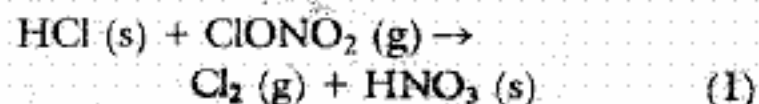


Observations of the Nighttime Abundance of OClO in the Winter Stratosphere Above Thule, Greenland

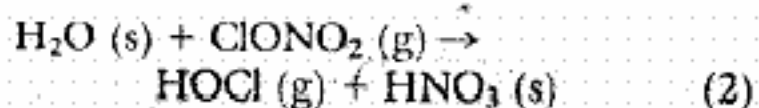
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Observations at Thule, Greenland, that made use of direct light from the moon on 2, 3, 4, 5, and 7 February 1988 revealed nighttime chlorine dioxide (OClO) abundances that were less than those obtained in Antarctica by about a factor of 5, but that exceeded model predictions based on homogeneous (gas-phase) photochemistry by about a factor of 10. The observed time scale for the formation of OClO after sunset strongly supports the current understanding of the diurnal chemistry of OClO. These data suggest that heterogeneous (surface) reactions due to polar stratospheric clouds can occur in the Arctic, providing a mechanism for possible Arctic ozone depletion.

THE COLUMN CONTENT OF OZONE (O_3) over Antarctica during the spring has decreased by ~50% during the past decade (1). Several studies (2, 3) suggested that this depletion at that particular season and latitude could be related to the enhanced abundance of polar stratospheric clouds (PSCs) there, in association with prevailing extreme low temperatures. The PSCs form abruptly when stratospheric temperatures drop below about -80°C (4), and play a critical role by providing an ice surface on which halogen compounds can engage in heterogeneous reactions (5), such as



or



The net effect of these reactions is to liberate reactive chlorine (ClO_x) from the relatively inert chlorine reservoir species, HCl and ClONO_2 , and thus enhance the potential for halogen chemistry to catalytically destroy O_3 over the height range where the PSCs are located [roughly 10 to 25 km as shown, for example, in (4)].

The chemistry of halogen species in the lower stratosphere is closely coupled to that of reactive nitrogen species (NO_x) because of the rapid formation of nitrates, specifically ClONO_2 and BrONO_2 . For reactions

such as 1 and 2 to effectively enhance the net abundance of ClO_x radicals, the lower stratospheric NO_x content must be greatly reduced so that reformation of ClONO_2 does not limit their accumulation (2, 3). Reactions 1 and 2 both produce reactive ClO_x radicals at the expense of their long-lived reservoirs and convert reactive nitrogen to the much less reactive species, HNO_3 . Additional heterogeneous reactions involving N_2O_5 (5) and the direct condensation of HNO_3 at temperatures below about -80°C (6) are likely to further inhibit the gas-phase abundance of NO_x species, so that PSC chemistry produces an atmosphere rich in ClO_x radicals and depleted in NO_x radicals.

Sunlight is also involved in Antarctic O_3 depletion. For example, the Cl_2 produced in reaction 1 must first photolyze to form two chlorine atoms, which then react rapidly with O_3 and initiate its catalytic destruction (3, 7). Thus the depletion of Antarctic O_3 is believed to involve the following primary elements: PSC formation at temperatures below about -80°C , subsequent surface chemistry that enhances chlorine free radicals and suppresses reactive nitrogen species, and fast photochemical depletion processes that require sunlight (2, 3, 5, 7).

Measurements of the stratospheric composition in Antarctic spring have revealed that the photochemistry of this region must be profoundly different from that found elsewhere, in a manner consistent with the identification of the ozone hole as a largely chlorine-induced phenomenon (although

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particular dynamical conditions are also required for such chemistry to occur). The abundances of ClO (8) and OClO (9) are elevated during the Antarctic spring by about a factor of 20 to 50, compared with predictions based solely on gas-phase photochemistry. The observed abundances of HCl, ClONO₂, NO₂, H₂O, and NO_x in Antarctic spring are also inconsistent with homogeneous gas-phase photochemical mechanisms, but in broad agreement with perturbations likely to be induced by heterogeneous PSC chemistry (10-13).

