°S). The solid and dashed lines are visual guides passing through the HCl and ClO + 2
Cl₂O₂ observations.
$\Delta$CINO$_O_2$ by itself does not bring any additional information as it depends on $\Delta$HCl and CIO (according to our definitions in equations (10) and (7)). It is, however, a useful quantity to consider in parallel with $\Delta$HCl, because it allows us to illustrate the behavior of both chlorine reservoirs at the same time.

By convention, and for simplicity, the sign in these expressions is such that for a net loss in HCl, $\Delta$HCl is positive (the same applies for CINO$_O_2$). Webster et al. [1993] demonstrated how the values of $\Delta$HCl, $\Delta$CINO$_O_2$, and CIO + 2 Cl$_2$O$_2$ associated with each air parcel can give us information on the stoichiometry of PSC processing, since the net effect of heterogeneous reactions (1)-(3) is to increase $\Delta$HCl, $\Delta$CINO$_O_2$, and CIO + 2 Cl$_2$O$_2$. Because of the large temperature dependence of heterogeneous reactions (1) - (3) the degree of chlorine activation depends on a balance between exposure time to cold temperatures and on the time spent in sunlight, which allows reformation of CINO$_O_2$.

Compact relationships between losses in chlorine reservoirs and production of reactive chlorine gases are seen for ASHOE/MAESA flights during the Antarctic winter. As we will show, these relationships are consistent with the stoichiometry of recent heterogeneous processing. Figure 3 presents $\Delta$HCl and $\Delta$CINO$_O_2$, as a functions of CIO + 2 Cl$_2$O$_2$. All the mixing ratios have been normalized to Cly to account for variations in chlorine loading between air parcels (for a simple conversion to mixing ratios, the air parcels in the vortex generally contained 1.8-2.2 ppbv of inorganic chlorine). In early June 1994 (Figure 3a), reactive chlorine accounted for up to 50% of Cly in the southern-most part of the flight, where HCl had been reduced by about 50%. Chlorine activation is more extensive at the end of July and in early August (Figure 3b), where in some air masses, up to 90% of chlorine was in the form of reactive chlorine and little HCl was observed.

Simultaneous measurements of HCl and CIO were previously made in the Arctic vortex aboard the ER-2 [Webster et al., 1993; Toohey et al., 1993] during the Airborne Arctic Stratospheric Experiment II (AASE II) campaign. In their analysis of the AASE II observations, Webster et al. [1993] saw a striking 1:2 slope for the correlation between $\Delta$HCl and CIO + 2 Cl$_2$O$_2$ corresponding to the stoichiometry of the heterogeneous reaction (1), by which one HCl is converted to one Cl$_2$, as depicted in Figure 4a for the AASE II flights of December 12, 1991, and January 20, 1992. For the highest values of active chlorine, the observations of HCl and inferred CINO$_O_2$ depart from the 1:2 slope. This departure was not seen as clearly in Webster et al. and is caused here by the use of Cl$_2$O$_2$ cross sections based on Huder and DeMore [1995] (instead of Burkholder et al. [1990]), which results in enhanced Cl$_2$O$_2$*, as discussed in section 3.1. CIO + 2 Cl$_2$O$_2$* exceeds Cly for some points inside the vortex, but one has to keep in mind that the total uncertainty in Cl$_2$O$_2$ is close to 50%.

For ASHOE/MAESA flights the slope of the correlation is close to 1:2, providing further evidence for the occurrence of reaction (1). However, there is a vertical offset. In other words, $\Delta$HCl > 1/2 (CIO + 2 Cl$_2$O$_2$). The points that fall on the parallel 1:2 lines correspond to latitudes poleward of 64°S. The offset (or the non zero y intercept) reflects a net gain of CINO$_O_2$ and loss of HCl compared with the relationships derived from observations in the fall.

Pure photochemical relaxation of the HCl/CINO$_O_2$ ratio could occur as a response to the decreased amount of sunlight as the vortex goes from fall to winter. From time-dependent photochemical calculations we evaluate that this effect could generate a decrease of 70 ppbv/month for HCl in the edge region of the vortex, accounting for up to a third of the observed offset. As discussed in section 3.1, the air that was sampled by the ER-2 in early June and late July could be air that originated from a higher altitude inside the vortex and as a result was not seen by the ER-2 in the fall. However, profiles of HCl obtained by HALOE in the fall of 1994 show that inside the vortex the HCl/Cly ratio is fairly constant in the 20-30 km region at 70% (J. Russell, personal communication, 1996). Thus the decrease in HCl/Cly could not be caused by descent. Finally, cold temperatures below 200 K are pervasive in fall/winter high latitudes, and heterogeneous reactions on sulfate aerosols could have partially converted HCl to Cl$_2$. With sufficient sunlight, some of the reactive chlorine in turn could have been converted back to CINO$_O_2$, thus changing the partitioning between HCl and CINO$_O_2$. The succession of reactions taking place can be summarized as follows.

