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# MEASUREMENTS OF THE VERTICAL PROFILE, DIURNAL VARIATION, AND SECULAR CHANGE OF ClO IN THE STRATOSPHERE OVER THULE, GREENLAND, FEBRUARY-MARCH, 1992

*R.L. de Zafra, L.K. Emmons, J.M. Reeves, and D.T. Shindell*

Physics Dept., State Univ. of N.Y.
Stony Brook, N.Y., 11794

**Abstract.** We report observations of stratospheric chlorine monoxide over the altitude range ~16 to 50 km at Thule, Greenland from Feb. 8 to Mar. 24, 1992. A new, more sensitive ground-based mm-wave spectrometer was employed for these measurements[1], similar in principle to that used earlier for the discovery of low altitude ClO in the Antarctic springtime[2,3]. In this report, we discuss different aspects of vertical distribution, secular trends, and diurnal variation of ClO in the Arctic stratosphere, based on a preliminary analysis of our Thule data. We see *no* evidence for large (~1.2-1.5 ppb) amounts of ClO in the lower stratosphere at any time during February or March, in agreement with UARS-MLS findings for this period, and in marked contrast to findings reported for the Arctic in January. We have some evidence for small enhancements (~0.2-0.5 ppb) in the 18-30 km range in late February-early March, which might be associated with volcanic aerosol, rather than PSC, processing.

**Introduction:** Low altitude ClO, occurring in the 15-25 km range, is the particular signature as well as the causal agent of the massive ozone destruction which has been characteristic of the Antarctic springtime in recent years. A limited number of previous ClO measurements have been made in the early Arctic spring in an attempt to understand similarities and differences in northern polar chemical processing, but until 1992, none at a time corresponding to the equivalent photochemical period when major ozone destruction occurs over Antarctica.

Free ClO is not normally found in the 15-25 km range of the stratosphere, due to rapid reaction with $NO_2$ to form chlorine nitrate ($ClONO_2$). Short wavelength absorption by ozone above 25 km limits the photolysis of chlorine nitrate to very small values at 15-25 km, severely limiting ClO formation in this region. Furthermore, the very low concentration of atomic oxygen renders the 'standard' catalytic chlorine cycle ineffective in depleting ozone, even though small amounts of ClO may be formed by "dead-end" photochemical processes. Only in situations where $NO_2$ has been effectively removed from the lower stratosphere by heterogeneous chemical processing is ClO formed in large enough concentrations to promote rapid ClO dimer formation (which depends on the square of ClO concentration). The alternate catalytic cycle proposed by Molina and Molina[4] then becomes effective in ozone destruction without the need of atomic O. These conditions now regularly occur in the Antarctic springtime stratosphere.

Above ~30 km, $ClONO_2$ photolyses rapidly after daybreak and destruction of ozone occurs during daylight hours through the standard catalytic chlorine reaction. This yields a diurnal cycle of ClO formation and ozone destruction centered around 40 km altitude at non-polar latitudes[5].

Our 1992 March observations at Thule covered a period of similar solar exposure at very nearly the same polar latitude (76.3 N) as our various measurements during September at McMurdo Station (77.5 S)[2,3,6]. $NO_2$ column measurements showed very low values within the Arctic region during the winter of 1991-92[7], yet at no time during the entire February-March observing interval did we see evidence for low altitude formation of ClO approaching the ~1.5 ppb of ClO we have consistently found over McMurdo at ~20 km. This is in sharp contrast to a ~20 km altitude layer of ClO observed over much of northern Europe in the first half of January by the MLS mm-wave spectrometer onboard UARS, and by more limited ER-2 aircraft sampling over eastern Canada and the northeastern U.S.[8]

Thule lies at 76.3 N, 68.4 W, on the northwest coast of Greenland. Defining the polar vortex region in terms of temperature contours in the vicinity of 20 km (30 mb), Thule was generally well outside the vortex core, which remained over northern Scandinavia and the Barents Sea during most of February and March[9]. Northwest Greenland *did* remain in the rim of circulation around this core, as defined by potential vorticity contours, through the first week in March, but after March 8-10, both potential vorticity contours and maps of wind speed and direction at ~20 and 25 km show a pronounced shift to circulation from outer portions of the Aleutian high. During February and March, the stratosphere near Thule was never much colder than 215 K between 12 and 25 km. For most of the period covered here, in fact, temperatures throughout the Arctic region were typically_>205 K, well above that associated with either Type I or II polar stratospheric cloud (PSC) formation. The comprehensive meteorological coverage of the European Arctic Stratospheric Ozone Experiment (EASOE) campaign reported no significant PSC activity anywhere in the Arctic after late January.

On the other hand, the massive aerosol cloud injected into the lower stratosphere by the eruption of Mt. Pinatubo in the early summer of 1991 exerted a strong perturbing influence on Arctic stratospheric chemistry, photolysis, and transport during the winter of 1991-92, as determined by extensive measurements from EASOE and NASA's second Arctic aircraft campaign. The Arctic winter-spring stratosphere of 1992 was thus far from normal, and presents many puzzles and challenges for correct interpretation.

