

Stratospheric Chemistry: Polar Ozone Depletion

AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: <http://www.atmos.umd.edu/~rjs/class/spr2017>

Today:

- **Processes that govern the formation of the Antarctic ozone hole**
- **Compare & contrast Antarctic and Arctic ozone depletion**
- **Arctic Ozone 2011**

Problem Set #3 is due on Thursday
No Admission Ticket for Thursday's Lecture

In 1976 and 1977, use of CFCs as aerosol propellants was banned first by the United States, then by Canada, Norway, and Sweden

Lecture 15
4 April 2017

Polar Ozone Depletion

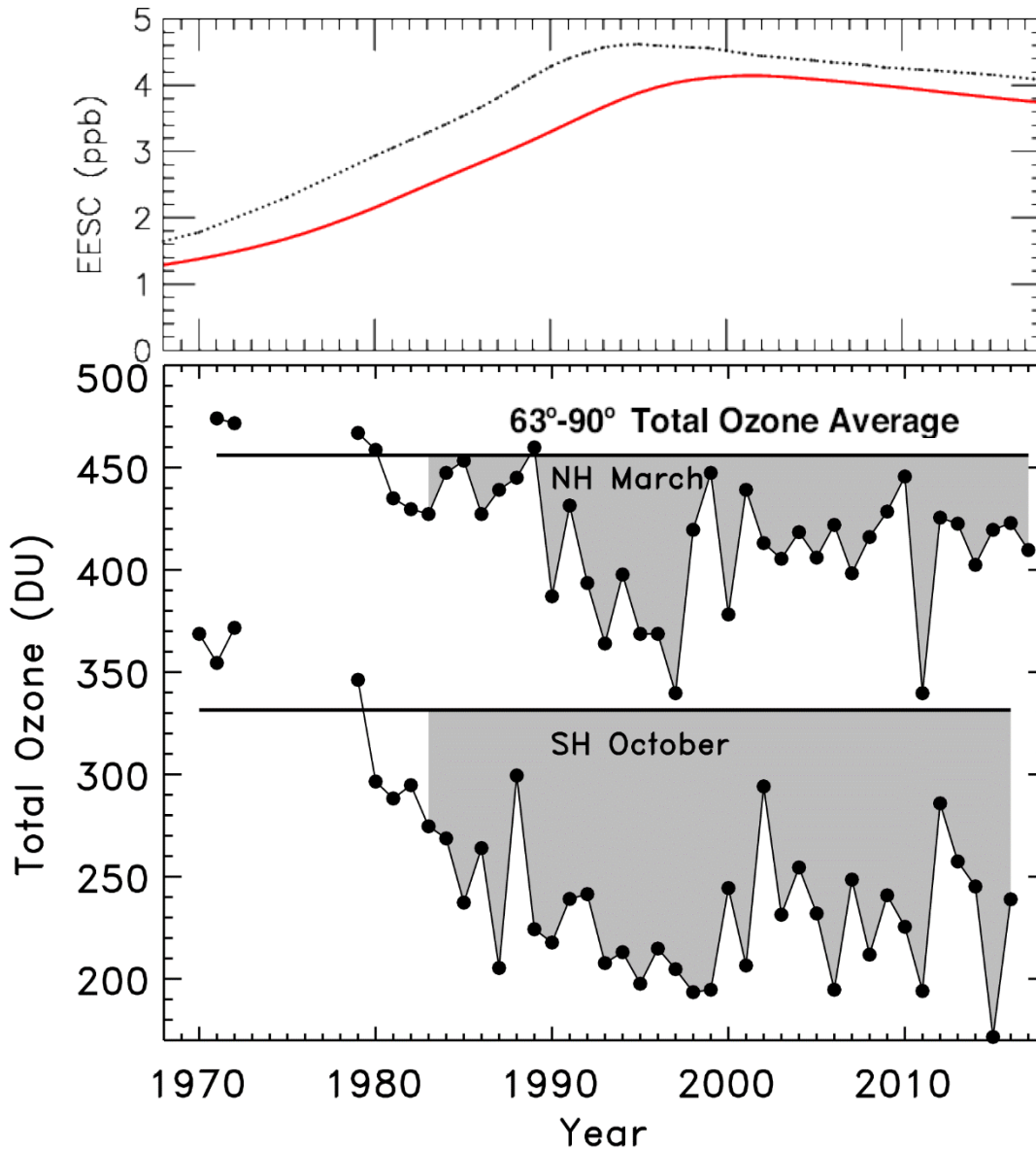
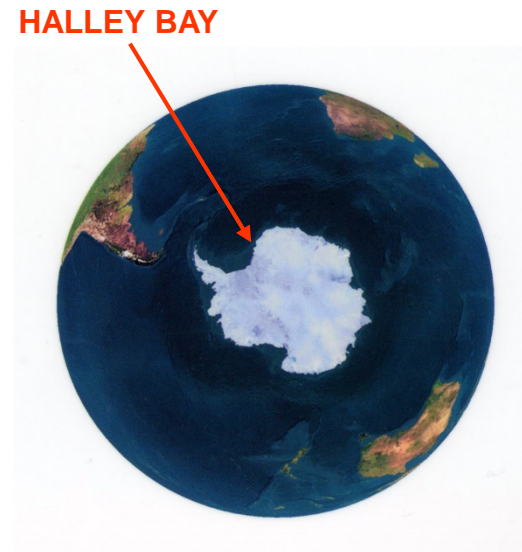
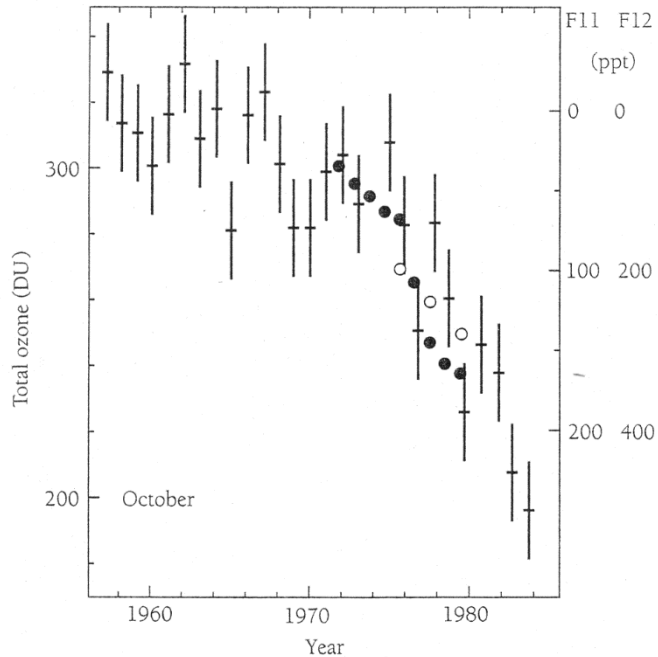