The formation of PSCs also occurs in the Arctic. Satellite observations demonstrate that the frequency of PSC occurrence is about ten times greater during the Antarctic winter and spring than during the corresponding Arctic seasons (14). This difference is due to the differences in climatology between the two hemispheres, with the Northern Hemisphere being considerably warmer on average due to its greater tendency for dynamical disturbances, particularly minor and major stratospheric warmings (15). These effects are strongly coupled to such factors as the differences in surface topography between the two hemispheres at middle and high latitudes. However, unusually low Northern Hemisphere winter temperatures can approach those typical of Antarctic winter, thus complicating comparisons based on limited data series. It is also important to determine the extent to which the chemical mechanisms that deplete Antarctic O₃ might also operate in the Arctic, both in relatively warm and relatively cold years.

The Arctic O₃ abundance has not decreased in the spectacular manner found in the Antarctic, but recent analyses have derived statistically significant total O₃ decreases in the Arctic (by about 5 to 10%), with the greatest changes during winter (16). Because these changes are so much smaller than the Southern Hemisphere depletions, it is difficult to establish conclusively whether the Arctic depletions exceed natural variability. Complementary information may be found by measuring the chemical species that could be responsible for such a perturbation. In Antarctica, for example, the O₃ change of 50% is accompanied by an apparent enhancement in OClO of about a factor of 50 compared with homogeneous photochemical model calculations or mid-latitude observations (see below). The latter perturbation is far easier to measure than the former and points toward mechanisms involving chlorine chemistry as the cause of the O₃ depletion.

OClO is of particular importance because it is believed to be produced primarily from the reaction



Thus the abundance of OClO is directly related to those of ClO and BrO. The latter two species are of central importance in chemical schemes for Antarctic O₃ depletion because they participate in the rate-limiting steps of the catalytic cycles that can destroy O₃ (3, 7). A measurement of OClO is useful as a proxy for the free radicals involved in O₃ loss provided that the photochemistry of OClO is well understood (17). During the day, the production of OClO is balanced by the rapid photolysis reaction



but at night, large levels of OClO can build up.

With these considerations in mind, we carried out spectroscopic measurements of the composition of the Arctic stratosphere over Thule, Greenland (76.5°N), during the period from 29 January 1988 through 16 February 1988, with the same instruments as those used at McMurdo Station, Antarctica (77.8°S), during September and October of 1986 and 1987 (9, 11, 18). The choice of timing for the experiment was difficult. Note that the OClO observations made at Thule were carried out several weeks earlier in the spring season than the earliest conjugate available observations in Antarctic spring. The solar forcing at high latitudes changes rapidly during this time, so caution must be exercised in comparing observations from the two polar regions for this reason alone, quite apart from other important differences in temperatures and dynamical conditions. Also, observations have established that Antarctic O₃ decreases occur predominantly during September [see references in (13)], probably because it is too warm during later months in the spring season and too dark during earlier months. Although the conjugate northern month for September in the Southern Hemisphere is March, the low temperatures required for PSC formation (below about -80°C) seldom persist even as late as February in the warmer Arctic environment (15).

Antarctic measurements revealed large abundances of OClO at night during September 1986 ($\sim 1.0 \times 10^{14} \text{ cm}^{-2}$), about 20 times greater than theoretical estimates neglecting heterogeneous chemistry, but in surprising agreement with those including it (17, 19). Even greater values ($\sim 2.5 \times 10^{14} \text{ cm}^{-2}$) were obtained in a single night of measurements on 30 August 1987 (18). These data represent the earliest available spring Antarctic OClO measurements at night. Furthermore, measurements of the daytime abundance of OClO in Antarctica displayed greater daytime levels in late Au-

gust than those in late September (9, 18) during both 1986 and 1987. These sets of measurements demonstrated that the abundance of OClO in Antarctic spring decreases as the spring season progresses. Thus we hoped that useful information regarding the influence of heterogeneous chemistry could be obtained by making measurements in the Arctic in February, although the photochemical conditions that are likely to lead to substantial O₃ depletion probably do not have the potential to occur until March there, and may therefore be limited to unusually cold and extensive Arctic winters. These considerations along with the timing of the full moon in 1988 prompted us to attempt measurements of OClO at Thule in early February.