\[
\begin{align*}
\text{HCl} + \text{CINO}_O_2 + 2 \text{O}_1 + \text{HNO}_3 & \rightarrow 2 \text{CINO}_O_2 + 2 \text{O}_2 + 2 \text{OH}. \\
\text{HCl} + \text{CINO}_O_2 & \rightarrow \text{Cl}_2 + \text{HNO}_3 \\
\text{Cl}_2 + \text{hv} & \rightarrow 2 \text{Cl} \\
2[\text{Cl} + \text{O}_3] & \rightarrow \text{CIO} + \text{O}_3 \\
2[\text{HNO}_3 + \text{hv}] & \rightarrow \text{NO}_2 + \text{OH} \\
2[\text{CIO} + \text{NO}_2 + \text{M}] & \rightarrow \text{CINO}_O_2 + \text{M} \\
\text{Cl}_2 + \text{hv} & \rightarrow 2 \text{Cl} \\
\text{Cl}_2 + \text{hv} & \rightarrow 2 \text{Cl} \\
\text{Cl}_2 + \text{hv} & \rightarrow 2 \text{Cl} \\
\text{Cl}_2 + \text{hv} & \rightarrow 2 \text{Cl} \\
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\end{align*}
\]
We estimate that 5-6 exposures to temperatures in the 197-199 K range for a few hours at a time would be enough to account for a decrease in HCl by a few tenths of ppbv (and increase ClONO₂ by twice that amount), due to heterogeneous reaction (1) on sulfate aerosols followed by excursions to lower latitudes. In this manner a large part of the offset can be attributed to prior processing of chlorine reservoirs on background sulfate aerosols or on PSCs. Thus while the 1:2 slope in Figure 3 comes from the stoichiometry of (1), the y intercept can be interpreted as the extent of past PSC processing, or the "memory" of chlorine activation through (1) for HCl. ClONO₂ on the other hand can recover through (4), resulting in the net stoichiometry of (14). As noted above, the AASE II data do not show such a non zero y intercept. This would suggest that the processed air encountered had been exposed to only one PSC event in the Arctic vortex, where PSCs are not as extensively present as in the Antarctic.

The compactness of the slopes in Figures 3 and 4 indicate that the process of activation/deactivation is very similar for all the air parcels sampled and that their temperature histories followed fairly similar evolutions for each individual flight. This is what we would expect, as the ER-2 flight tracks during ASHOE/MAESA were usually designed to follow potential temperature surfaces. Under adiabatic conditions, air is transported along such surfaces of constant potential temperature. At the edge of the Antarctic vortex, temperatures are cold enough for multiple processing events to take place, interrupted by excursions into sunlight that allow partial recovery of ClONO₂. However, in Figure 3 a, the 1:2 slope is not present due to the low ClONO₂ values, possibly indicating the occurrence of (2). Note that without temperature history considerations and knowledge of the type of PSC formed, we cannot a priori distinguish between cases 4.2 and 4.4.

From these observations it seems that even though processing begins with more HCl than ClONO₂, partial recovery of ClONO₂ through the net reaction (14) allows near complete heterogeneous loss of HCl. Interestingly, this would suggest that the conversion to active chlorine is HCl-limited in the edge region of the Antarctic vortex. Excursions of air parcels to lower latitudes provide enough sunlight to produce NOx, which combines with ClO (via reaction (4)) to produce small amounts of ClONO₂. Similarly, production of HOx at lower latitudes results in small amounts of HOCl (via ClO + HO₂). Subsequently, as the parcel returns to higher latitudes and colder temperatures, heterogeneous reactions of HCl with both reservoirs via (1) and (3) continue to deplete HCl [Jaegele, 1996].

In this manner, reaction (1) is responsible for the rapid early winter loss of HCl, until all of ClONO₂ has been consumed. Reactions (1) and (3) then combine to continue this process, at a rate determined by the rate of heterogeneous conversion, which can be expressed as a function of ClO (via reaction (4)) to produce small amounts of ClONO₂. Similarly, production of HOx at lower latitudes results in small amounts of HOCl (via ClO + HO₂). Subsequently, as the parcel returns to higher latitudes and colder temperatures, heterogeneous reactions of HCl with both reservoirs via (1) and (3) continue to deplete HCl [Jaegele, 1996].

4.1. On going Processing: $\Delta$HCl = $1/2(\text{ClO} + 2 \text{Cl}_2\text{O}_3^*)$

Reaction (1) dominates the conversion process and yields a 1:2 net stoichiometry, in which one HCl is converted to one Cl₂O₃ (which is then rapidly converted to 2 (ClO + 2 Cl₂O₃))). The AASE II flights of December 12, 1991, and January 20, 1992, fall into this category (Figure 4 a) [Webster et al., 1993].

4.2. Recovery of ClONO₂: $\Delta$HCl = Constant

Following event 4.1., if there is sufficient sunlight, NO₃ is produced from HNO₃ decomposition (photolysis and reaction with OH) and reacts with ClO to form chlorine nitrate. Thus ClONO₂ increases and $\Delta$ClONO₂ decreases linearly with reactive chlorine, with a slope of 1, following the stoichiometry of (4). This can be seen during the AASE II flights of February 13 and 17, 1992. HCl recovers much more slowly, as indicated by the small slope of $\Delta$HCl in Figure 4 b.

4.3. Multiple Processing: $\Delta$HCl = $1/2(\text{ClO} + 2 \text{Cl}_2\text{O}_3^*) + c$

At the edge of the Antarctic vortex, temperatures are cold enough for multiple processing events to take place, interrupted by excursions into sunlight that allow partial recovery of ClONO₂. Events 4.1. and 4.2. can follow each other several times until all of HCl has been consumed. The ASHOE/MAESA flights in Figure 3 show a 1:2 slope with a y intercept of 20-30% Cl₂, implying that the accumulated effect of 4.1. and 4.2. could have been to convert a fraction of Cl₂ back to ClONO₂, through the net reaction (14). (From our discussion above, a third of that offset could be due to pure gas phase repartitioning at high latitudes.)

4.4. Low HCl Levels: $\Delta$HCl = Constant

When most of HCl has been consumed, the rate for (1) becomes very slow. At cold enough temperatures, ClONO₂ can be directly converted to HOCl through (2) on sulfate aerosols or type II PSCs (this reaction is ineffective on NAT; see Figure 5). Such a case would be translated into a slope of 1:1 for $\Delta$ClONO₂ and of zero for $\Delta$HCl. In Figure 3 b, $\Delta$HCl is seen to depart from the 1:2 line for high (ClO + 2 Cl₂O₃)/Cl₂ values, implying that the accumulated effect of 4.1. and 4.2. could have been to convert a fraction of Cl₂ back to ClONO₂ through the net reaction (14). (From our discussion above, a third of that offset could be due to pure gas phase repartitioning at high latitudes.)
slower rate, limited by excursions into sunlight. Thus the near-
total removal of HCl that was observed in this study and in
airborne column measurements [Toon et al., 1989] can take place
from excursions in and out of sunlight, with a resupply of HOCl
and ClONO₂, which provide oxidation partners for HCl. Deeper
inside the vortex it has been suggested that HO₂ and NO₃
production by galactic cosmic rays [Müller and Crutzen, 1993]
could replace the role of these excursions in generating total loss
of HCl [Liu et al., 1992] via (1) and (3).

