

01 Aug 2000

Observation of Stratospheric Ozone Depletion associated with Delta II Rocket Emissions

Martin N. Ross

Darin W. Toohey

W. T. Rawlins

E. C. Richard

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/phys_facwork/146

Follow this and additional works at: https://scholarsmine.mst.edu/phys_facwork

 Part of the [Chemistry Commons](#), and the [Physics Commons](#)

Recommended Citation

M. N. Ross and D. W. Toohey and W. T. Rawlins and E. C. Richard and K. K. Kelly and A. F. Tuck and M. H. Proffitt and D. E. Hagen and A. R. Hopkins and P. D. Whitefield and J. R. Benbrook and W. R. Sheldon, "Observation of Stratospheric Ozone Depletion associated with Delta II Rocket Emissions," *Geophysical Research Letters*, vol. 27, no. 15, pp. 2209-2212, American Geophysical Union (AGU), Aug 2000. The definitive version is available at <https://doi.org/10.1029/1999GL011159>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Physics Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Observation of Stratospheric Ozone Depletion Associated With Delta II Rocket Emissions

M. N. Ross¹, D. W. Toohey², W. T. Rawlins³, E. C. Richard⁴, K. K. Kelly⁴,
A. F. Tuck⁴, M. H. Proffitt⁵, D. E. Hagen⁶, A. R. Hopkins⁶, P. D. Whitefield⁶,
J. R. Benbrook⁷, and W. R. Sheldon⁷

Abstract. Ozone, chlorine monoxide, methane, and submicron particulate concentrations were measured in the stratospheric plume wake of a Delta II rocket powered by a combination of solid (NH₄ClO₄/Al) and liquid (LOX/kerosene) propulsion systems. We apply a simple kinetics model describing the main features of gas-phase chlorine reactions in solid propellant exhaust plumes to derive the abundance of total reactive chlorine in the plume and estimate the associated cumulative ozone loss. Measured ozone loss during two plume encounters (12 and 39 minutes after launch) exceeded the estimate by about a factor of about two. Insofar as only the most significant gas-phase chlorine reactions are included in the calculation, these results suggest that additional plume wake chemical processes or emissions other than reactive chlorine from the Delta II propulsion system affect ozone levels in the plume.

1. Introduction

Rockets used by the space launch industry employ a number of different propellant combinations and emit a variety of exhaust products directly into the stratosphere. While rocket exhaust currently represents a small fraction of the total impact of industrial activity on the stratosphere, prudence requires that we carefully evaluate its impact. Space launch traffic in general is widely expected to increase during coming decades so that the stratospheric impact of rocket emissions from all propellant types will increase. Previous investigations have focused mainly on the stratospheric impact of large solid rocket motors (SRMs) using ammonium perchlorate (NH₄ClO₄) oxidizer. Recent stratospheric measurements have shown that large solid fueled rockets

dramatically perturb stratospheric ozone in regions covering up to several hundred square kilometers for several hours after launch [Ross et al., 1997b].

Solid fueled rockets, however, represent only a portion of the emission inventory of the space launch industry. Another widely used propellant combination is liquid oxygen and kerosene (LOX/RP; RP refers to RP-1 or RG-1, kerosene distillations widely used as rocket fuel.) Careful study of LOX/RP combustion emissions is justified for several reasons. LOX/RP exhaust accounts for a significant fraction (about one fourth by mass in 1998) of the total stratospheric emission by rockets and several powerful LOX/RP rockets in development will increase the relative impact of these emissions. In this paper we present measurements obtained in the stratospheric plume wakes of a Delta II rocket that provide evidence that reactive chlorine gas may not be the only chemically active component of the Delta II emission.