Figure Q12-1, WMO/UNEP (2010), updated by Tim Canty

Polar Ozone Depletion

Discovery of the ozone hole:

Halley Bay (76°S)
October Mean

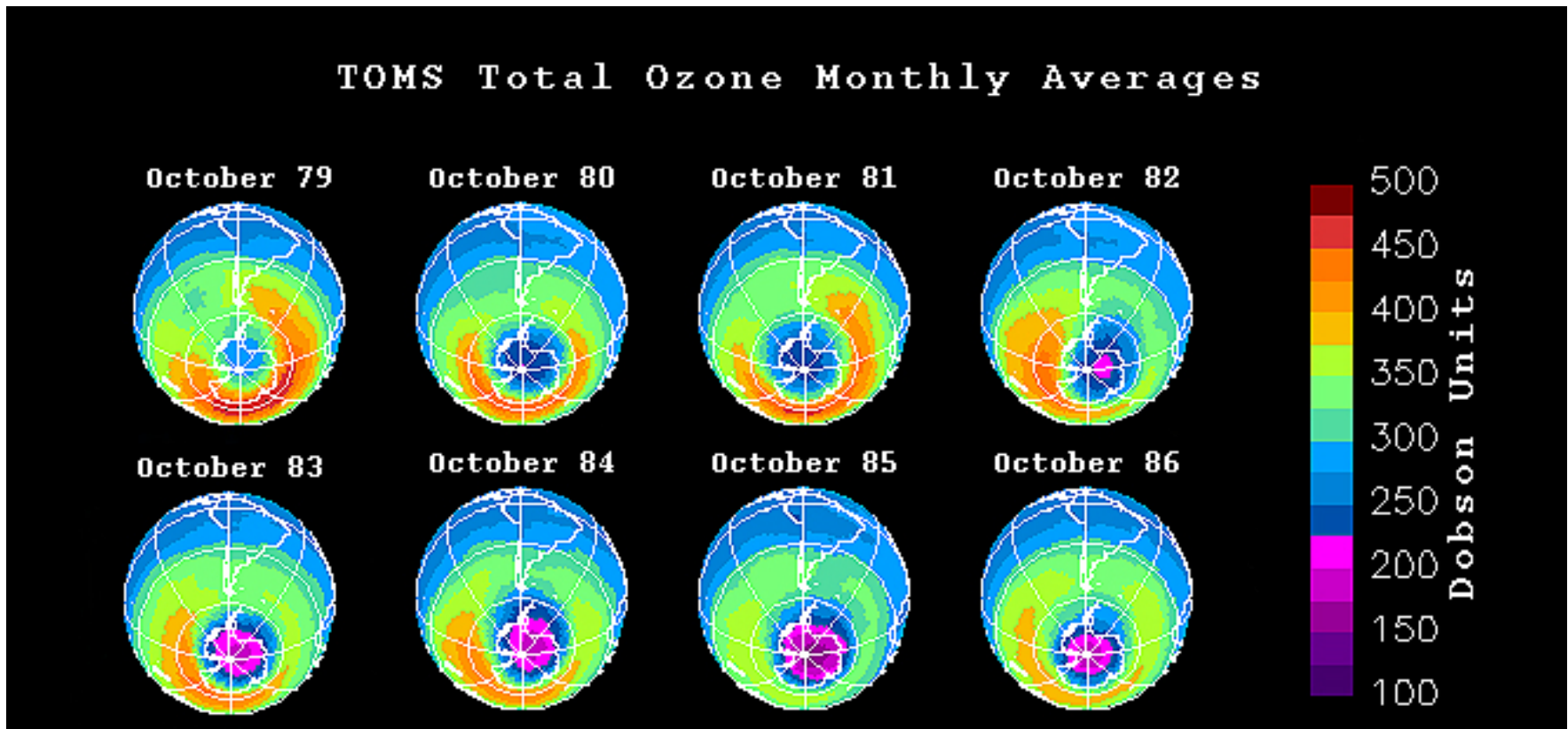


**Southern
Hemisphere**

Farman *et al.*, Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature*, 315, 207, 1985.

Polar Ozone Depletion

First view from space:



Stolarski *et al.*, *Nature*, 322, 808, 1986.

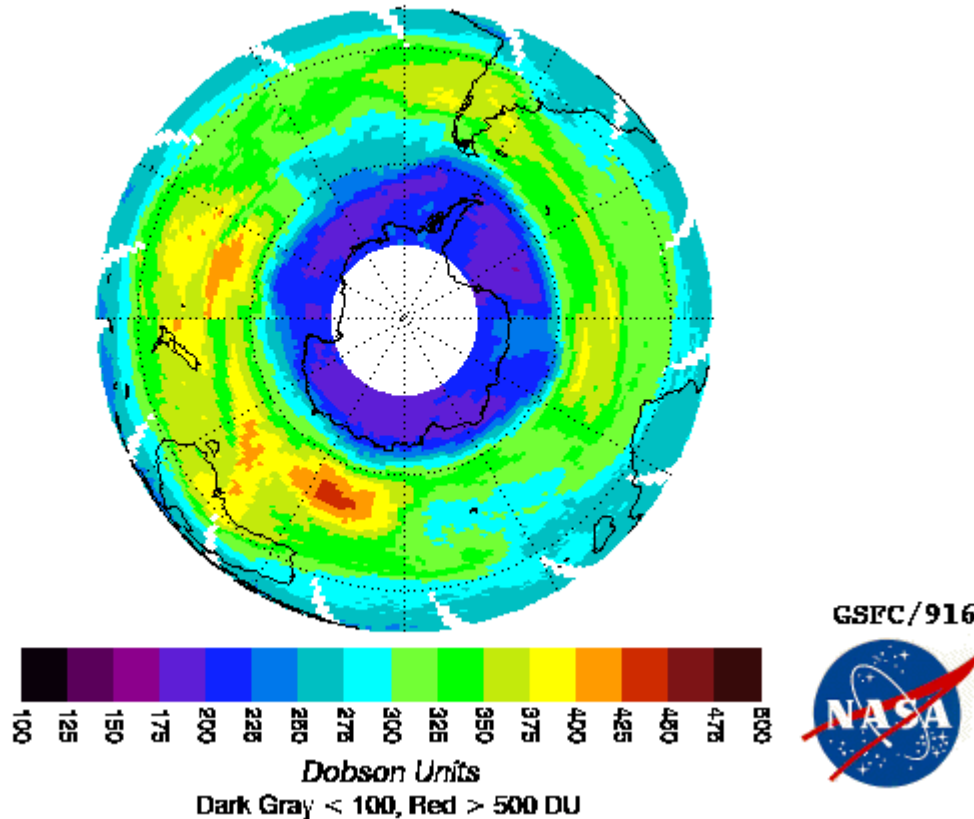
The paper showed data for Octobers of 1979 through 1985 in black & white contour diagrams. This image, produced soon after, showed color plots of total column ozone during Antarctic spring, including measurements for year 1986.

Polar Vortex Circulation

During winter:

- radiative cooling leads to cold air in polar stratosphere
- large scale low pressure region develops over pole
- strong “polar night jet” develops, isolating air at high latitudes from air at low latitudes
- T continues to fall in the “vortex like” circulation near the pole

EP/TOMS Total Ozone for Sep 1, 2001



GEN:271:2001

Polar Ozone Depletion Theories

Soon after the discovery of the ozone hole three theories emerged to explain the rapid springtime loss of ozone over Antarctica:

1. Chemistry due to enhanced levels of ClO, driven by heterogeneous reactions on the surface of polar stratospheric clouds (PSCs) [McElroy et al., *Nature*, 1986; Solomon et al., *Nature*, 1986]
 - a) two new catalytic cycles, both involving halogen radicals and requiring ~1 ppb of ClO to be effective ($\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{ClOOCl} + \text{M}$; $\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$)
[Molina and Molina, *JPC*, 1987; McElroy et al., *Nature*, 1986]
 - b) suggestion that PSC particles might be composed of HNO_3 and upon sedimentation could appreciably lower NO_x (which would prevent conversion of ClO to ClONO_2)
[Toon et al., *GRL*, 1986]
 - c) decreasing ozone column driven by rising ClO, due to buildup of chlorine from CFCs
2. Chemistry due to enhanced levels of NO_x , driven by variations in solar UV
[Callis and Natarajan, *Nature*, 1986]
3. Loss by transport due to upwelling of ozone poor air from the troposphere
[Tung et al., *Nature*, 1986]

Polar Stratospheric Clouds

- Studies prior to the discovery of the ozone hole documented :
 - high altitude (~20 km) “mother of pearl” clouds over Norway [e.g., Carl Stormer, Remarkable clouds at high altitudes, *Nature*, 1929]
 - greater prevalence of polar stratospheric clouds in SH compared to NH [e.g., McCormick et al., Polar Stratospheric Cloud Sightings by SAM II, *JAS*, 1982].

