GEOPHYSICAL RESEARCH LETTERS, VOL. 22, NO. 21, PAGES 2937-2940, NOVEMBER 1, 1995

UARS PSC, $ClONO_2$, HCl, and ClO measurements in early winter: Additional verification of the paradigm for chlorine activation

Marvin A. Geller,[1] Valery Yudin,[1] A. R. Douglass,[2] J. W. Waters,[3]
L. S. Elson,[3] A. E. Roche,[4] and J. M. Russell III[5]

Abstract. We present an example of observations within a single air mass of ClO, $ClONO_2$, and HCl from the instruments on the UARS spacecraft. A three-dimensional chemistry-transport calculation for HCl is used to show that this air mass has been transported through regions cold enough for polar stratospheric cloud formation and chlorine activation through heterogeneous chemical reactions. These data, together with modeling of HCl with and without heterogeneous loss as a qualitative measure of polar processing, indicate directly the transformation of the reservoirs HCl and $ClONO_2$ to reactive chlorine species.

1. Introduction

The discovery of the Antarctic ozone hole by Farman et al. (1985) has motivated extensive theoretical work, ground-based observations, and aircraft observations to better understand processes occurring in the Antarctic and Arctic that influence ozone loss. These impressive efforts have resulted in a generally accepted paradigm for polar processing of air on polar stratospheric clouds (PSCs) and the subsequent chemical reactions that deplete ozone.

This paradigm begins with lower stratospheric temperatures becoming very cold in polar regions in early winter, resulting in the formation of an intense westerly polar vortex. When the temperatures become low enough, PSCs form, and reaction (1) takes place

$$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2 \qquad (1)$$

Thus, we expect to see cold temperatures associated with enhanced PSC amounts (see Hanson and Mauersberger, 1988), and this should lead to decreases in the atmospheric inactive chlorine species HCl and $ClONO_2$. We also expect to see increases in active chlorine in the form of $ClO + 2Cl_2O_2 + Cl$.

Aircraft measurements have indicated that reaction (1) is occurring in the Antarctic and Arctic winters. Anderson et al. (1989) have measured the increases in ClO in the Antarctic and have shown that these ClO enhancements are highly correlated with O_3 losses. Brune et al. (1990) have shown similar increases in ClO occurring in the Arctic. Webster et al. (1993) have shown measured ClO enhancements, measured HCl depletions, and <u>inferred</u> $ClONO_2$ (actually residual inorganic chlorine species labeled as $ClONO_2^*$) depletions that indicate the polar processing reaction (1) has taken place. They used trajectory calculations to demonstrate that these regions of polar processed air had previously encountered air temperatures cold enough for PSCs to have formed, enabling reaction (1) to take place.

UARS measurements have also indicated that reaction (1) is occurring in the Antarctic and Arctic winters. Waters et al. (1993a, 1993b) have shown enhanced ClO regions in both the Arctic and Antarctic occurring where the polar vortex extends equatorward into sunlit regions. Roche et al. (1993b, 1994) have shown $ClONO_2$ depletions in both the Antarctic and Arctic winters. Russell et al. (personal communication) have shown examples of depletions of HCl in regions of enhanced aerosol extinctions in Southern Hemisphere winter, indicating that HCl is being depleted in regions that are cold enough for PSCs to form.

Thus, aircraft, ground-based, and satellite observations provide a great deal of evidence that reaction (1) takes place on PSC surfaces in the Antarctic and Arctic winters, transforming inactive chlorine to reactive chorine. The purpose of this paper is to present UARS observations that indicate conversion between the reservoir chlorine species HCl and $ClONO_2$ and the reactive species ClO. These UARS observations demonstrate that air which has encountered temperatures cold enough for PSCs to occur do show depletions of these inactive chorine species and that reactive chlorine species are enhanced in this same air mass. For clear identification of regions where $ClONO_2$ and HCl have been depleted by heterogeneous chemical processes, we use a 3-D polar processing model.