The high amounts of ClONO₂, inferred here, form the so-
called chlorine nitrate “collar,” first discovered in ground-based
measurements [Farmer et al., 1987] and remote soundings from
aircraft [Toon et al., 1989] in the springtime Antarctic and,
subsequently, measured in the Arctic [von Clarmann et al., 1993;
Toon et al., 1994; Oelhaf et al., 1994]. Observations aboard the
UARS satellite have revealed a global picture of this collar which
surrounds the Antarctic vortex between 50° and 60°S and is
present from July to September [Roche et al., 1993, 1994].

5. Photochemical Model Along Trajectories

To better understand the mechanisms responsible for the
repartitioning of chlorine species during the polar winter, we use
a Lagrangian photochemical model along trajectories [Nair,
1996] adapted from the Caltech-JPL model. The model includes
50 species in the NOₓ, Clₓ, Brₓ, HOₓ and Oₓ families. A full
methane oxidation scheme is included. Close to 200 gas phase
reactions, 50 photolytic reactions, and 6 heterogeneous reactions
on various surfaces are used. Most reaction rates are based on
the compilation by DeMore et al. [1994]. Absorption cross
sections are also taken from DeMore et al., except for HOB and
Cl₂O₃, for which more recent laboratory measurements by
Rattigan et al. [1996] and Huder and DeMore [1995] are used.
The photolysis rates are calculated using climatological ozone
profiles scaled to total ozone mapping spectrometer (TOMS)
overhead ozone corresponding to the end point of the trajectory.

The main heterogeneous reactions and their uptake
probabilities, corresponding to different types of surfaces adopted
in this work, are listed in Table 2. Figure 5 illustrates the
temperature dependence of the three most important
heterogeneous reactions (1) to (3) for different surface types.
Recently, the high reactivity of bromine compounds on
heterogeneous surfaces has been observed in the laboratory
[Hanson and Ravishankara, 1995; Abbatt, 1994]. In addition to
the hydrolysis of bromine nitrate (Table 2) we have included
other possible heterogeneous bromine reactions, such as HCl +
HOB and HBr + HOCl, and found that their effect was to
slightly increase chlorine activation. This effect was minor,
however, compared with reactions (1)-(3), as was shown by Lary
et al. [1995] and Danilin et al. [1996].

Elucidating the exact phase and composition of the PSC
particles is not in the scope of this work and is addressed
elsewhere [Del Negro et al., this issue; Dye et al., 1996]. Instead,
we use simplified assumptions for each flight examined, based on
the observed surface area and composition of the aerosols. Many
uncertainties still remain on the early phase of the formation and
growth mechanism of polar stratospheric clouds, which can be
characterized as type I or type II PSCs. The possible composition
of type I PSCs include nitric acid trihydrate (NAT), nitric acid
dihydrate (NAD), supercooled H₂O-HNO₃, supercooled ternary
solutions (STS) HNO₃/H₂SO₄/H₂O, and sulfuric acid tetrahydrate
(SAT) [Hanson and Mauersberger, 1988; Worsnop et al., 1993;
Tabazadeh et al., 1994; Molina et al., 1993; Zhang et al., 1993].
Type II PSCs are composed of water ice [Steene et al., 1983].

In the model the composition and volume growth of
supercooled ternary solution is obtained according to the
formulation of Carstew et al. [1995], and we assume heterogeneous
reactions on STS to take place with the same reactivities as on sulfate aerosols. The presence of NAT particles
is predicted as a function of H₂O and HNO₃ local partial
pressures, using the saturation vapor pressures given by
Hanson and Mauersberger [1988]. The corresponding surface area
is calculated from the amount of condensed species using a
specified radius of 1 μm. Similarly, ice particles are predicted as
a function of H₂O partial pressure, with the saturation vapor
pressure given by Marti and Mauersberger [1993]. For these
generally larger particles, we assume a 10 μm radius to calculate
the surface area. Condensed species are returned to the gas phase
when the clouds evaporate. An example of calculated growths
of STS and NAT and ice PSCs as a function of temperature is
shown in Figure 6.

We do not consider the effects of deminification in this study,
because it was generally not observed for the air masses sampled
during ASHOE/MAESA [Keim et al., this issue]. However, the
formation of NAT in the model temporarily sequesters HNO₃ in
the solid phase and thus can effectively slow the recovery of
ClONO₂.