The instrument, data analysis method, and primary sources of error have been discussed elsewhere (9, 11, 18, 20) and will be summarized only briefly here. The instrument used for the moon observations is a crossed Czerny-Turner spectrograph covering the wavelength range between about 400 and 450 nm in third order. The spectral features of OClO detected in this spectral interval in Antarctica were consistent with measurements in the shorter wavelength range from 330 to 370 nm where the maximum OClO absorption cross section occurs (9, 18). We report data obtained with the long-wavelength instrument in the spectral region from about 403 to 428 nm (9, 21).

The data were analyzed with a least-squares method (9, 11, 18, 20). The spectrum of each known molecular absorber was determined by laboratory measurements with the field instrument (22). Weak residual absorption due to unidentified absorbers is of the order of 0.1% (9) and is a potential source of error if there is strong overlap between these features and the spectral features of the molecule under consideration. In the observations at Thule, the absorption due to OClO represents as much as 0.1 to 0.2% for large lunar zenith angles near 80° to 85°. An absorber exhibiting a multiline spectrum is unlikely to be mimicked by spectral features of unknown absorbers. Strong support for the spectroscopic identification of OClO comes from consideration of the observed variation with increasing solar zenith angle and the observed diurnal change, as well as from simultaneous measurements made with identical instruments (9) and from the use of several spectral intervals from 330 to 370 nm as well as from 385 to 390 nm, along with those in the longer wavelength range from 400 to 428 nm (9, 18).

The lunar measurements extend over the period from 2 February through 7 February (23). The moon was full on 2 February.

Table 1. Background spectra used in reduction of lunar observations at Thule, February 1988.

Date	Observing sequence	Time (LT)	Lunar zenith angle (degrees)
2	Moonrise	19:08	70.9
3	Moonset	05:22	67.3
3	Moonrise	21:46	69.7
4	Moonset	05:51	71.4
5	Moonset	04:21	71.2
7	Moonset	05:22*	67.3

*On 7 February, the moon rose only to about 81°, so a background spectrum from 3 February was used to reduce the data from that particular night.

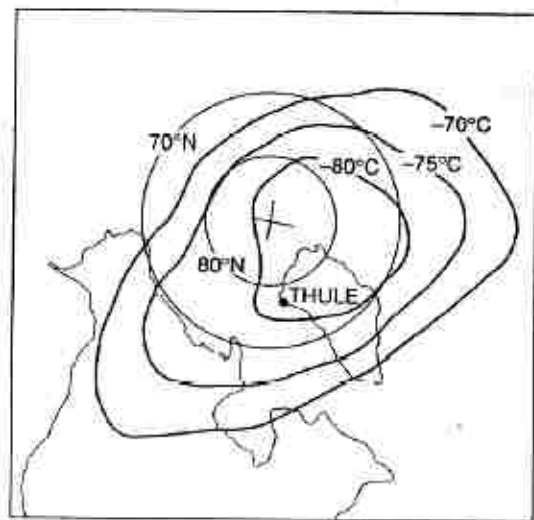


Fig. 1. National Meteorological Center (NMC) 30-mbar (~24-km altitude) temperature analysis 4 February 1988.