2. UARS Observations

In this paper, we use data from the UARS MLS, CLAES, and HALOE instruments (see Barath et al., 1993; Roche et al, 1993a; and Russell et al, 1993, for instrument descriptions). Both the MLS and CLAES instruments observe the atmosphere perpendicular to the spacecraft velocity vector in the direction away from the Sun. The UARS spacecraft is flying at an inclination of 57 ^{o} and an altitude of about 585 km, and its orbit is processing in local time. Because of this orbital precession, the UARS spacecraft must execute a yaw maneuver approximately every 36 days to ensure that the same side of the spacecraft always faces away from the Sun (Reber, 1993). This implies that the high latitudes of each hemisphere are viewed for alternative periods that are about one month long. For instance, when the cold side of UARS faces north, the emission sounders CLAES and MLS obtain data daily from about 33 ^{o}S to 80 ^{o}N. This also implies that the latitude that separates daytime UARS viewing from nighttime UARS viewing changes with time. This is particularly important for MLS ClO viewing since significant concentrations of ClO are only expected to be present under sunlit conditions (see Schoeberl et al., 1993). This precession

---

[1] Institute of Terrestrial and Planetary Atmospheres, State University of New York at Stony Brook.

[2] Laboratory for Atmospheres, NASA Goddard Space Flight Center, Greenbelt, Maryland.

[3] Jet Propulsion Laboratory, California Institute of Technology, Pasadena.

[4] Lockheed Palo Alto Research Laboratory, Palo Alto, California.

[5] NASA Langley Research Center, Hampton, Virginia.

Copyright 1995 by the American Geophysical Union.

Paper number 95GL01661
0094-8534/95/95GL-01661$03.00

also implies that the latitude of the HALOE solar occultation observations shows great variation over a month. All of these considerations imply that it is difficult to find days in which MLS and CLAES are looking into the winter hemisphere, and MLS is looking at high latitudes in sunlight, and HALOE is measuring at latitudes where polar processing is occurring.

Version 3 MLS, version 7 CLAES, and version 16 HALOE data are used in this paper. The quoted measurement accuracies and precisions are about 30% and 0.3 ppbv, respectively, for CLAES $ClONO_2$ (Roche at al., 1994) and 15% and 5%, respectively, for HALOE HCl (Russell et al., 1993). The individual measurement accuracy for MLS ClO is 0.4 ppbv (Waters, 1993b).

3. Polar Processing Modeling

In the same manner as Douglass et al. (1993), we use the NASA/Goddard Space Flight Center (NASA/GSFC) chemical-transport model (CTM) in which the temperatures and winds are derived from the STRATAN troposphere-stratosphere data assimilation at NASA/GSFC. The CTM has been run to derive depletions in HCl (DHCl), using a simple temperature threshold below which HCl loss occurs, for the first two Northern and Southern Hemisphere winters observed by UARS. (We emphasize that this is not a full chemistry model.) We use these model results for two purposes. One is to guide us in identifying days for which HALOE data are available in regions with substantial polar processing. The other is to interpret the HCl and $ClONO_2$ depletions and ClO enhancements.

4. Results

Figure (1) shows six Northern Hemisphere mapped products for January 10, 1992. In all of these, the North Pole is at the center, the dashed inner circle is at 60 ^{O}N, and the outer edge is at 30 ^{O}N. Proceeding from left to right along the top row, STRATAN temperatures (in ^{O}K), the Ertel potential vorticity (PV) in units of 10^{-5} ^{O}K m^2 s^{-1} kg^{-1}, and the modeled HCl depletions in ppbv (DHCl) are all plotted on the 465 ^{O}K potential temperature surface (near a pressure altitude of 46 hPa) at 12 GMT. Potential temperature is used as the vertical coordinate in displaying these model-derived parameters to clearly show the edge of the polar vortex. The wind vectors are plotted as arrows where the length of the arrows denote the wind speed according to the scale shown at the lower left of the temperature plot. The triangles in the DHCl plot are the locations of HALOE observations on that day. (The heavy dashed white circle about the pole shows the day-night boundary of the MLS observations). The bottom row shows CLAES aerosol extinction (in units of 10^{-5} km^{-1}) , nighttime CLAES $ClONO_2$ mixing ratios (in ppbv), and the daytime ClO mixing ratio (in ppbv) distribution from MLS, all plotted at 46 mbar. (For this mapping, daytime (nighttime) has been defined by the solar zenith angle being less (greater) than 90 ^{O}.) Pressure is used in these plots since this is the vertical coordinate in which these UARS observations are reported. On all of these plots, the HALOE observational track and the PV vortex boundary are shown.