2. Plume Wake Measurements and Analysis

The Delta II plumes were sampled following daytime launches on November 7, 1996 (1600 UT) from Cape Canaveral Air Station (28° 33' N, 80° 18' W) and on May 17, 1998 (2316 UT) from Vandenberg Air Force Base (120° 37' W, 34° 48' N). The altitudes of the plume encounters varied between 18 and 18.6 km. Measurements included O₃ [Sen et al., 1996] (University of Houston) and total (volatile and nonvolatile) aerosol concentrations [Ross et al., 1999] in 1996 and ClO [Pierson et al., 1999], CH₄, three independent O₃ measurements [Sen et al., 1996] (University of Houston); [Proffitt et al., 1989] (NOAA); and [Proffitt and Rawlins, 1998] (PSI) and total aerosol concentrations [Ross et al., 1999] in 1998. Following each launch, the WB-57F aircraft intercepted the plume wake six times. Only the 1998 data is comprehensive enough to support significant conclusions regarding the details of plume wake chemistry and we focus on that data shown in Figure 1. The plume encounters are clearly visible as large departures from the background for all species except CH₄, which shows a modest decrease only during the fifth encounter. The sixth encounter does not conform with the trends in composition (progressively greater ozone loss) and duration (progressively longer) observed in the preceding encounters, apparently because the aircraft intercepted an edge of the main plume. Since the encounters occurred at slightly different altitudes (between 18 and 18.6 km), the aircraft sampled distinct plume segments.

Representative of the first three encounters, Figure 2 shows expansions of the second encounter when the plume was 12 minutes old. At the center of the generally symmetric plume, ozone concentration was reduced by 70% from the

¹M. N. Ross, Environmental Systems Directorate, The Aerospace Corporation, PO Box 92957, Los Angeles CA 90009.

²D. W. Toohey, Program in Atmospheric Sciences, University of Colorado, Boulder CO 80309

³W. T. Rawlins, Physical Sciences, Incorporated, 20 New England Business Center, Andover MA 01810

⁴E. C. Richard, K. K. Kelly, A. F. Tuck, Aeronomy Laboratory, NOAA, 325 Broadway, Boulder CO 80303

⁵M. H. Proffitt, The Environmental Division, World Meteorological Organization, 7 bis, Avenue de la Paix, Geneva, Switzerland

⁶P. D. Whitefield, D. E. Hagen, A. R. Hopkins, Cloud and Aerosol Sciences Laboratory, University of Missouri-Rolla, Rolla MO 65401

⁷J. R. Benbrook and W. R. Sheldon, Physics Department, University of Houston, Houston TX 77204

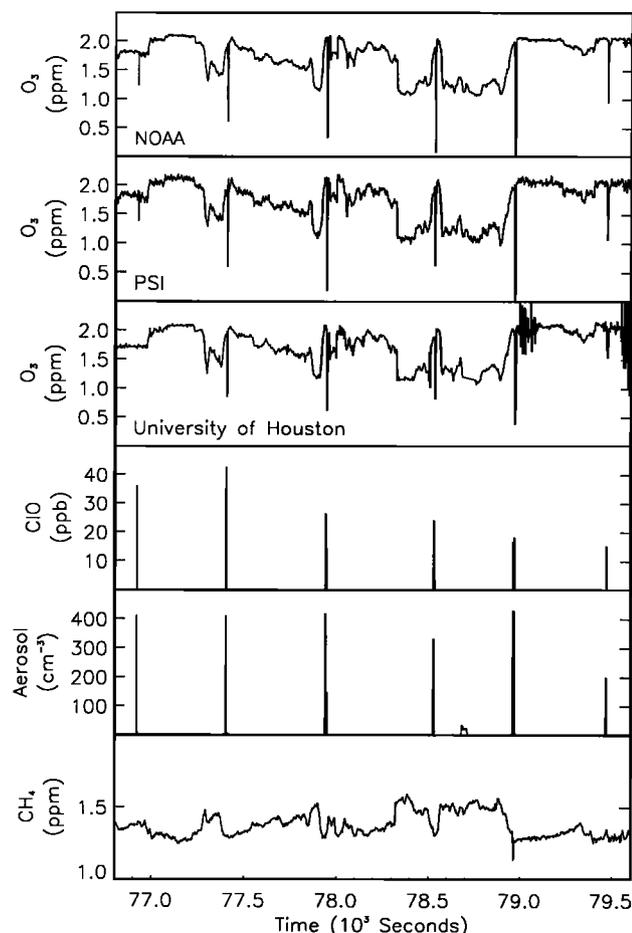
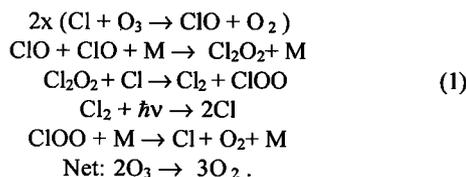