Surface weather conditions were generally excellent (24); clouds interfered with the observations only on the night of 6 February. The moon was above the horizon during nearly all of this period. Observations were obtained whenever the moon was unobstructed by clouds or surface topography and was bright enough to detect against the sky background (in a few cases, at solar zenith angles as small as 94°, although the sun was well below the horizon at angles greater than 100° for the great majority of the observations). Generally, the moon rose in the evening hours before midnight and set in the early morning hours. On the nights of 2 to 3 and 3 to 4 February, the moon rose approximately at sunset and set approximately at sunrise. These nights allow detailed study of the night growth of OCIO after sunset, as shown below. Scattered sky spectra obtained by pointing the instrument straight up at the zenith sky were also collected daily during the period from 29 January through 16 February 1988 whenever the solar zenith angle was less than about 95° (9, 11, 18, 20). Observations of daytime O_2 and O_3 derived from the scattered sky measurements are discussed in (25).

As in all absorption measurements, the

data spectrum must be divided by a background spectrum. The background spectra used in the analyses here are lunar spectra obtained at a lunar zenith angle of about 65°, generally as close as possible in time to a data spectrum series obtained at larger lunar zenith angles. Thus, for example, a measurement when the moon was near its zenith at about 65° near midnight on 2 February was used as the background spectrum to reduce lunar data obtained at larger angles as the moon set on the morning of 3 February. This procedure allowed us to measure the change in slant column absorber amount relative to that in the background spectrum. The measured change in slant column then reflects a combination of two factors: (i) the change in airmass factor as the moon sets (which can be calculated accurately from geometric considerations) and (ii) any changes in the vertical column amount due to diurnal photochemistry or air mass motions. The effects of each will be discussed below. The local time and lunar zenith angles used as the background spectra in the analysis of each set of lunar data are presented in Table 1.

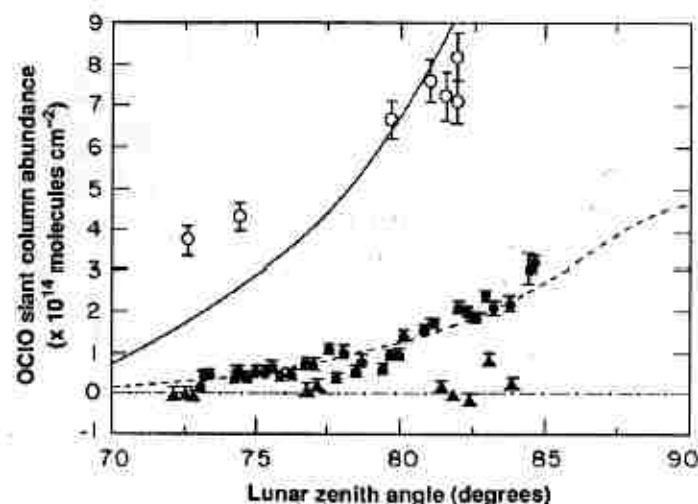
The meteorological conditions at Thule were excellent in the stratosphere and troposphere during the observing period. A minor warming did occur during December 1987, which caused a general warming of the Arctic stratosphere, but conditions were unusually quiet for the rest of the winter, and by late January the temperatures at the 30-mb level had decreased to -80°C and lower at the vortex center, comparable to Antarctic winter temperatures. Indeed, the February 1988 temperatures at 30 and 50 mbar were unusually low, about -80° to -85°C (15). At lower altitudes near 100 mbar, however, the temperatures remained of the order of -70° to -75°C, which is greater (by ~10°C) than the corresponding Antarctic temperatures in August at these levels, suggesting that the potential for PSC formation was restricted to a higher, nar-

rower altitude range during these measurements than in Antarctic winter and spring. In spite of some slight motion, the geopotential minimum at the center of the polar vortex remained very near Thule over the entire period of observation. During the period of the moon observations discussed here, the center of the vortex was nearly over Thule (Fig. 1). Temperatures at 30 mbar over Thule on this particular day were -85°C.