Note that on January 10, 1992, temperatures colder than 195 ^{O}K are seen near 60 ^{O}N and 0 ^{O}E just inside of the vortex edge. Enhanced aerosol extinction is also seen in this region, indicating the presence of PSCs. On this date the polar vortex, as defined by the PV field, is filled with polar processed air, as defined by the modeled DHCl. Thus, the air circulating within the polar vortex has passed through regions cold enough for the existence of PSCs and should have experienced heterogeneous chemistry depleting the inactive chlorine species HCl and $ClONO_2$ and enhancing reactive chlorine. Evidence that this is the case is seen in the agreement between the low values of CLAES $ClONO_2$ and the polar processed air within the polar vortex. ClO enhancements are seen where the polar processed air is in sunlight. In darkness, most of the reactive chlorine should be in the dimer form Cl_2O_2. Figure (2) shows the measured $ClONO_2$, measured HCl, and modeled HCl at 47 ^{O}N (along the HALOE measurement track) at 46 hPa (about 20 km) on the left and HCl + $ClONO_2$ and ClO averaged over a zonal band extending from 46-54 ^{O} N, at the same altitude, on the right. Note that the figure (2) results are consistent with the results shown in figure (1) in that both HALOE and the CTM give HCl depletions in a region around 0 ^{O}E along the HALOE track of observations.

5. Summary and Discussion

As indicated earlier, previous ground-based and aircraft observations and satellite data provide compelling evidence for reaction (1), or some other reactions converting the inactive chlorine species HCl and $ClONO_2$ to active chlorine species, to be occurring on PSC surfaces. Previous UARS observations have supported this picture. The present work strengthens this evidence by using UARS observations directly to show HCl and $ClONO_2$ depletions within the same air mass and ClO enhancements when this air mass is exposed to sunlight. The accompanying modeling shows that this air mass had previously encountered air temperatures cold enough for PSCs to be present, and the UARS measurements demonstrate that PSCs are in fact present in regions of sufficiently cold temperatures.

From figure (2), we see in the left-hand panel that outside of the polar vortex region (the polar processed air) the $ClONO_2$ mixing ratios are about 1.2 ppbv, rising to about 1.8 ppbv near 60 ^{O}W, while the HCl mixing ratios are about 0.9 ppbv. Thus, outside of the polar vortex, at this latitude, the HCl amounts are somewhat less than the $ClONO_2$ amounts except in the region of enhanced $ClONO_2$ concentrations near 60 ^{O}W where the $ClONO_2$ concentrations are much higher than those of HCl. Looking at the right-hand panel, we see that inside the polar processing region, ClO mixing ratios reach about 1.5 ppbv while the HCl + $ClONO_2$ concentrations drop from about 2 ppbv outside the vortex to about 0.9 ppbv inside. These observations are consistent with there being more inorganic chlorine at this level inside the polar vortex than outside (due to enhanced descent inside the vortex). These UARS measurements provide compelling evidence for reaction (1) taking place in regions where sufficiently cold temperatures exist for PSCs to form. We have looked at higher levels (520 ^{O}K and 600 ^{O} K) and find maximum depletions in inactive chlorine taking place at 465 ^{O}K, with little evidence for depletions in inactive chlorine being seen at 600 ^{O}K and above.

Recently, a great deal of attention has been paid to the apparent inconsistency between the chlorine partitioning implied by aircraft measurements (see Webster et al., 1993, 1994). Briefly, that fraction of inorganic chlorine that is found in the form $ClONO_2$ appears to exceed that derived from models. It is difficult for us to address this problem with these UARS data. We have found no good way of deriving Cl_y from the UARS data for the January period presented here. If we use the relationship between N_2O and Cl_y in Webster (1993) together