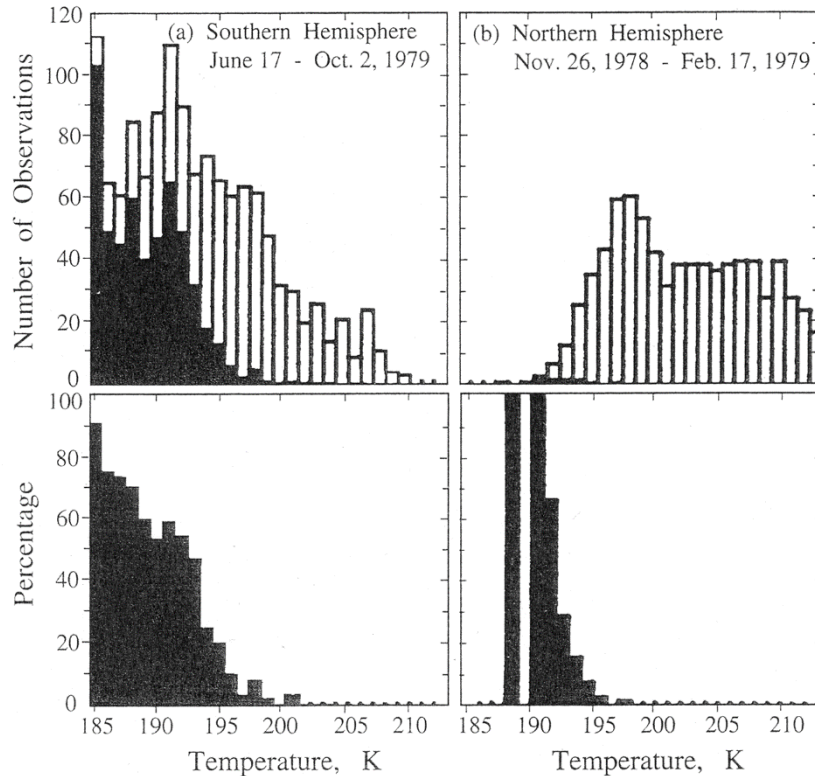


FIGURE 4.20 The top panels show a histogram of the total number of vertical temperature profiles having a given minimum temperature for the Antarctic and Arctic winters. The darkened bars represent observations of PSCs. The lower panel shows the frequency of PSC observations as a percentage of the total events with the same minimum temperature (McCormick et al., 1982). All events for temperatures ≤ 185 K are included in the 185 K bin.