Figure 1. Time series of measurements during the 46 minute period that included the six plume encounters. Units are mixing ratio in parts per million by volume (ppmv), parts per billion by volume (ppbv), and total (volatile and nonvolatile) aerosol number density in the size range 0.3 to 4 μm . The small aerosol event after the fourth plume encounter is interpreted as an encounter with the WB-57F's own exhaust. The bottom axis is Universal Time on 17 May 1998.

background value. The maximum ClO concentration was 45 ± 15 ppbv, about a factor 20 greater than in the South Polar springtime vortex [Pierson et al., 1999]. Methane concentration in the plume was not different from the ambient background. A proposed description of gas phase SRM plume photochemistry features a ClO dimer catalytic cycle unique to warm (≈ 215 K) SRM plumes [Ross, 1996; Ross et al., 1997b]:



The set of reactions (1) can reasonably be taken to describe the main aspects of SRM plume kinetics because all of the chlorine species are in significant excess ($\approx 10^2$) of ambient species that might play a role in the plume kinetics (HO_x and NO_x for example) and because all other Cl_x family reactions are slow compared to those that make up (1). Our desire is not to

explain all the details of the plume kinetics (nor is that presently possible, given the many uncertainties regarding the actual Delta II emissions). Rather, we seek to evaluate the ability of the reaction set (1) to explain the observed ozone loss.

Within a few minutes after launch, the principal chlorine species are in a slowly varying steady-state and the reactions (1) can be solved to yield a relationship between $[\text{ClO}]$ (in units of cm^{-3}) and total reactive chlorine $[\text{Cl}_x] \equiv [\text{ClO}] + [\text{Cl}] + 2[\text{Cl}_2] + 2[\text{Cl}_2\text{O}_2]$:

$$[\text{Cl}_x] = 1.5 [\text{ClO}] + 5.4 \times 10^{-11} [\text{ClO}]^2 \quad (2)$$

The numerical coefficients were determined using DeMore et al. [1997] for temperature and pressure equal to 215 K and 65 mbar, respectively, and ambient O_3 mixing ratio of 2 ppmv; the coefficients are not greatly sensitive to these conditions. Detailed kinetics calculations [Rawlins et al., 1998] verify the analytic result (2) and show that about 90% of the Cl_x is in the form of Cl_2 during the steady-state. We average the plume ingress and egress data (to reduce the influence of small scale structure in the plume) and fit a linear expression to describe the radial dependence of $[\text{ClO}]$ and, therefore, $[\text{Cl}_x]$ using (2). Integrating derived $[\text{Cl}_x]$ across the plume and taking into account the known uncertainty in measured $[\text{ClO}]$ we find that the total abundance of reactive chlorine in the plume, $\{\text{Cl}_x\}$ (brackets indicating the horizontal integration), does not exceed 0.9 moles per meter of altitude (Mm^{-1}).