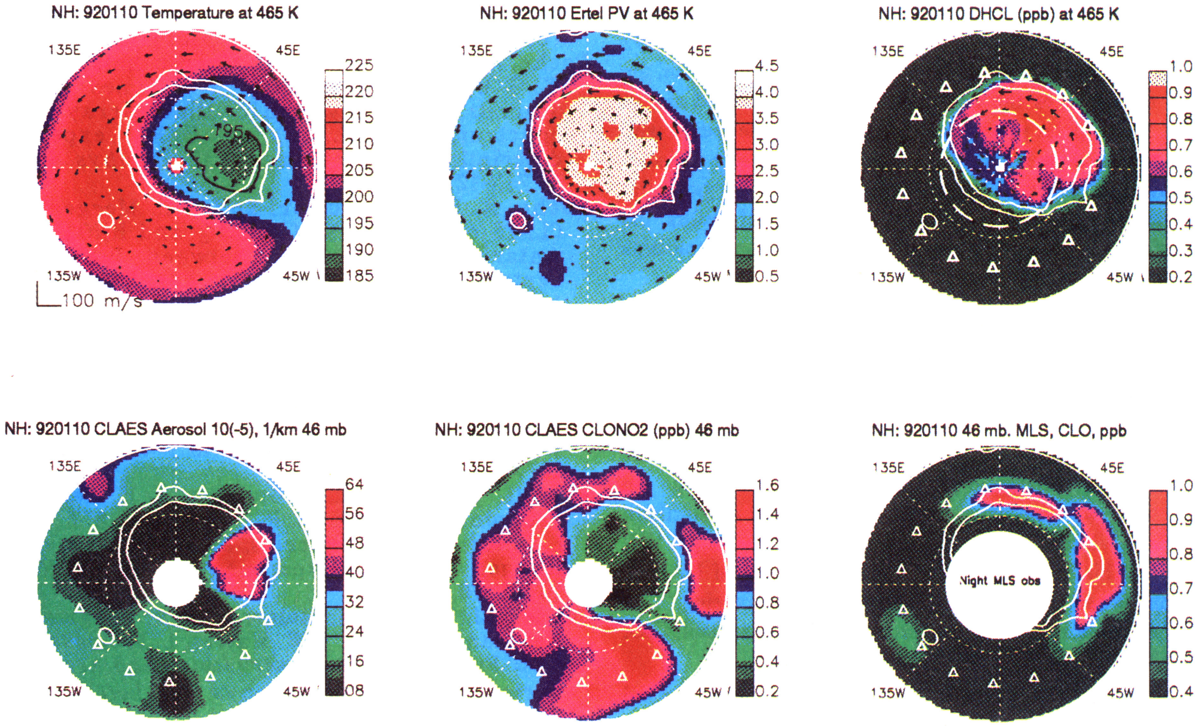

Figure 1. Maps are for January 10, 1992, centered at the North Pole with their outer boundary at 30 ^{O}N. The latitude 60 ^{O}N is shown as a white dashed circle. Top left - STRATAN temperatures at 12 GMT on the 465 ^{O}K potential temperature surface in units ^{O}K; Top middle - Potential vorticity (PV) at 12 GMT at 465 ^{O}K in units 10 $^{-5}$ ^{O}K m^{2} s^{-1} kg^{-1}, two curves that indicate the approximate boundary of the polar vortex are shown; Top right - Modeled DHCl at 12 GMT at 465 ^{O}K in ppbv, triangles show locations of HALOE measurements on that day; Bottom left - Aerosol extinction measured by CLAES at 46 hPa in units of 10^{-5} km^{-1}; Bottom middle - Nighttime ClONO$_2$ measured by CLAES; Bottom right - Daytime ClO measured by MLS.

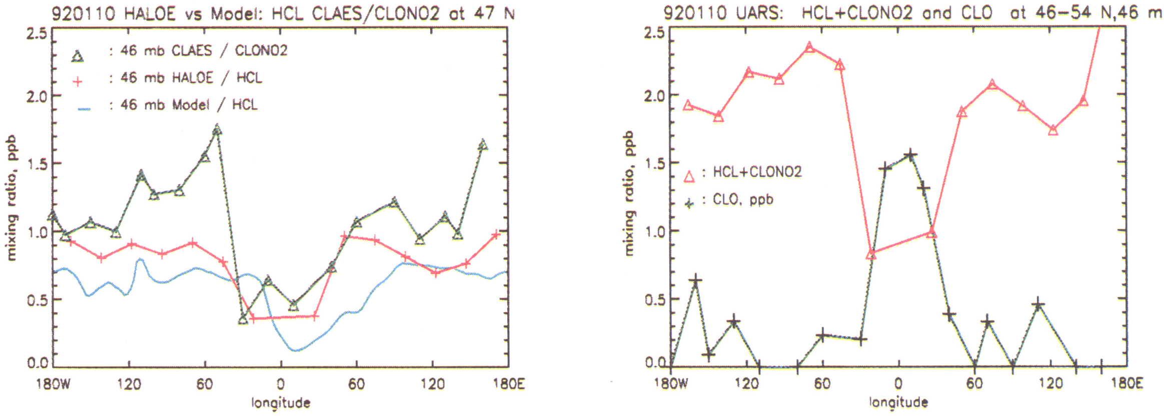

Figure 2. Left panel: CLAES ClONO$_2$, HALOE HCl, and CTM modeled HCl at 47 ^{O}N and 46 hPa on January 10, 1992, all in ppbv, as a function of longitude. Right panel: Measured HCl + ClONO$_2$ and ClO averaged over the zonal band 46-54 ^{O}N and 46 hPa on January 10, 1992, all in ppbv, as a function of longitude.