An important check on the validity of any column measurement of atmospheric constituents is its consistency as a function of zenith angle of the light source. As the light source sets, for example, the slant path through the atmosphere increases dramatically, increasing the slant column of absorber and hence the measurement absorption and the signal-to-noise. Since we suspect that the large abundances of OCIO observed in polar regions result from PSC chemistry, results obtained at high latitudes must be compared with those of mid-latitudes. In Fig. 2 measurements of the postmidnight increase in slant column abundance of OCIO for lunar zenith angles greater than ~65° are compared, as determined at McMurdo Station (78°S), Thule (76.5°N), and Fritz Peak, Colorado (40°N). Also included are lines indicating what the slant column behavior would be assuming particular constant values of the vertical column, illustrating the increase in slant column abundance with increasing lunar zenith angle discussed above. Note that error bars indicate the 1- σ standard error of the spectral fit, not the total error (22).

The observations in Antarctica in late August revealed large abundances of OCIO, ~2.5 $\times 10^{14}$ cm⁻², that increased systematically with increasing angle. In sharp contrast to the Antarctic observations, OCIO could not be detected in this (or any other) series of measurements at Fritz Peak, Colorado (40°N). A conservative value for the upper limit implied by the data in Fig. 2 is

Fig. 2. Observations of the increase in OCIO slant column abundance as a function of increasing lunar zenith angle at Fritz Peak, Colorado (\blacktriangle , 40°N), on 3 January 1988, at Thule, Greenland (\bullet , 76.5°N), on 3 February 1988, and at McMurdo Station, Antarctica (\circ , 78°S), on 30 August 1987. The background spectrum used in the analysis in all cases was taken near 65° lunar zenith angle on the indicated nights. Lines indicate the expected response for OCIO vertical column abundances of (—) 0, (---) 4.5×10^{13} , and (—) 2.5×10^{14} molecules cm⁻².



$1.0 \times 10^{13} \text{ cm}^{-2}$. "Standard" homogeneous gas-phase theory suggests an expected vertical column amount of $\sim 5.0 \times 10^{12} \text{ cm}^{-2}$ (17), consistent with this value.

The measurements at Thule lie between these two values. The observations follow a consistent pattern of growth as a function of zenith angle, suggesting a vertical column abundance of $\sim 4.5 \times 10^{13} \text{ cm}^{-2}$ during the particular moonset depicted in Fig. 2. These values are about a factor of 5 lower than the measurements at McMurdo in late August, but are about a factor of 10 greater than model estimates that include only homogeneous chemistry (17), suggesting that heterogeneous chemistry may indeed occur in the Arctic.

A composite of all the Thule moonset observations is shown in Fig. 3 (moonrise data are discussed separately). The observations on all nights are consistent with vertical column abundances between 3×10^{13} and $6 \times 10^{13} \text{ cm}^{-2}$ (The systematic variation with lunar zenith angle on individual nights is discussed below).

We performed a simplified model calculation to study the diurnal chemistry of OCIO over the altitude range from about 10 to 30 km. The background temperatures used in the calculations are those appropriate to Thule based on NMC maps and Thule radiosonde observations for 3 February. We adopt an abundance of BrO of 7 parts per trillion by volume (pptv) and prescribe the vertical distribution of ClO_x (defined as the sum of Cl + ClO + HOCl + Cl₂O₂ + OCIO) from our two-dimensional (2-D) photochemical dynamical model of the stratosphere (26) at the appropriate season and latitude for the altitudes between its lower boundary at 16 and 30 km, in 2-km intervals. From 16 to 10 km, the values from the 2-D model are extrapolated linearly to zero. We consider the detailed diurnal chemistry of Cl₂O₂, OCIO, and ClO by using full spherical geometry for all photolysis calculations, but neglecting the coupling to NO_x by setting the NO_x abundance to

zero (for example, to simulate severe NO_x depletion by PSCs). The chemical scheme is discussed in more detail in (18).