In view of this, we have begun a careful analysis of

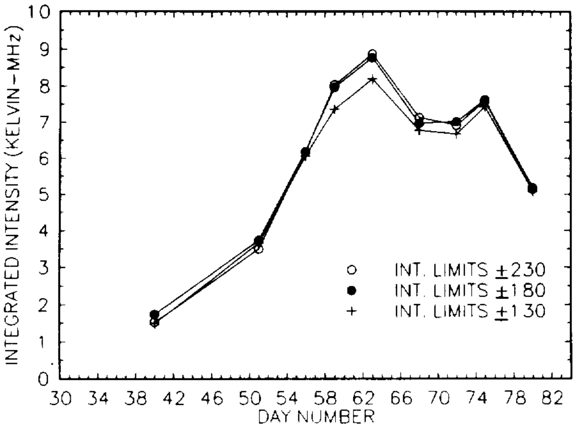

**Fig.1.** Integrated ClO signal intensity vs time during February and March, 1992. Feb 9 = Day 40, Mar 24 = Day 84. Mid-day data have been grouped over 3 to 5 day intervals for most of the points shown. See Fig.2 for details. Results for three different integration limits are given: ±230, 180, and 130 MHz each side of the emission line center. Integrated intensity values plotted here for the widest limits will give approximate column density in molecules per $cm^2$ above 17 km when multiplied by $3.4x10^{13}$. Estimated uncertainties are ±15 to 20 %.

a nearly two month record of ClO observations. This record contains information on diurnal and secular changes in the column density and vertical profile of ClO in the Thule region.

**Secular changes in column density:** We start with the variation of integrated column density. Our present mm-wave spectrometer has a bandwidth of 512 MHz, sufficient to allow analysis of pressure-broadened line shapes down to an altitude of ~16 km. In Fig.1, the mid-day integrated line intensity for the 278 GHz ClO emission line is shown as a function of day number. (Day 61 = March 1.) Typically, three adjacent days are grouped together to improve signal/noise ratio and to help average out residual baseline artifacts. During some periods, poor weather prevented daily observations, and a longer time span is covered: e.g., days 61-66 for early March. Within these intervals, whenever conditions were favorable, observations were made continuously in integration intervals of 20 minutes each.

There is a steady increase by more than 4-fold in the total column of ClO from our initial average over Feb 8-10 to that over Mar 1-6, after which the total column amount drops again. Exposure to sunlight at 16 km varied from about 4.3 hrs on Feb 9 (day 40) to 14.5 hrs on Mar 20 (day 80), and the respective values for 40 km altitude are about 6.5 hrs and 17 hrs. The noon solar zenith angle at 16 km also decreased from 92 to 77.5 degrees during this period. The increase in total column amount is thus primarily driven by the daily increase in solar exposure time. In contrast, we believe that the drop-off in the total column of ClO after early March is directly related to a "re-noxification" of the lower and middle stratosphere occurring about this time. We discuss this further below.

Another significant feature is present in Fig.1. Integration has been carried out over three different windows spanning intervals of ±130, 180, and 230 MHz around the line center (with the same zero baseline for each). It is clear that integration over the two wider intervals gives essentially identical values for each data point, while integrated intensities for the narrowest window fall consistently below these between ~days 56 and 70 (Feb 25 to Mar 10), and are in good agreement otherwise. This indicates that the ±130 MHz limits are too narrow to encompass the whole lineshape during the Feb 25 - Mar 10 interval, i.e., there is evidence for at least a small enhancement of ClO in the mid-to-lower stratosphere during this interval. We look further at this in the next section.

**Evolution of vertical profiles:** The mid-day spectral lineshapes that were integrated to obtain the data for Fig.1 are shown in Fig.2. In Fig.3, the mid-day average over Feb 27-Mar 6 (the interval showing the greatest evidence of low-altitude ClO enhancement), as well as the spectrum for Mar 17-24, are contrasted with the mid-day lineshape recorded at McMurdo Station, Antarctica, as an average over Sept 20-24, 1987. The contrast in pressure-broadened (hence low altitude) line wing intensity is very pronounced. Note that the Mar 17-24, 1992 data and the Sep 20-24, 1987 data each fall at equal times after the respective winter solstice, and that each location is about equidistant from the respective pole, so that diurnal insolation was essentially the same for each. What is of course different is the vortex size, duration, temperature minima, and location relative to respective poles.

The low-to-vanishing intensity of line wings in our 1992 Thule data pose a considerable test for recovery of vertical profiles in the 16-25 km altitude range.

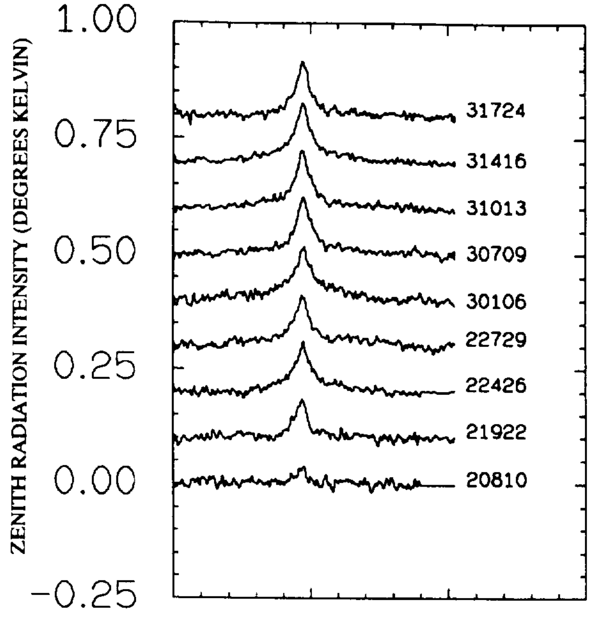

**Fig 2.** Evolution of mid-day emission line spectra for the 278 GHz rotational transition of ClO, during Feb-Mar, 1992 over Thule, Greenland. Integrations produced the data points in Fig.1. Identification numbers are in the format M-DD-DD so that 30106 is a sum of available data over the period Mar 1-6, etc. Days with usable data = Feb 8,10,19,21,22,24-29, Mar 1,6-10,12-17,20, and 24. The ordinate gives radiation intensity in equivalent black-body temperature units. The abscissa is in spectrometer channel number, at 1 MHz per channel.

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