When Cl_x is greatly in excess of O_3 , Cl_2 photolysis ($J = 0.22 \text{ min}^{-1}$ for the relevant local conditions, P. F. Zittel and P. K. Swaminathan, personal communications) controls the rate of ozone destruction and the horizontally integrated cumulative ozone loss in the plume and $\{\Delta\text{O}_3\}$ during a time Δt can be approximated by

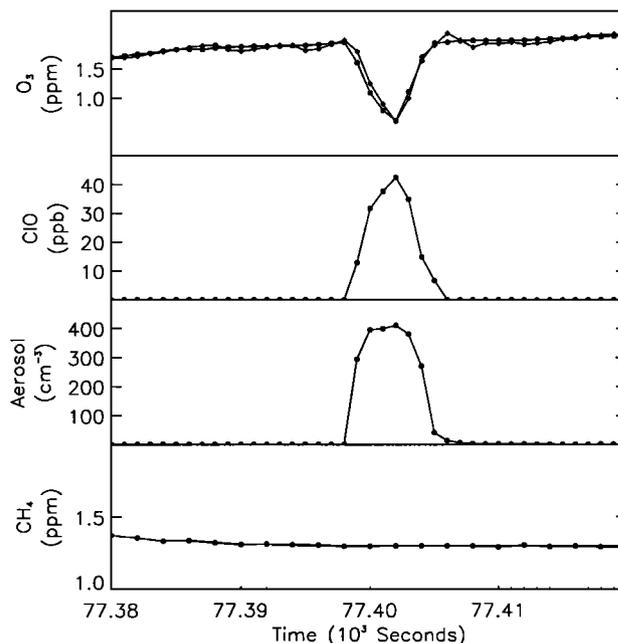


Figure 2. Expanded time series for the second plume encounter. In the topmost panel data from the NOAA and PSI instruments are given by circles and squares, respectively. Data rates are 1 Hz except for CH_4 which is 0.5 Hz. The bottom axis is Universal Time on 17 May 1998. WB-57F airspeed is about 190 ms^{-1} .

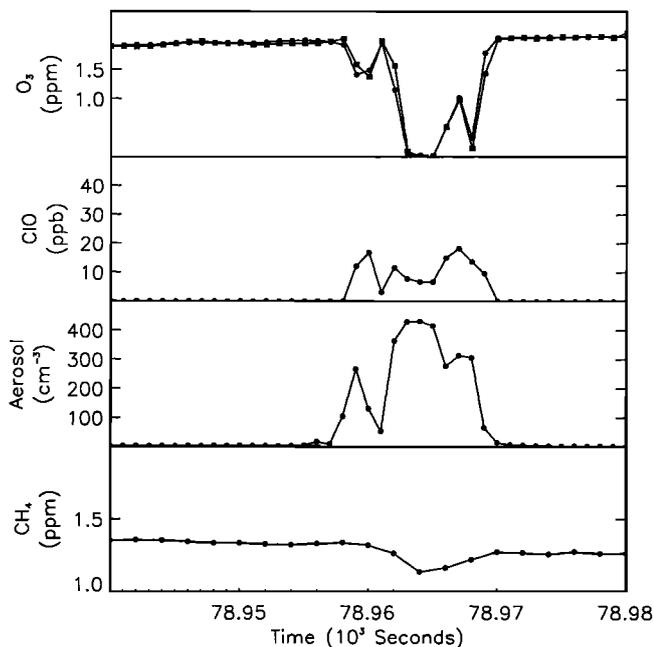


Figure 3. As for Figure 2, except for the fifth plume encounter.

$$\{\Delta O_3\} \approx J \{Cl_X\} \Delta t \quad (3)$$

The approximation (3) likely overestimates the cumulative ozone loss for several reasons. First, detailed kinetics calculations [Rawlins et al., 1998, for example] show that for the Cl_X concentrations in this plume, ≈ 100 ppbv, (3) overestimates the cumulative ozone loss by about 30%, a result that follows from the nonlinear nature of Cl_2O_2 production in the scheme (1). Second, reactive chlorine is thought to be emitted by SRMs almost entirely as Cl_2 [Ross et al., 1997a] and so the actual ozone loss rate will be less than implied by (3) for several minutes after launch as the Cl_2 photolyzes and a steady-state is established. The estimated ozone loss $\{\Delta O_3\}$ at the time of the second encounter is 2.1 ± 0.3 Mm^{-1} . The observed ozone loss (following a procedure similar to the one used to calculate $\{ClO\}$) during the second encounter was 4 ozone Mm^{-1} . Thus, a substantial fraction of the ozone loss appears to be caused by a reaction(s) not accounted for by the gas-phase reactions (1) and the derived reactive chlorine abundance (2).