National Ozone Expedition: McMurdo Station, 1986

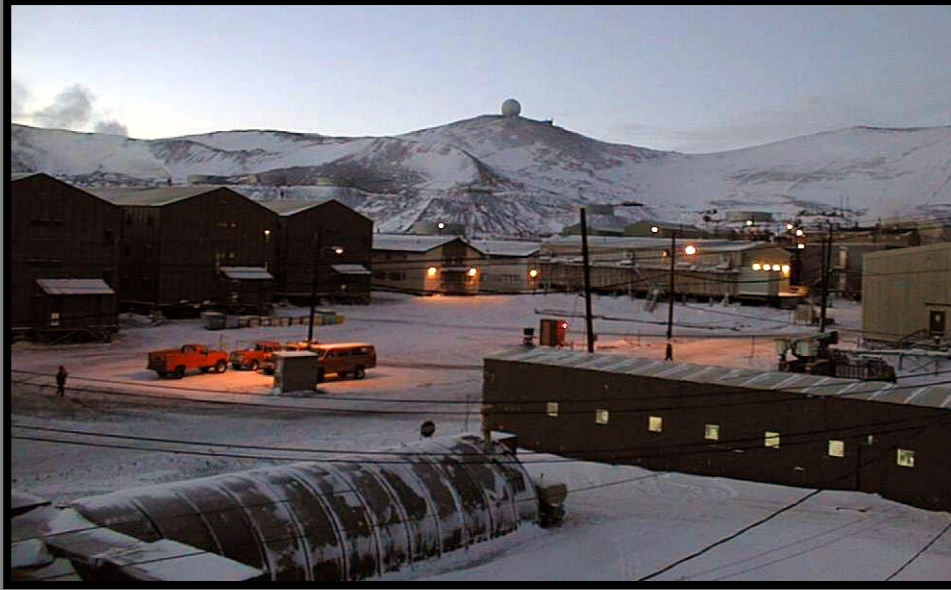
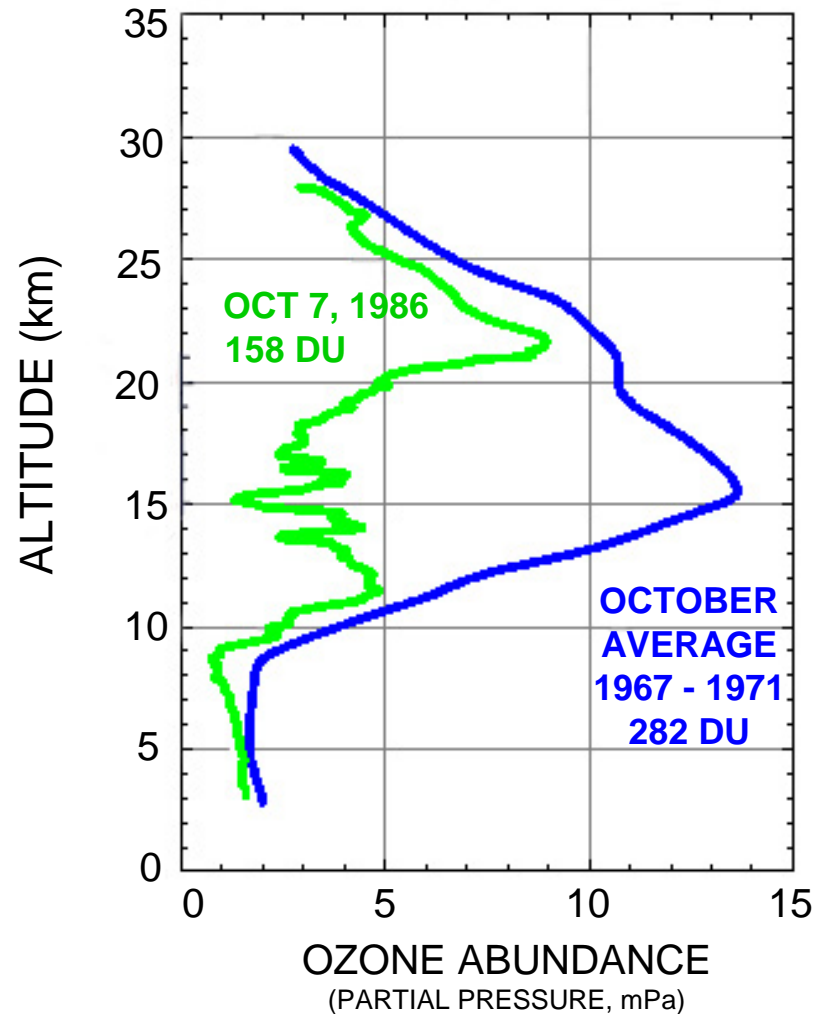


Photo © Geoff Toon

National Ozone Expedition: McMurdo Station, 1986

Balloon-borne ozonesondes showed:

Region of nearly complete removal of ozone between ~12 and 20 km:

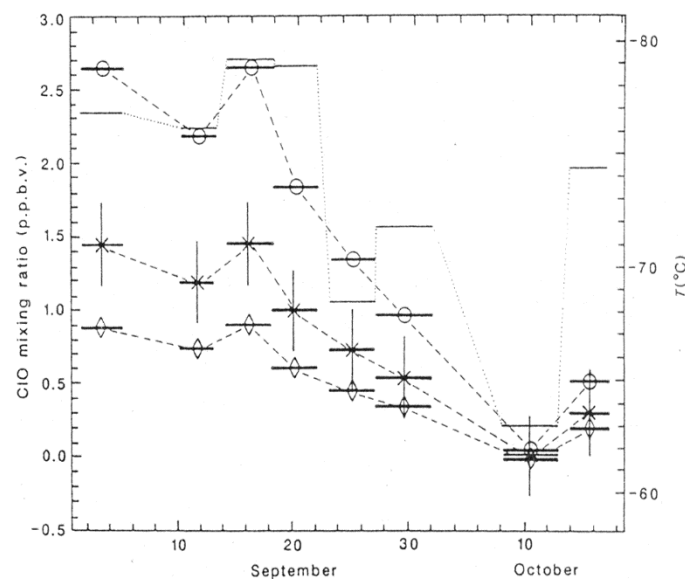
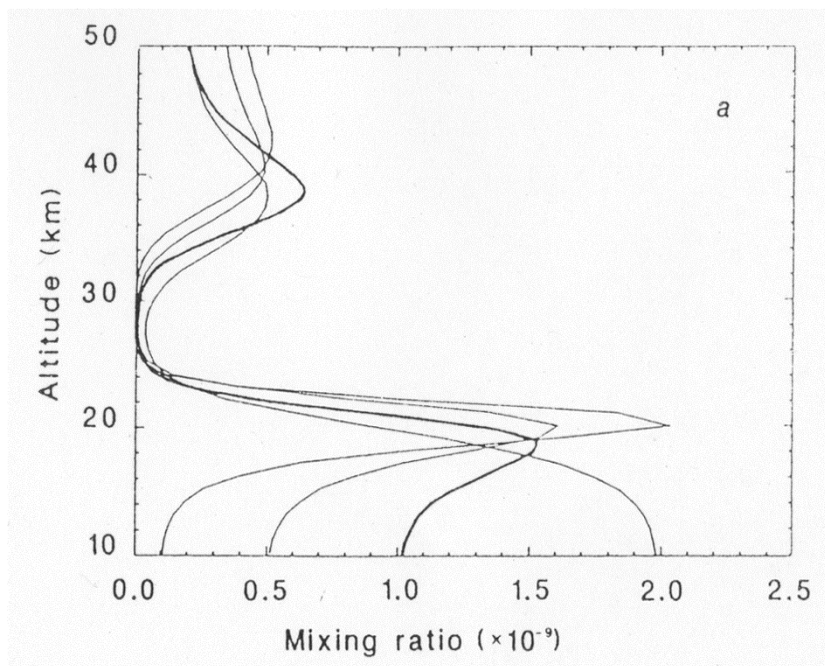