Unless otherwise specified, H₂O, CH₄, and O₃ are kept fixed
at their measured values. If no measurements are available for a
particular flight, these species are obtained from empirical tracers

Table 2. List of Heterogeneous Reaction Probabilities

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Surface</th>
<th>type</th>
<th>ke</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ClONO₂ + HCl → Cl₂ + HNO₃</td>
<td>(b)</td>
<td>(d)</td>
<td>0.2 (a)</td>
</tr>
<tr>
<td>(2) ClONO₂ + H₂O → HOCI + HNO₃</td>
<td>(b)</td>
<td>0.001 (a)</td>
<td>0.1 (a)</td>
</tr>
<tr>
<td>(3) HOCl + HCl → Cl₂ + H₂O</td>
<td>(c)</td>
<td>(f)</td>
<td>= NAT 0.3 (a)</td>
</tr>
<tr>
<td>(4') N₂O₄ + H₂O → 2HNO₃</td>
<td>0.1 (a)</td>
<td>0.0003 (a)</td>
<td>0.1 (a)</td>
</tr>
<tr>
<td>(5') BrONO₂ + H₂O → HOB + HNO₃</td>
<td>0.5 (g)</td>
<td>0.006 (b)</td>
<td>= NAT 0.3 (a)</td>
</tr>
<tr>
<td>(6') N₂O₅ + HCl → ClONO₂ + HNO₃</td>
<td>0.003 (a)</td>
<td>0.03 (a)</td>
<td></td>
</tr>
</tbody>
</table>

(a) DeMore et al. [1994]; (b) Hanson and Ravishankara [1994]; (c) Hanson et al. [1994]; (d) Hanson and Ravishankara [1993];
(e) Zhang et al. [1993]; (f) Abbatt and Molina [1992]; (g) Hanson and Ravishankara [1995]; (h) Lary et al. [1996].
Figure 5. Heterogeneous reaction probabilities as a function of temperature on sulfuric acid (line, H₂SO₄), nitric acid trihydrate (dashed-dotted, SAT), nitric acid tetrahydrate (short dashed, NAT), and ice (diamonds) for reactions (1) HCl + ClONO₂ → Cl₂ + HNO₃, (2) ClONO₂ + H₂O → HOCI + HNO₃, and (3) HOCI + HCl → Cl₂ + H₂O. The dependence on HCl levels is shown for reactivities on sulfuric acid (long dashed, low HCl = 0.01 ppbv).

Figure 6. Model-calculated aerosol surface area growth as a function of temperature. Supercooled ternary solution (line, formulation of Carslaw et al., [1995]), nitric acid trihydrate (short dashed, with assumed radius = 1 μm), and ice (dashed dotted, with assumed radius = 10 μm) surface areas as a function of temperature. Conditions used: p = 55 mbar, H₂O = 5 ppmv, HNO₃ = 10 ppbv, H₂SO₄ = 0.5 ppbv.
partitioning of chlorine species and other reactive species. To that end we focus on a detailed analysis of two ER-2 flights made on July 28, 1994, and August 6, 1994. During this period of austral winter, temperatures are generally very cold throughout the vortex. Intense heterogeneous processing has been taking place since early June [Waters et al., 1993; Santee et al., 1994].

6. On-going Heterogeneous Processing: July 28

Observations obtained during the flight of July 28, 1994, are shown in Plates 2 a and 2 b, as a function of latitude. During this flight, temperatures as cold as 190 K were measured southward of 60°S (top panel in Plate 2 b), and the ER-2 flew through a polar stratospheric cloud between 65.5° and 67.5°S. Ten-day back trajectories show that the air had been rapidly cooling over the 12 hours prior to being sampled by the ER-2 (Figure 7 a). Inside the vortex (the maximum horizontal wind was observed at 64°S), CIO mixing ratios reached a maximum of 0.85 ppbv, while HCl levels decreased to values lower than 0.2 ppbv (Plate 2 a), close to the detection limit of the instrument.

6.1. Model Results along Trajectories

In a first step we assume in our calculations that the aerosols are in the liquid phase and that they grow by condensation of

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Plate 2 a. Flight of July 28, 1994. Comparison between observations and results from 10-day photochemical trajectory calculation for chlorine species. (b) HCl, (c) CIO, (d) ClO₂, (e) ClONO₂. All species with stars are calculated from observations assuming steady state (see text). N₂O and altitude are represented in the top panel as well as the specific air parcel locations used in the analysis. The model results assume heterogeneous reactions on background sulfate aerosols and growth of supercooled ternary solutions (STS) particles as a function of temperature (see Figure 6). The solid squares connected with lines (case 1) represent model calculations at the end of the 10-day trajectory assuming no previous processing of chlorine, while the triangles (case 2) show the model results assuming an initialization with 0.35 ppbv of HCl (or 20% of Cl₂) having been previously heterogeneously processed. The plus at 67°S (case 3) and the star at 64°S (case 4) correspond to model cases assuming formation of types I and II PSCs, and frozen SAT particles (see text), respectively. The vertical line going through all the panels indicates the southern most latitude reached (~67.5°S).

Plate 2 b. Same as for Plate 2 a but for (b) NO, (c) OH, (d) HO₂, and (e) HOCl⁻. Temperature and solar zenith angle along the ER-2 flight track are presented in the top panel. The vertical bars show the range of temperatures encountered in the previous 10 days, as obtained from back trajectory calculations.

---

significance. Recent measurements of CIO uptake on sulfuric acid [Abbott, 1996] indicate that this reaction would be too slow to compete with the other heterogeneous reactions. For this reason we have not included considerations of missing chemistry in this study.

In the following two sections we examine whether the model simulations can account for the observed amounts of HCl lost and CIO produced as a result of a PSC encounter. In particular, we pose the question of whether different aerosol surfaces and temperature histories leave specific fingerprints on the
Plate 3a. Flight of August 6, 1994. Same as Plate 2a. The solid squares connected with lines (case 1) represent model calculations assuming no previous processing of chlorine, while the triangles (case 2) show the model results assuming that 0.35 ppbv of HCl have been heterogeneously processed. Both cases assume heterogeneous reactions on sulfate aerosols and STS. The plus symbols (case 3) show model results assuming pre-processing and formation of NAT and ice PSCs.