Typical of the fourth and fifth encounters, where ozone has fallen to nearly zero, Figure 3 shows expansions of the latter, 39 minutes after launch. Ozone was completely removed from a small portion of the plume center ("core") about 0.4 km across. CH_4 was also reduced in the core region by 12 ± 0.5 %.

ClO was reduced by about 50% in the core relative to the plume edges so that the ClO distribution assumed an annular form [Ross, 1996].

Complete removal of ozone from the plume air provides a second method of calculating $\{Cl_X\}$, independent of the ClO -based method applied to the second encounter. After the quasi steady-state regime is established in the plume, ozone loss proceeds until titrated out of the plume, initially at the center then spreading radially with time. Once ozone is removed, ClO , Cl_2O_2 , and Cl_2 production ends and the significant remaining reactions are Cl_2 photolysis and CH_4 loss by reaction with Cl , photolysis being the slower reaction. Since Cl_2 accounts for more than 90% of the Cl_X budget in the steady-state, after a sufficiently long period of time has elapsed from the moment of ozone titration to allow for Cl_2 photodissociation, a close correspondence will exist between lost CH_4 and Cl_X in the plume. Figure 1 (NOAA) shows that ozone titration was first reached sometime between the third and fourth encounter, at least 8 minutes before the fifth encounter and long enough to ensure that the observed CH_4 deficit serves as a good proxy for Cl_X in the core region. Measured methane loss and therefore inferred $[Cl_X]$ were about 170 ± 7 ppbv in the core. We assume a linear relationship between $[Cl_X]$ and aerosol concentration throughout the plume (gas and micron-sized aerosol mixing are not different on a timescale of 10^3 seconds) and follow the previous procedure to calculate total abundance, $\{Cl_X\}$. Table 1 shows that $\{Cl_X\}$ was 1.5 Mm^{-1} and the estimated ozone loss of 13 ozone Mm^{-1} was exceeded by the integrated ozone loss by about 7 ozone Mm^{-1} . Figure 3 shows that the encounter five plume was more structured than encounter two, though the observed symmetry still justifies the integration procedure.

Without measurement of a well characterized plume tracer, we can not compare plume abundances from one encounter to another (which are not, as noted above, the same plume parcel) on an absolute basis. We can, however, normalize $\{Cl_X\}$ by the integrated particulate abundance ($< 1\%$ uncertainty) and compare one encounter to another in a relative sense. Table 1 shows that normalized $\{Cl_X\}$ in the second and fifth encounters determined using the independent methods closely agree, giving us confidence that (1) in fact describes the main points of the gas-phase chlorine chemistry as proposed.

3. Discussion

That two independent methods of inferring the $\{Cl_X\}$ abundance agree is a strong, though not conclusive, argument that the chlorine chemistry is not very different from the picture presented by (1) - (3). This means that additional or different ozone loss mechanism(s) are suggested active in the

Table 1. $\{Cl_X\}$ abundances and cumulative ozone losses $\{\Delta O_3\}$ for the second and fifth plume encounters.

Plume Encounter	Absolute $\{Cl_X\}$ Abundance	Absolute Particle Abundance	Normalized $\{Cl_X\}$ Abundance	Observed $\{\Delta O_3\}$ loss	Estimated $\{\Delta O_3\}$ loss
2	$0.8 \pm .12$	2.5	$0.32 \pm .05$	4.0	2.1 ± 0.3
5	$1.5 \pm .06$	5.3	$0.27 \pm .01$	20	13 ± 0.1

Estimated $\{\Delta O_3\}$ loss is based on the approximation (3).

Units are moles per meter of altitude except Absolute Particle Abundance which has units of 10^{14} particles per meter of altitude and Normalized $\{Cl_X\}$ Abundance which has units of moles per 10^{14} particles.