with CLAES measurements of N$_2$O, we find that the Cl$_y$ concentrations are smaller than the sum of HCl and ClONO$_2$ outside of the polar vortex. Therefore, the N$_2$O-Cl$_y$ relationship is inconsistent with the measured values of N$_2$O, HCl, and ClONO$_2$. All we are able to say is that the measured amounts of HCl and ClONO$_2$ are approximately equal both inside and outside the polar vortex, except in some regions where ClONO$_2$ amounts are clearly enhanced. Since chorine partitioning depends on O$_3$ concentrations, we note that the O$_3$ measured by HALOE at 46 mbar are about 3.5-4 ppmv outside of the polar vortex, decreasing to values as low as 2 ppmv inside of the polar vortex at 46 mbar (or about 465 ^{O}K in potential temperature). The sharp gradient in ClONO$_2$ near 60 ^{O}W coincides with a sharp gradient in O$_3$.

Unfortunately, not many days exist in which HCl, ClONO$_2$, and ClO are measured together in regions of polar processing by the UARS instruments. This follows from the different nature of the MLS and CLAES emission instruments, from whose measurements daily maps can be obtained, and the HALOE occultation instrument which gives measurements along a fixed latitude circle on a given day. We have used the polar processing model to see where the HALOE measurement latitude intersects an air mass within which polar processing is believed to take place. Only a few such days during early Arctic winters 91/92 and 92/93 have been found in the UARS data set. Even then, the HALOE track grazes the edge of the polar processed air, as indicated by our polar processing model. This is the reason why we have presented the UARS measurements on pressure surfaces. If we interpolate these observations to the same potential temperature surfaces used in displaying the model results, the interpolations are not able to properly resolve the sharp gradients in $ClONO_2$ that are seen on pressure surfaces.

We have inspected HALOE HCl data during the end of December and the first few weeks of January 91/92 and 92/93 when HALOE occultation coverage is near the boundary of the winter polar vortex. We find significant HCl depletions in the HALOE data, such as is seen in figure (1), during the period January 9-16, 1992, when the model results indicate that the sampled air has undergone significant polar processing. In contrast, there were no days during the early part of Northern Hemisphere winter 92/93 that showed similarly large HCl depletions. This is because the air at the latitudes of HALOE measurements had not undergone as much polar processing. This was also apparent in UARS measurements of less aerosol, ClO, and $ClONO_2$ depletion during this period.

In this paper, we have focused on reaction (1) as the chemical pathway by which inactive chlorine species are converted to reactive chlorine on PSC surfaces. In fact, the observational evidence shown here implies chemical reactions taking place at temperatures cold enough for PSCs to form, but chemical pathways other than reaction (1) whose net results are decreases in HCl and $ClONO_2$ and increases in ClO (and presumably Cl_2O_2), can explain these observations equally well.

References

Anderson, J. G., W. H. Brune, and M. H. Proffitt, Ozone destruction by chlorine radicals within the Antarctic vortex: the spatial and temporal evolution of ClO-O_3 anticorrelation based on in situ ER-2 data, *J. Geophys. Res., 94*, 11,465-11,479, 1989.

Barath, F. T., M. C. Chavez, R. E. Cofield, D. A. Flower, M. A. Frerking, M. B. Gram, W. M. Harris, J. R. Holden, R. F. Jarnot, W. G. Kloezeman, G. J. Klose, G. K. Lau, M. S. Loo, B. J. Maddison, R. J. Mattauch, R. P. McKinney, G. E. Peckham, H. M. Pickett, G. Siebes, F. S. Soltis, R. A. Suttie, J. A. Tarsala, J. W. Waters, and W. J. Wilson, The Upper Atmosphere Research Satellite Microwave Limb Sounder, *J. Geophys. Res., 98*, 10,751-10,762, 1993.

Brune, W. H., J. G. Anderson, and K. R. Chan, In situ observations of ClO in the Arctic stratosphere: ER-2 aircraft results from 59 °N to 80 °N latitude, *Geophys. Res. Lett., 17*, 505, 1990.

Douglass, A., R. Rood, J. Waters, L. Froidevaux, W. Read, L. Elson, M. Geller, Y. Chi, M. Cerniglia, and S. Steenrod, A 3D simulation of the early winter distribution of reactive chlorine in the north polar vortex, *Geophys. Res. Lett., 20*, 1271-1274, 1993.