Plate 3b. Flight of August 6, 1994. Same as Plate 3a, but for (a) temperature and altitude, (b) NO, (c) OH, (d) HO₂, and (e) HOCI⁻.
Figure 7. Back trajectory temperatures for end points on (a) July 28, 1994, at 67°S, 172.5°E (parcel 11 in Plate 2a) and (b) August 6, 1994, at 67.2°S, 172.5°E (parcel 12 in Plate 3a). The dotted lines show the NAT formation temperatures, \(T_{\text{NAT}}\) [Hanson and Mauersberger, 1988], for (a) 7.2 ppbv HNO and 4.8 ppmv \(\text{H}_2\); (b) 10.3 ppbv HN\(_3\) and 5 ppmv \(\text{H}_2\). The dashed line corresponds to the ice formation temperature \(T_{\text{ICE}}\). The variations in both \(T_{\text{NAT}}\) and \(T_{\text{ICE}}\) reflect the changes in pressure along the trajectories.

Figure 8. Evolution of model calculations along a trajectory starting July 18 (day 200) and ending July 28, 1994 (67°S, 172.5°E, at 22:34 UT). Parcel 11 in Plate 2a. Values of the species as observed by the ER-2 are represented by the symbols with error bars at the end of the trajectory. Temperatures along the trajectory are shown in Figure 7a.

As discussed by Hanson and Ravishankara [1995] and Lary et al. [1995], BrONO\(_2\) hydrolysis on sulfate aerosols leads to increased HOBr levels, which via photolysis produces higher levels of HO\(_x\), especially close to sunrise. Not including BrONO\(_2\) hydrolysis in our calculations would result in HO\(_x\) values 20% lower at a SZA of 75° and 65% lower at a SZA of 85°.

If we now study parcel 11 of Plate 2a, with a temperature history shown in Figure 7a, we obtain model calculations for the evolution of individual species during the 10 days prior to the ER-2 measurement, as shown in Figure 8. These results correspond to the initialization in case 2, assuming pre processing of HCl. When the temperature decreases below 200 K (on day 207.5), the reaction of HCl and CINO\(_2\) on STS becomes fast enough to deplete slightly both chlorine reservoirs and to increase Cl\(_x\).

The precipitous drop in temperatures for the last 12 hours of the trajectory causes the reactivity of (1) to increase by an order of magnitude. While at the same time, the uptake of HNO\(_3\) generates the growth of aerosols (Figure 6) to form supercooled ternary solutions. As a consequence of high reactivity and increased surface area, HCl and CINO\(_2\) are rapidly converted to Cl\(_2\) (through reaction (1)) which itself is transformed to ClO and Cl\(_2\)O. Heterogeneous reactions of HCl with HOC1 (reaction (3)) and of CINO\(_2\) with H\(_2\)O (reaction (2)) result in less than 0.02 ppbv of additional ClO production. Model-calculated HCl, CINO\(_2\), CIO, Cl\(_2\)O\(_2\) compare very well with the observed and
derived quantities at the intercept of the trajectory with the ER-2 flight track. The high levels of ClO suppress NO$_3^-$ via reaction of ClO and NO$_2$ to form CIONO$_2^-$. Indeed, the NO levels are below the detection limit of the instrument.

The analysis we presented in section 4 showed that the stoichiometry of the reaction converting HCl and CIONO$_2$ to active chlorine is 1:2, suggesting a dominant role for CIONO$_2^-+HCl \rightarrow Cl_2+HNO_3^-$. In our model simulations, where heterogeneous reactions with laboratory measured reaction rates are included, we see the same behavior as illustrated in the bottom right-hand panel of Figure 8, where we plot the loss in HCl as a function of model-produced active chlorine over the course of the 10-day trajectory. Thus, as expected, the overall stoichiometry of the heterogeneous reactions listed in Table 2 is close to that of reaction (1).

The bottom right-hand panel in Figure 8 illustrates the evolution of reservoir losses and active chlorine production for a given air parcel as a function of time rather than an instantaneous snapshot for many air parcels as in Figure 3 and 4. The slopes of these figures are similar because they show, in one case, the changes in HCl and CIONO$_2$ for a given moment in a suite of parcels that have experienced cold temperatures for different lengths of time (Figure 3 and 4), and in the other case, the time evolution of HCl and CIONO$_2$ in a parcel as it encircles the pole, steadily increasing the length of time exposure to cold temperatures (Figure 8).

6.2. Heterogeneous Reaction HOCl + HCl $\rightarrow$ Cl$_2$ + H$_2$O

When temperatures fall below 198 K, reaction (3) begins to be important and HOCl rapidly reacts with HCl to produce Cl$_2$ (see Figure 5). HOCl* itself is mainly formed by the reaction ClO + HO$_2$ $\rightarrow$ HOCl + O$_3$ as well as heterogeneously via (2) (which contributes to up to 40% of HOCl production under the July 28 conditions). In this manner, as pointed out by Prather [1992] and Crutzen et al. [1992], reaction (3) acts as an effective sink for HO$_3^-$ in the polar stratosphere. HO$_3^-$ observations inside the vortex during ASHOE/MAESA provide direct evidence for reaction (3) (also see K96): panels c and d in Plate 2 illustrate how levels of OH and HO$_2$ are indeed suppressed inside the vortex, with mixing ratios of $-0.025 \pm 0.01$ pptv and 0.10 $\pm 0.03$ pptv respectively. The trajectory model results are consistent with this effect, predicting HO$_3^-$ values slightly lower than observed. If we compare these mixing ratios with a model calculation in which we do not include reaction (3), predicted OH and HO$_2$ levels would be more than a factor of 10 higher. Not including either (2) or (3) results in modeled HO$_3^-$ being 5 times higher than observations. Note that ClOO is measured with 50% efficiency in the HO$_2$ channel, and that this could introduce a bias in the HO$_3^-$ observations by up to 15% inside the vortex.

The steady state assumption for HOCI* (reaction (6)) no longer holds for temperatures below 195 K. In these regions, rates for heterogeneous and gas phase loss become similar, and our time-dependent model calculations yield HOCl* values 50% lower than steady state calculations would predict. We have therefore included a correction factor for the HOCl* values derived from measured ClO and HO$_2$ poleward of 66°S (panel c in Plate 2 b).