Delta II plume. SRMs conceivably emit radical species other than chlorine. Combustion models predict that SRMs emit only small amounts of NO_x [Brady et al., 1997] but those predictions have not been validated. HO_x emissions have not yet been modeled. Chlorine activation reactions on alumina particulate surface have been shown to possibly play a role in the global impact of SRM emissions [Molina et al., 1997; Jackman et al., 1998]; they might also play a role in the local plume wake, enhancing the net reactivity of Cl_x emitted by the SRMs, for example.

Alternately, some component of the LOX/RP engine exhaust might play an active role in the plume wake chemistry, either directly or through interaction with chlorine from the SRMs. The main constituents of LOX/RP exhaust are thought to be H_2 , H_2O , CO_2 , and CO , with lesser emissions of carbon particulate (soot), HO_x , NO_x , and sulfate aerosol. There are few relevant theoretical predictions and no measurements of these species in LOX/RP exhaust plumes [Brady et al., 1997], all of which are known to promote a variety of reactions that could play important roles in plume wake kinetics. Given the complex nature of cross family radical kinetics, it is not clear how enhanced HO_x or NO_x emissions from the LOX/RP engine or active heterogeneous reactions would influence ozone loss in the plume; the required models have not been developed.

The general behavior of ozone loss in Delta II plume wakes is confirmed by data taken during the 1996 (data not shown) plume encounters. Comparison of the 1998 and 1996 data indicates that the significant ozone loss in Figure 1 is not unusual for the Delta II rocket. Following the analysis procedure described earlier, the 1996 data show that 65 minutes after launch the cumulative ozone loss $\{\Delta\text{O}_3\}$ was about 30 Mm^{-1} , exceeding the 21 Mm^{-1} loss from (3) using the $\{\text{Cl}_x\}$ values found in the 1998 plume. Since ClO and CH_4 were not measured in 1996, we can not compare inferred Cl_x from these two plumes; the ozone loss comparison is illustrative nevertheless.

The cumulative ozone losses observed in these two Delta II plumes are in fact comparable to the $\{\Delta\text{O}_3\}$ loss observed in the plume wakes of much larger Titan IV rockets that use solid propellant exclusively [Ross et al., 1997b] in the lower stratosphere. As the Titan IV SRM emission is about a factor of 11 larger than the Delta II SRM emission, we conclude that ozone loss in SRM plume wakes does not linearly scale with rocket size, a feature not apparent in models of plume wake chemistry [Ross, 1996; Danilin, 1993; Brady et al., 1997].

4. Summary

Our measurements obtained in the plumes of Delta II rockets reveal that the prompt stratospheric response to rocket motor emissions, and possibly the emissions themselves, are more complex than previously assumed. It is difficult to reconcile the observed ozone loss with the simple representation of the gas-phase chlorine catalytic cycle thought to control chemical evolution in SRM plume wakes. Assuming that Cl_2 is the only significant reactive gas-phase component of SRM emissions, several circumstances might explain the data: (1) the plume could contain significantly more Cl_x than implied by measured ClO , (2) heterogeneous reactions on alumina or soot particulate could accelerate ozone loss beyond the photolysis limited rate; (3) the gas-phase plume chemistry is substantially more complicated than represented here, (4) the Delta II SRMs or LOX/RP engines might emit significant

quantities of reactive gases other than chlorine that contribute to ozone loss. Since complex mixing and chemical processes control the composition of rocket plume wakes, the discrepancy between observed and predicted ozone loss may well be reduced or eliminated using a model that realistically includes these processes. Local [Danilin, 1993; Ross, 1996;] and global [Jackman et al., 1998] models of rocket emission impacts generally do not address the possible influence of rockets powered by other than solid propellant; our conclusions reasonably suggest some revision to this qualification.