Hofmann et al., *Nature*, 326, 59, 1987.

National Ozone Expedition: McMurdo Station, 1986

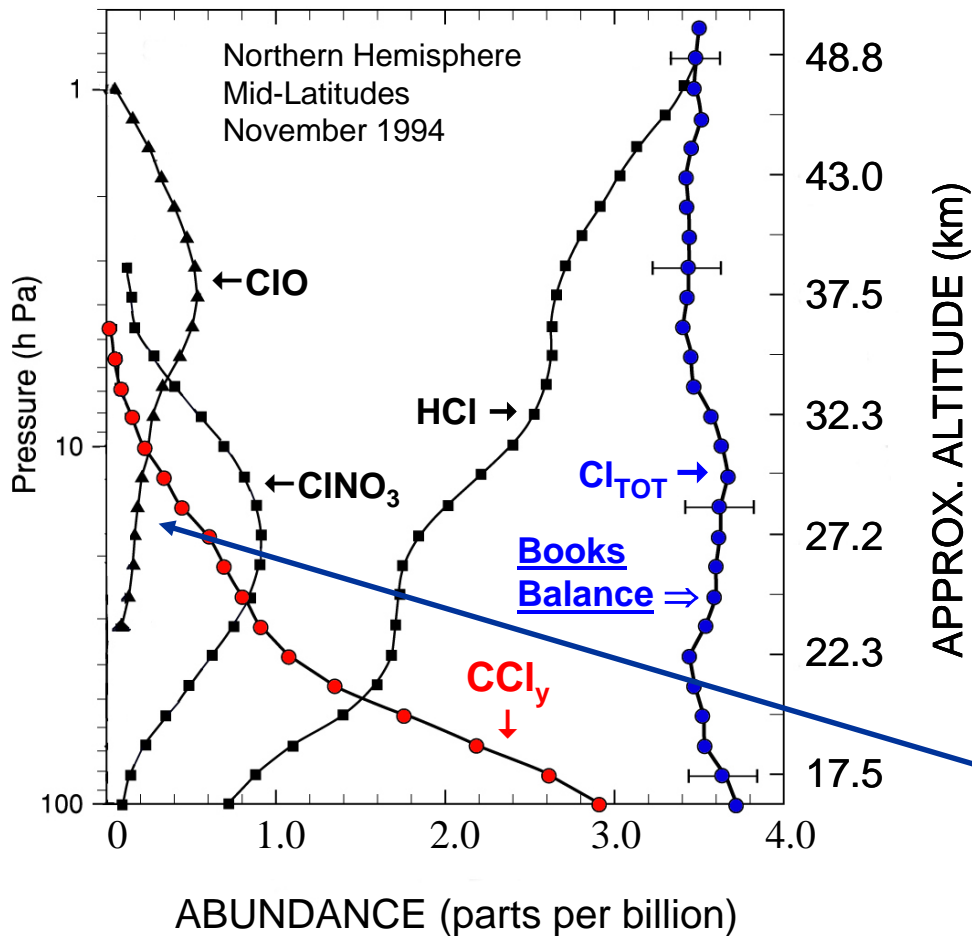
Ground based measurements revealed:

- Presence of ~1 ppb of ClO over Antarctica
 - Decreasing column HNO_3 throughout springtime and suppressed column HCl and ClONO_2 , consistent with existence of large amounts of ClO
- [Farmer et al., *Nature*, 1987]



Left: ClO profiles retrieved over McMurdo Station based on ground based microwave spectra acquired 1-22 Sept 1986, for initial mixing ratio guesses of 0.1, 0.5, 1.0, and 2.0 ppb. Because pressure broadening $>$ spectral bandwidth below ~ 15 km, the initial guess is unaltered by the retrieval algorithm below ~ 15 km. **Right:** Time series of ClO over McMurdo, assuming constant ClO mixing ratio vs altitude between 15-20 km (circles), 15-22 km (crosses), or 15-24 km (diamonds). Thin lines connected by dots are stratospheric temperature at 18 km. From *DeZafra et al.*, *Nature*, 1987 and *P. Solomon et al.*, *Nature*, 1987.