Direct heterogeneous loss of OH itself on sulfate aerosols via OH + HNO$_3^- \rightarrow H_2O + NO_3^-$ is too slow to compete with the similar homogeneous reaction [Danilin et al., 1994a], and the heterogeneous loss of HO$_2^-$ on sulfate aerosol via reaction HO$_2^- + HO_2 \rightarrow H_2O_2$ is very minor in importance compared with other gas phase reactions [Danilin et al., 1994a].

A more thorough discussion of the relative importance of (2) and (3) on the HO$_3^-$ budget in the polar environment is presented by K96 in the context of the July 30, 1994, ASHOE/MAESA ER-2 flight.

6.3. Role of Aerosol Surface Type

In all of the above we have assumed that aerosols were present in the form of supercooled ternary solutions H$_2$SO$_4$/HNO$_3$/H$_2$O which grow in volume as HNO$_3$ and H$_2$O condense at temperatures below ~193 K (Figure 6). Observations of total nitrogen for this flight indeed show the presence of HNO$_3$ in the aerosol phase [Del Negro et al., this issue]. In situ observations of the particle composition and phase suggest a rather more composite picture during this flight. In particular, aerosol samples collected at 67°S inside a PSC show the presence of type I and type II particles with an effective radius of 7 μm on July 28 the high C10 levels seem to have been mainly caused by heterogeneous reaction (1) on supercooled sulfate aerosols surfaces. These results are in agreement with independent studies by Kawa et al. [1997], Dye et al. [1996] and Del Negro et al. [this issue] for the same ASHOE/MAESA flight. Because of their low observed concentrations, the contribution of types I and II PSCs to the total surface area is small (less than 5%, Goodman et al., [1997]).

Our calculations show an additional increase in chlorine activation of less than 2% if we include, in addition to supercooled aerosols, both types I and II aerosols (at a surface area of 0.2 μm$^2$/cm$^3$ for the last 12 hours of the trajectory, corresponding to the observations by Goodman et al.). This particular model calculation is illustrated by the plus symbol in Plate 2 a (case 3). Furthermore, wire impactor measurements during this flight show that up to 30% of the sulfate aerosols were frozen at 64°S on the northbound leg of the flight [Goodman et al., 1997]. If we assume that frozen sulfate aerosols were present with a surface area of 0.8 μm$^2$/cm$^3$, in addition to background aerosols, we obtain 0.03 ppbv more C10 (star symbol in Plate 2 a, case 4).

Thus for the ER-2 flight of July 28 the high C10 levels seem to have been mainly caused by heterogeneous reaction (1) on supercooled sulfate aerosols surfaces. These results are in agreement with independent studies by Kawa et al. [1997], Dye et al. [1996] and Del Negro et al. [this issue] for the same ASHOE/MAESA flight. Because of their low concentrations, types I and II PSCs did not contribute much to chlorine activation. When present, frozen aerosols have the potential of increasing chlorine activation, but under the conditions studied here, their role was comparable to sulfate aerosols.

6.4. Dependence on Temperature History

For the last 12 hours before ER-2 observations the temperature histories derived from the NMC analysis [Kawa et al., 1997] compare well with the ECMWF trajectories used in this study: the onset of the rapid cooling is very similar in the two analyses. The slightly colder temperatures (by up to 2 K) from NMC result in chlorine activation which is 10% higher than shown in Plate 2 a. Between days 200 and 208 (see Figure 7 a), the NMC analysis yields temperatures 2-3 K colder than ECMWF, but as temperatures are generally above 200 K, very little chlorine activation takes place and this does not affect our results.

7. Recent Heterogeneous Processing: August 6

Observations during the flight of August 6, 1994, are summarized in Plate 3 a and 3 b. The temperatures measured aboard the ER-2 were, on the average, 10 K warmer than on July
The lowest temperatures reached were close to 200 K (top of Plate 3 b). Ten-day back trajectories show that southward of 64°S this air was repeatedly exposed to temperatures well below NAT formation temperatures (Figure 7 b) and had been warming on the last few days before being sampled by the instruments aboard the ER-2. HCl levels outside the vortex (equatorward of 64°S, as defined by the polar jet maximum) are generally higher than for July 28 because the air sampled contained more Cl\textsubscript{y}, as indicated by the lower \textsubscript{N}2O values measured.

7.1. Model Results Along Trajectories

As in section 6.1, we first assume that the aerosols are in the liquid phase and that they incorporate HNO\textsubscript{3} to form STS at low temperatures. Model calculations along trajectories are compared to the observations in Plate 3. The latitudinal extent of enhanced ClO and Cl\textsubscript{2}O\textsubscript{2} is well reproduced by the model. If we assume no previous processing event, modeled HCl levels poleward of 65°S are much too high: over the 10 days of the calculation, most of Cl\textsubscript{NO}_2 has been consumed, and HCl lacks a partner to be further depleted. In a fashion similar to that described for the previous flight, we initialize the chlorine reservoirs assuming that 30% of Cl\textsubscript{y} has been processed and repartitioned into Cl\textsubscript{NO}_2 (case 2, triangles), as suggested by observations on July 28, 1994.

In this case, model results for HCl are in better agreement with the observations south of 64°S. The total depletion of HCl, however, generates levels of OH and HO\textsubscript{2} inside the vortex that are too high by a factor of 2 compared to observations (Plate 3 b).

Furthermore, model calculations for OH predict a local maximum inside the vortex, while observations show a minimum. This reflects the accumulation of HOCI in the model which can no longer react with HCl via (3) and as a consequence acts as a source of HO\textsubscript{2}.