We have already emphasized the important coupling between nitrogen and halogen chemistry. Note that the nighttime column abundance of OCIO is even more sensitive to the local NO_x abundance than is ClO, which arises because the BrO necessary to form OCIO at night can be converted to BrONO₂ during twilight if NO₂ abundances exceed a few parts per trillion by volume (18). Typical calculated NO₂ values from our 2-D model for the conditions of these measurements are much greater (>100 pptv). Thus these observations of OCIO require not only significant perturbations to the predicted ClO_x, but even more drastic perturbations in NO₂ compared with homogeneous model predictions. The two levels are likely to be closely related through PSC chemistry. The measured column abundances of NO₂ at Thule (25) were as low as those obtained in Antarctic spring at McMurdo Station (10, 11). These abundances for NO₂ are among the lowest obtained at any latitude or season in the earth's atmosphere. The measurement of an integrated total column abundance does not allow a definitive statement to be made regarding the local NO₂ mixing ratios at any particular point in the column, but the similarity between the Antarctic and Arctic measurements certainly suggests that heterogeneous removal of NO_x took place in the stratosphere above Thule.

For the purpose of this discussion, we make no attempt to explicitly model the interaction between NO_x and ClO_x. Rather, we seek to examine only crudely to what extent the model fails to reproduce the observations by evaluating how large a scaling factor must be applied to the model ClO_x abundances in order to obtain OCIO levels near those observed. We found that the model ClO_x abundances must be multiplied by a factor of 10 to obtain total OCIO column abundances in the postmidnight pe-

riod of the order of those observed, in general agreement with other calculations (17). Assuming a BrO abundance of 7 pptv, this implies ClO abundances of about 100 to 150 pptv near 20 km. In situ measurements on the edge of the Arctic vortex western Canada on 13 February 1988 at 61°N near 20 km indicated ClO mixing ratios of about 65 pptv (27), which are much greater than those at mid-latitudes (28), but somewhat lower than the values deduced from the OCIO measurements, which would be expected only near the center of the Arctic vortex (Fig. 1). The diurnal variation in vertical OCIO column abundance calculated with these assumptions is shown in Fig. 4A. Clearly, an alternate approach would be to perturb the ClO abundance by larger factors only in those layers where the temperatures fall below about -80°C , rather than prescribing a scaling factor that is independent of altitude, but this would not greatly alter the interpretation we present.

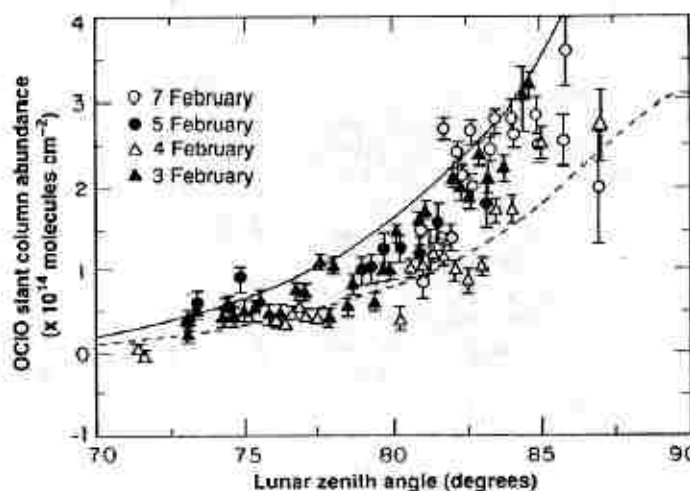


Fig. 3. Observations of the increase in OCIO slant column abundance as a function of increasing lunar zenith angle for all moonset data obtained at Thule in February 1988. See Table 1 for background spectra used on each night. Lines indicate the expected response for OCIO vertical column abundances of (---) 3×10^{13} and (—) $6 \times 10^{13} \text{ molecules cm}^{-2}$. The background lunar zenith angle was approximately 65° to 70° .