Chlorine Abundance, Mid-Latitude Stratosphere



Note: Below ~30 km,
 $\text{ClO} \ll \text{ClNO}_3$ and HCl

Zander *et al.*, *GRL*, 1996

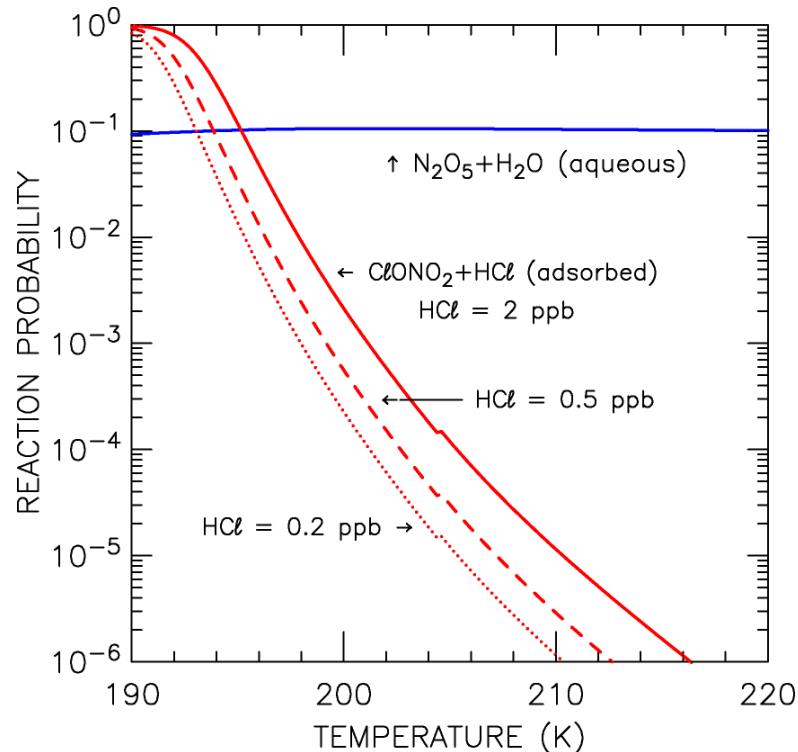
Lecture 14

Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

- a) What type of aerosol particles are present in the mid-latitude stratosphere?
- b) What heterogeneous chemical reaction occurs on the aerosol particles present in the mid-latitude stratosphere and how is ClO affected by this reaction?
- c) What type of particles are present in the polar stratosphere during winter?
- d) What is the effect of these particles on the chemical composition of the polar stratosphere?
Scientists have shown that chemical reactions occurring on the surface of these particles convert species such as Cl_2 and Br_2 (that do not deplete ozone) and HOCl and HOBr that do not cause harm to the ozone layer in the dark of winter.
- e) Following the return of sunlight, significant levels of what radical compound builds up inside the Antarctic stratosphere, leading to rapid loss of ozone?
- f) Why does the ozone hole occur only over Antarctica?

Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

In all cases, γ must be measured in the laboratory



Reaction probabilities given for various surface types, with formulations of various degrees of complexity, in **Section 5** of the JPL Data Evaluation.

Atmospheric Chemistry and Physics by Seinfeld and Pandis provides extensive treatment of aqueous phase chemistry, properties of atmospheric aerosol, organic aerosols, etc.