On the other hand, if we assume formation of NAT PSCs (case 3, pluses), our model calculations are in better agreement with the observations of HO\textsubscript{2} at the inner vortex edge. Indeed, as the temperature was oscillating well below 195 K for air parcels inside the vortex 10 days prior to the intercept, we might expect the phase of the aerosols to be NAT, water ice, and/or frozen particles, depending on the temperature thresholds reached. We next examine the sensitivity of our model calculations to the assumed aerosol composition, which has an impact on both the surface reactivities and the growth properties of the particles.

7.2. Model Sensitivity to Aerosol Composition

For the August 6, 1994, flight, no continuous aerosol measurements are available. However, the samples collected by the Ames wire impactor experiment [Pueschel et al., 1989] show a relatively low amount of background aerosols (~1 \textmu m\textsuperscript{2} cm\textsuperscript{-3}), all in the liquid phase. This is consistent with volume observations obtained a few days later on August 8 and 10, 1994, with the continuous aerosol measurements, which are a factor of 2 lower than on July 28 and 30, 1994 (~2-3 \textmu m\textsuperscript{2} cm\textsuperscript{-3} outside of the PSC). One possible explanation for this phenomenon could be the growth and subsequent sedimentation of large aerosols (>1

![Figure 9](image-url)
Figure 10. Inside the vortex: same as Figure 9, assuming NAT (when $T_{\text{Nat}} < T < T_{\text{NAT}}$) and ice (when $T < T_{\text{Ice}}$) PSC formation.

The stratospheric temperature at which NAT particles are formed is not well known and seems to depend on the state of background particles [Rosen et al., 1993] as well as on the amount of condensing vapors [Hanson and Maurerberger, 1988]. Observations imply a barrier to the thermodynamic formation of NAT, which tends to form 3 K below $T_{\text{NAT}}$ [Fahey et al., 1989]. It is possible that surfaces need some 'accommodation' before NAT readily forms [Zhang et al., 1996]. Or, in a more complex manner, cooling and warming cycles could cause selective formation of different surface types [Tabazadeh and Toon, 1995].

We can construct the following scenario. During the first cooling cycle NAT forms on background liquid aerosols at 3 K supersaturation ($T_{\text{Nat}} - 3K$). Once $T > T_{\text{NAT}}$, NAT evaporates and leaves behind liquid aerosols and SAT. The next formation cycle may take place at 0 K supersaturation, due to preactivation of the background surfaces [Zhang et al., 1995]. When temperatures decrease below the ice formation temperature (for parcels 13 to 15, as numbered on Plate 3 a), we assume formation of type II PSCs with a radius of 10 μm. In these calculations we do not include the effects of aerosol sedimentation out of the considered air parcel or originating from air masses above. This phenomenon was observed in the redistribution of H$_2$O and NO$_y$ observations during the ER-2 dive (~16 km) during this flight [Tuck et al., 1995], but not elsewhere [Keim et al., this issue].

In Figures 9 and 10 we compare the different behavior of reactive species for the STS case and for the described PSC scenario, with sulfate aerosols acting as the background surfaces. These Lagrangian calculations correspond to the temperature history shown in Figure 7 b (parcel 12), and they assume previous processing of HCl as discussed above. For the STS case in Figure 9, ClONO$_2$ and HCl are rapidly lost via reaction (1). Once all the HCl has been consumed on day 210, the heterogeneous processing of ClONO$_2$ continues through (2) and generates very high levels of HOCI (~0.75 ppbv). As illustrated in Figure 5, the hydrolysis of ClONO$_2$ on sulfate aerosols proceeds more rapidly if there is no competition from its reaction with HCl. Small excursions of the air parcel to lower latitudes (up to 58°S) allow ClONO$_2$ to reform by reaction of ClO with NO$_3$, resulting from the photochemical conversion of HNO$_3$ (at times 212.5 and 216). Repeated exposures to cold temperatures continue the processing of ClONO$_2$ via (2) and maintain high ClO and HOCI levels. Note the strong, diurnal variation of ClO which is due to fine photolysis of ClO$_2$ during the day. At night the ClO dimer is the dominant Cl$_2$ species. For the PSC scenario in Figure 10, further depletion of ClONO$_2$ after day 210 takes place through hydrolysis of ClONO$_2$ on ice (which forms in the model on day 210.25 for 12 hours, when temperatures decrease below $T_{\text{Ice}} = 189$ K). Hydrolysis of ClONO$_2$ on NAT surfaces is much slower than on ice or sulfate aerosols; therefore, the high levels of HOCI first produced on day 210 cannot be maintained through (2) on NAT and slowly decrease via photolysis, and heterogeneous reaction with both HCl and HBr. After 2-3 days, HOCI levels are controlled by pure gas phase chemistry. As a consequence of these lower HOCI mixing ratios, the resulting OH and HO$_2$ are in better agreement with observations for the PSC case (case 3 in Plate 3 b) rather than for the STS case (case 2).

We have tested the sensitivity of our results on the occurrence of ice PSCs on day 210 (8 days prior to the ER-2 flight) and found...
that the formation of ice and assumptions on surface area have very little impact (± 10%) on the HOx levels at the end of the trajectory, due to the rapid relaxation time of HOCl.

Note that both model cases predict very low HCl (0.05 ppbv), while the observations seem to suggest a higher value (0.17 ± 0.2 ppbv) at these mixing ratios. The signal-to-noise ratio is poor as reflected by the large error bars, and it is difficult to determine how much HCl is present.

We have used a sticking coefficient of 0.001 for (2) on NAT as recommended by DeMore et al. (1994). However, laboratory results range between 10⁻⁴ and 0.02 [Leu et al., 1991; Moore et al., 1990]. If we use a value of 0.01, our calculations yield slightly larger HOCl levels and further improvement in the agreement with the HOx observations.