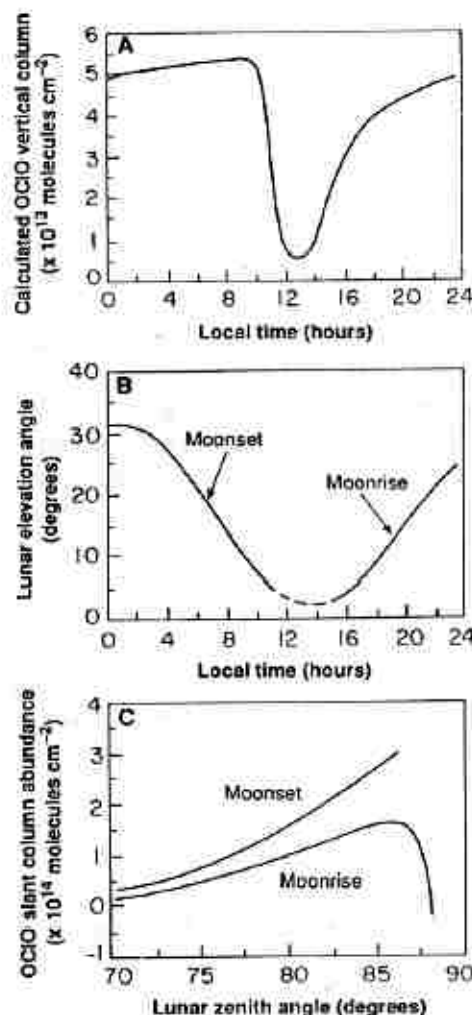
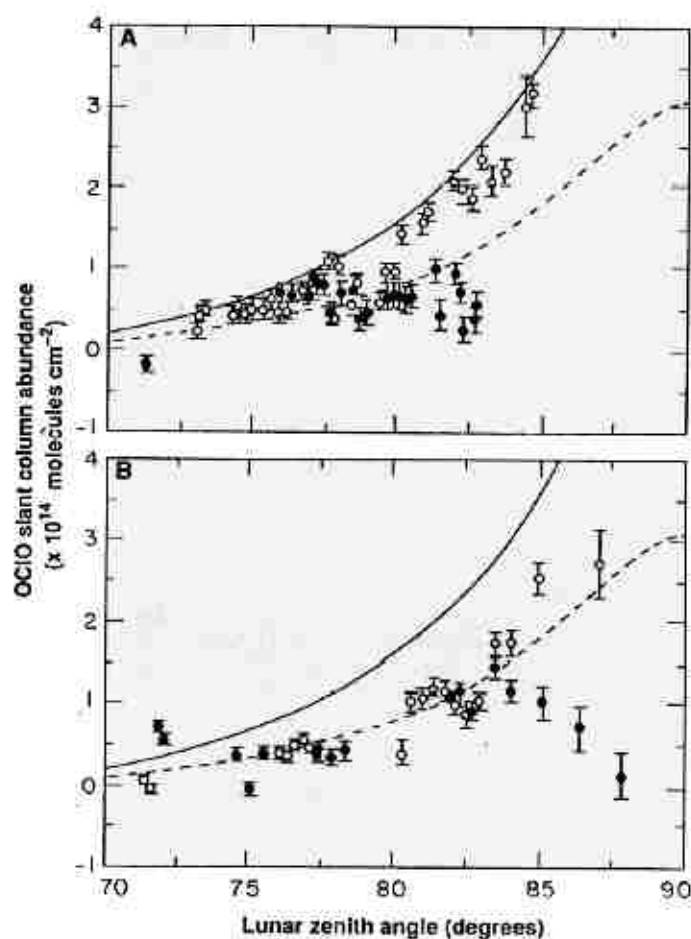


Fig. 4. (A) Calculated diurnal variation of the OCIO vertical column abundance obtained by multiplying the reactive chlorine abundances of the model by Garcia and Solomon (26) by a factor of 10 (see text). (B) Lunar elevation angle as a function of local time on the night of 3-4 February 1988 at Thule, Greenland. (C) Calculated variation of OCIO slant column abundance versus lunar zenith angle based on that in (A) and (B), assuming a background lunar zenith angle of 65° .

Fig. 5. (A) Observations of the change in OCIO slant column abundance as a function of increasing lunar zenith angle for (●) the moonrise of 2 February 1988 (local times from about 1430 to 1900) and (○) the moonset of 3 February 1988 (local times from about 0500 to 1100). Calculated vertical moonset data: (---) 3.0×10^{13} and (—) 6.0×10^{13} molecules cm^{-2} . (B) As in (A), but for (●) moonrise 3 February 1988, and (○) moonset 4 February 1988.