Farman, J. C., B. G. Gardiner, and J. D. Shanklin, Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature, 315*, 207-210, 1985.

Hanson, D. and K. Mauersberger, Laboratory studies of the nitric acid trihydrate: implications for the south polar stratosphere, *Geophys. Res. Lett., 15*, 855-859, 1988.

Reber, C. A., The Upper Atmosphere Research Satellite (UARS), *Geophys. Res. Lett., 20*, 1215-1218, 1993.

Roche, A. E., J. B. Kumer, J. L. Mergenthaler, G. A. Ely, W. G. Uplinger, J. F. Potter, T. C. James, and L. W. Sterritt, The cryogenic limb array etalon spectrometer (CLAES) on UARS: experiment description and performance, *J. Geophys. Res., 98*, 12,763-12,775, 1993a.

Roche, A. E., J. B. Kumer, and J. L. Mergenthaler, CLAES observations of $ClONO_2$ and HNO_3 in the Antarctic stratosphere, between June 15 and September 17, 1992, *Geophys. Res. Lett., 20*, 1,223-1,226, 1993b.

Roche, A. E., J. B. Kumer, J. L. Mergenthaler, R. W. Nightingdale, W. G. Uplinger, G. A. Ely, J. F. Potter, D. J. Wuebbles, P. S. Connell, and D. E. Kinnison, Observations of lower stratospheric $ClONO_2$, HNO_3, and aerosol by the UARS CLAES experiment between January 1992 and April 1993, *J. Atmos. Sci., 20*, 2877-2902, 1994.

Russell, J. M. III, L. L. Gordley, J. H. Park, S. R. Drayson, W. D. Hesketh, R. J. Cicerone, A. F. Tuck, J. E. Frederick, J. E. Harries, and P. J. Crutzen, The Halogen Occultation Experiment, *J. Geophys. Res., 98*, 10,777-10,797, 1993.

Schoeberl, M. R., R. S. Stolarski, A. R. Douglass, P. A. Newman, L. R. Lait, J. W. Waters, L. Froidevaux, and W. G. Ready, MLS ClO observations and Arctic polar vortex temperatures, *Geophys. Res. Lett., 20*, 2861-2864, 1993.

Waters, J. W., L. Froidevaux, W. G. Read, G. L. Manney, L. S. Elson, D. A. Flower, R. F. Jarnot, and R. S. Harwood, Stratospheric ClO and ozone from the Microwave Limb Sounder on the Upper Atmosphere Research Satellite, *Nature, 362*, 597-602, 1993a.

Waters, J. W., L. Froidevaux, G. L. Manney, W. G. Read, and L. S. Elson, MLS observations of lower stratospheric ClO and O_3 in the 1992 Southern Hemisphere winter, *Geophys. Res. Lett., 20*, 1219-1222, 1993b.

Webster, C. R., R. D. May, D. W. Toohey, L. M. Avallone, J. G. Anderson, P. Newman, L. Lait, M. R. Schoeberl, J. W. Elkins, and K. R. Chan, Chlorine chemistry on polar stratospheric particles in the Arctic winter, *Science, 261*, 1130-1133, 1993.

Webster, C. R., R. D. May, L. Jaeglé, H. Hu, S. P. Sander, M. R. Gunson, G. C. Toon, J. M. Russell III, R. M. Stimpfle, J. P. Koplow, R. J. Salawitch, and H. A. Michelson, Hydrochloric acid and the chlorine budget of the lower stratosphere, *Geophys. Res. Lett., 21*, 2575-2578, 1994.

Marvin A. Geller, Valery Yudin; Institute for Terrestrial and Planetary Atmospheres; SUNY/Stony Brook; Stony Brook, NY 11794-5000

A. R. Douglass; NASA Goodard Space Flight Center; Code 916; Greenbelt, MD 20071.

J. W. Waters, L. S. Elson; Jet Propulsion Laboratory; Mail Code 183-701; 4800 Oak Grove Drive; Pasadena, CA 91109.

A. E. Roche; Lockheed Palo Alto Research Laboratory; Dept. 91-20, Bldg. 201; 3251 Hanover Street; Palo Alto, CA 94304.

J. M. Russell III; NASA/Langley Research Center; Mail Stop 401B; Hampton, VA 23665-5225.

(Received November 9, 1994; Revised March 9, 1995; Accepted April 19, 1995)