Thus, compared to the July 28 flight, during August 6, relatively high levels of OH and HO₂ were measured inside the vortex: 0.1 (± 0.03) and 0.5 (± 0.15) pptv, respectively, as opposed to 0.025 and 0.1 pptv on July 28 for similar solar zenith angles. This source of HO₃ is supplied by high HOCl mixing ratios on August 6 (Plate 3 b). In this case, the sustained near-zero HCl mixing ratios contribute to turning off the main sink for HOCl reaction (3). Comparison between model calculations and observations support the laboratory measured small reactivity of (2) on NAT surfaces, as opposed to the faster rates for the same reaction on sulfate aerosols and type II PSCs.

The bottom right-hand panels of Figure 9 and 10 show the two types of slopes obtained for ΔHCl and ΔCINO₂ which were discussed in section 4 for case 4.4.: as reaction (1) proceeds, the 1:2 slope develops, but when all the HCl is depleted, CINO₂ continues to produce active chlorine through (2) on sulfate aerosols or type II PSCs, forming the 1:1 slope. The different PSC composition assumed for these two cases do not have a large effect on active chlorine and HOx levels, and therefore there is not much difference in the patterns on these two bottom plots.

The wire impactor measurements on July 28, 1994, have clearly shown that SAT could be present in the polar environment. Thus we have conducted a test case where we have assumed the background aerosols to be all frozen (at a surface area of 1 μm² cm⁻²), once ice formation temperature is reached and that NAT subsequently forms on these surfaces. The results obtained are very similar to those shown in Figure 10, due to heterogeneous reactivities for SAT which are comparable to those on sulfate aerosols.

From our photochemical analysis of the ER-2 observations, we deduce that the amount of chlorine activation is fairly independent of the composition of PSCs (STS, NAT, ice), due to the very similar reactivity of (1) on all these surfaces (Figure 5). However, the composition of PSCs can have a large impact on the amount of nitric acid in the vortex [Del Negro et al., this issue]. Thus on the basis of CIO and HOCl observations alone, no differentiation is possible. On the other hand, reaction (2) has very different rates for these surfaces, and its impact on HOCl levels has been used to deduce the possible formation of type I PSCs in air sampled on August 6, 1994. In this manner, OH and HOCl can be very sensitive indicators of the degree of processing of HCl and may exhibit different signatures depending on the type of heterogeneous surfaces that affected chlorine activation.

7.3. Dependence on Temperature History

The temperature histories obtained with the isentropic NMC fields tend to be 3 K colder than the ECMWF trajectories close to the edge of the vortex (62°-66°S) for August 6, 1994. The temperatures begin to diverge after one day along the back trajectory. This difference has a large impact on the photochemical calculations: the colder NMC temperatures lead to 2-5 times more chlorine activation near the edge of the vortex (the latitudinal calculations in model-calculated CIO is displaced in latitude by 1.5° north compared to ER-2 observations). Outside of the vortex (south of 62°S) and deeper inside the vortex (north of 66°S), the analyses are similar and yield very similar results for HCl, CIO, HOCl, and NO. The observed difference could be due in part to the strong cooling rate at the edge of the vortex which is taken into account in the ECMWF three-dimensional trajectories but not in the GSPC isentropic trajectories. Future comparisons between observed and derived cooling rates would be required to resolve these differences.

7.4. Implications for Ozone Loss

In response to the chlorine activation, ozone begins to decrease in June continuing until the springtime when higher sun levels fuel the chemical cycles involving halogens [Molina and Molina, 1987; McElroy et al., 1986]. In situ O₃ observations during ASHOLE/MAESA show that 25% of O₃ has been depleted by early August [Tuck et al., 1995].

Figure 10 shows that active chlorine levels had been elevated for at least 1 week prior to the ER-2 flight on August 6, 1994. From our photochemical back trajectory calculations for this 10-day period, we obtain an average ozone loss of 30 ppbv day⁻¹. If this rate of loss can be maintained, then by mid-October, very little ozone is left. Indeed, air with extremely depleted O₃ levels (95% loss) was sampled by the ER-2 on two occasions on October 10 and 13 (W96b). However, more generally ER-2 observations at this time show ozone losses in excess of 75% at the highest latitudes. These different amounts of ozone loss observed in the edge region of the vortex probably reflect varying degrees of mixing and exposure to sunlight which result in separate regimes of chlorine recovery (W96b).

8. Summary and Conclusions

Measurements of HCl and CIO during the Antarctic winter of 1994 indicate chemical processing of the chlorine reservoir HCl to active chlorine via the heterogeneous reaction HCl + CINO₂ → CIO + HNO₃. This processing is diagnosed by large losses in HCl, increases in CIO, and a slope of 1:2 for AHCl versus CIO + 2 Cl₂O₂, consistent with the stoichiometry of the above reaction. The high amounts of CINO₂ inferred in this study (and forming the CINO₂ "collar") are generated by PSC processing followed by excursions into sunlight. While chlorine activation begins with 60-70% of Cl₂ as HCl, the near-total removal of HCl can take place from excursions in and out of sunlight, with resupply of CINO₂ and HOCl which provide oxidation partners for HCl.

Examination of two separate ER-2 flights with a box model along trajectories has confirmed the dominant role of reaction (1) in generating the observed HCl loss and CIO production. Evidence of the reaction HCl + HOCl on sulfate aerosols was found by its impact on HOCl levels. On the basis of high HOCl observations under very low HCl conditions, we deduce the likely formation of type I PSCs identified by their slow rate for CINO₂ + H₂O → HOCl + H₂O. Furthermore, in this environment, the exact physical and chemical state of the surfaces providing sites for heterogeneous reactions does not significantly change the amount of chlorine activation generated.

Together, these findings quantitatively confirm the central role of heterogeneous chemistry on sulfate aerosols and PSCs in the Antarctic stratosphere and point to the importance of
latitudinal excursions in the edge region of the vortex. The
consistency between model calculations and observations
strengthens our confidence in the current understanding of
stratospheric gas phase and heterogeneous polar chemistry
controlling chlorine activation.

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