Acknowledgments. We appreciate the efforts of the WB-57F air and engineering crews, and the range support personnel at Cape Canaveral Air Station and Vandenberg Air Force Base. We thank C. H. Jackman, P. F. Zittel, P. K. Swaminathan, and D. W. Fahey for helpful discussions and comment. This work is supported by the Air Force Launch Programs Office, the Air Force Office of Scientific Research, NOAA Aeronomy Laboratory, the National Science Foundation, Thiokol Propulsion, Alliant Techsystems, and the University of Missouri-Rolla.

References

- Brady, B. B., L. R. Martin, and V. I. Lang, effects of launch vehicle emissions in the stratosphere, *J. Spacecr. Rockets*, 34, 774-779, 1997.
- Danilin, M. Y., Local stratospheric effects of solid-fueled rocket emission, *Ann. Geophys.*, 11, 828-836, 1993.
- DeMore, W. B. et al., Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation No 12, Jet Propulsion Laboratory, California Inst. Tech., Pasadena, Calif., 1997.
- Jackman, C. H., D. B. Considine, and E. L. Fleming, A global modeling study of solid rocket aluminum oxide emission effects on stratospheric ozone, *Geophys. Res. Letts*, 25, 907-910, 1998.
- Ko, M. K., N.-D. Sze, and M. J. Prather, Better Protection for the Ozone Layer, *Nature*, 367, 505-509, 1994.
- Molina, M. J., L. T. Molina, R. Zhang, R. F. Meads and D. D. Spencer, The reaction of ClONO_2 with HCl on aluminium oxide, *J. Geophys. Res.*, 24, 1619 - 1622, 1997.
- Pierson, J. M., K. A. McKinney, D. W. Toohey, A. Engel, and P. A. Newman, An investigation of ClO photochemistry in the chemically perturbed Arctic vortex, *J. Atmos. Sci.*, 32, 61-81, 1999.
- Proffitt, M. et al., In-situ ozone measurements within the 1987 Antarctic ozone hole from a high-altitude ER-2, *J. Geophys. Res.*, 94, 16547, 1989.
- Proffitt, M. H., and W. T. Rawlins, RISO WB-57F measurements and intercomparisons of stratospheric ozone depletion in the exhaust plume of a Delta II rocket, American Geophysical Union 1998 Fall Meeting, Paper A31B-04, *EOS Trans. AGU*, (Abstract), 1998.
- Rawlins, W. T. et al., Kinetics of stratospheric ozone depletion in the exhaust plume of a Delta II rocket as observed in RISO, American Geophysical Union 1998 Fall Meeting, Paper A31B-03, *EOS Trans. AGU*, (Abstract), 1998.
- Ross, M. N., Local effects of solid rocket motor exhaust on stratospheric ozone, *J. Spacecr. Rockets*, 33, 144-153, 1996.
- Ross, M. N., Ballenthin, J. O., Gosselin, R., Meads, R. W., Zittel, P. F., Benbrook, J. B., Sheldon, W. R., In-situ measurement of Cl_2 and O_3 in a stratospheric solid rocket motor exhaust plume, *Geophys. Res. Letts.*, 24, 1755-1758, 1997a.
- Ross, M. N., J. R. Benbrook, W. R. Sheldon, P. F. Zittel, and D. L. McKenzie, Observation of Stratospheric Ozone Depletion in Rocket Plumes, *Nature*, 390, 62-65, 1997b.
- Ross, M. N., P. D. Whitefield, D. Hagen, and A. R. Hopkins, In Situ measurement of the aerosol size distribution in stratospheric solid rocket motor exhaust plumes, *Geophys. Res. Letts.*, 26, 819-822, 1999.
- Sen, B., Benbrook, J. R., and Sheldon, W. R., Ultraviolet absorption photometer for measurement of ozone on a rocket-boosted payload, *Applied Optics*, 35, 610-614, 1996.
- WMO, World Meteorological Organization Scientific Assessment of Ozone Depletion -Report No. 25, Chap. 10, World Meteorological Organization, Geneva, Switzerland, 1991.

(Received October 18, 1999; revised April 11, 2000; accepted May 15, 2000.)