The abundances of chlorine and nitrogen free radicals are critically dependent on the downward transport occurring within the polar vortex, which is only crudely approximated in 2-D models. The influence of zonal asymmetries (waves) is also a potentially critical factor that is completely neglected in 2-D models. Homogeneous gas-phase processes such as the rate of photolysis of N_2O_5 might also contribute to the large observed OCIO abundances if current estimates of the rates of those processes are greatly in error. We do not intend to discuss all of the uncertainties and factors that might influence the calculated abundance of OCIO, but rather to show that conventional chemical dynamical models that use current best estimates of photochemical reaction rates and that neglect heterogeneous chemistry fall far short of matching the observations.

In Fig. 4A the calculated time-dependent behavior of the vertical column abundance of OCIO is shown for 4 February when the ClO_2 is multiplied by a factor of 10. Note that the vertical column abundance of OCIO increases relatively slowly in the evening post-twilight period due to the time scale for reaction 3. In Fig. 4B, corresponding lunar zenith angles for the night of 3–4 February are displayed, and Fig. 4C shows the calculated changes in OCIO slant column abundances corresponding to Fig. 4, A and B. The moonset data shown in Figs. 2 and 3 were obtained when the OCIO abundance is expected to be near its asymptotic nighttime

value and changing only very slowly, whereas the moonrise period just after sunset is expected to be associated with large changes in the OCIO vertical column as well as in the lunar angle.

In Fig. 5, A and B, the measured slant column abundances during the moonrises and moonsets of 2–3 February and 3–4 February are shown. The largest moonrise lunar zenith angles were those obtained on the night of 3–4 February and hence these display the largest change in slant column abundance (compare with Fig. 4C). On the night of 3–4 February, the time scale for the rise of OCIO is about 2.5 hours. The data in Fig. 5 demonstrates that the absorption identified as that of OCIO is due to a diurnally varying species, whose time scale for formation is consistent with that of OCIO.

The OCIO levels about Thule were significantly enhanced during February 1988 compared with theoretical predictions that used only gas-phase photochemistry. Even more dramatic perturbations of the local NO_2 abundances (decreases from greater than 100 to a few pptv) are needed to explain the highly elevated nighttime OCIO column amounts observed, consistent with concurrent observations of extremely low NO_2 column abundances (25). Thus we suggest that the chemical "preconditioning" that occurs through heterogeneous PSC chemistry in the Antarctic winter and early spring probably also took place to some

extent in the Arctic in the (relatively cold and undisturbed) winter and spring of 1988. The data we present thus suggest that the relatively modest O_3 depletions reported for the present northern high latitudes in late winter (16) may be related in part to halogen chemistry. However, the observed chemical state of the Arctic vortex described here probably represents an extreme, since the monthly mean stratospheric temperature over the North Pole in February 1988 were the lowest observed since 1956 (15). Further, such preconditioning is a necessary, but not sufficient, condition for extensive O_3 depletion. Note that the observed Antarctic O_3 depletion is essentially confined to the month of September, when temperatures there remain low enough for PSCs to be present and when the solar illumination increases dramatically. The historical record of stratospheric temperatures extends from 1956 to the present. The lowest temperature ever obtained in the monthly mean over the North Pole in the conjugate month of March (15) was -72°C in 1967. Such conditions are believed to be much too warm for PSC formation, suggesting that the much earlier stratospheric warming of the more dynamic Northern Hemisphere plays a critical role in the dramatically different O_3 depletion found in the two hemispheres. Although this behavior is likely to protect the Northern Hemisphere from massive O_3 depletion in the immediate future irrespective of chemical processes taking place earlier in winter, the possibilities of increasing future total chlorine abundances due to continuing releases of chlorofluorocarbons, and decreasing stratospheric temperatures due to CO_2 emissions, must be considered in attempts to predict the longer term future of the ozone layer.

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