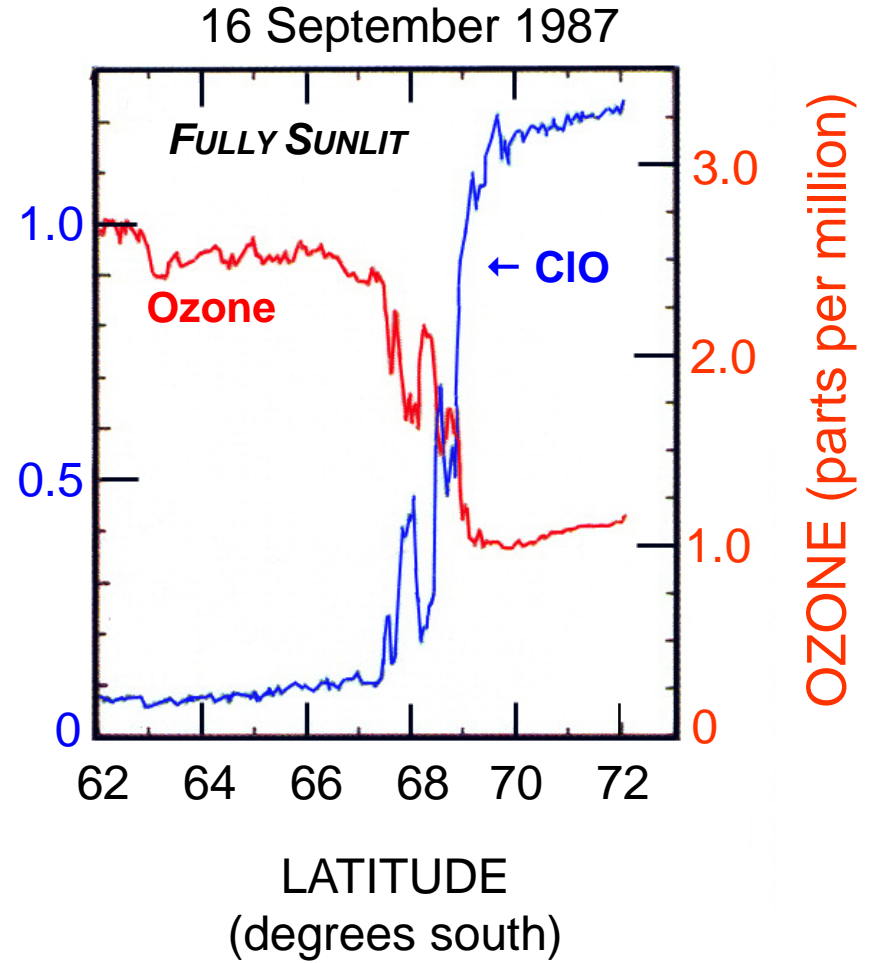
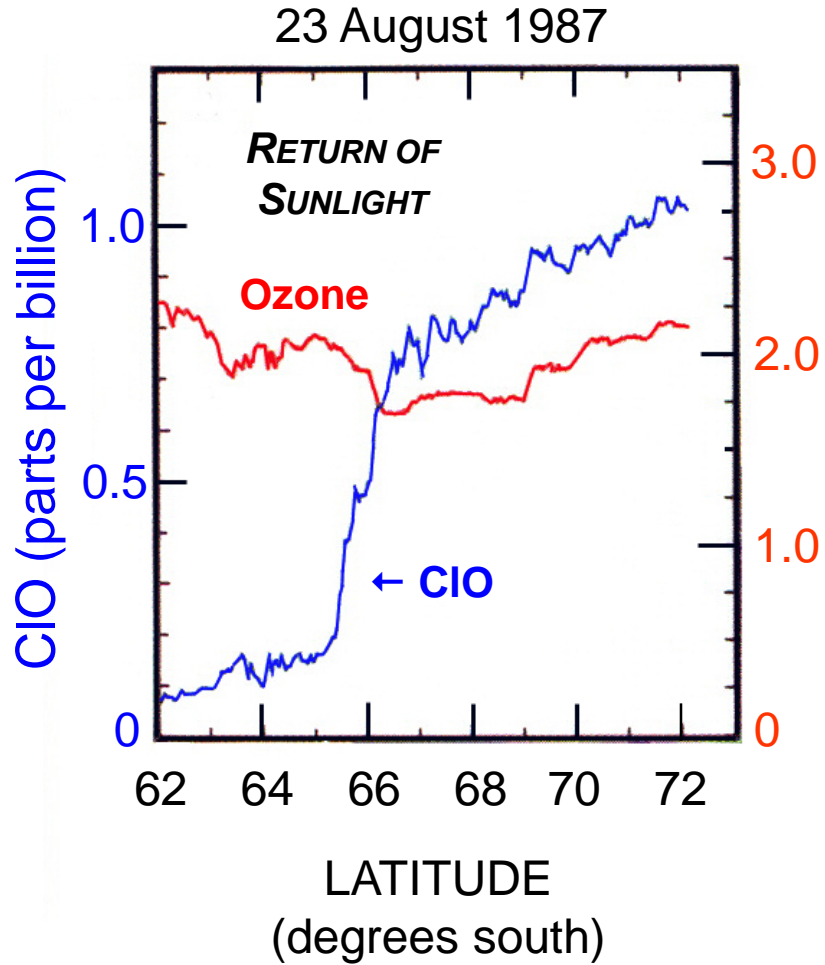
POLAR OZONE LOSS

- COLD TEMPERATURES → POLAR STRATOSPHERIC CLOUDS (PSCs)
- REACTIONS ON PSC SURFACES LEAD TO ELEVATED ClO
 - $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 \text{ (gas)} + \text{HNO}_3 \text{ (solid)}$
 - $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$
 - $\text{Cl}_2 + \text{SUNLIGHT} + \text{O}_3 \rightarrow \text{ClO}$
 - $\text{HOCl} + \text{SUNLIGHT} + \text{O}_3 \rightarrow \text{ClO}$
 - HNO_3 SEDIMENTS (PSCs fall due to gravity)
- ELEVATED **ClO** + SUNLIGHT DESTROYS O_3
- BrO : REACTION PARTNER FOR ClO ⇒ ADDITIONAL O_3 LOSS





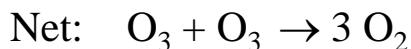
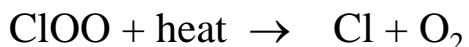
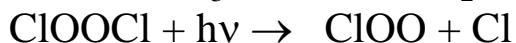
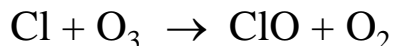
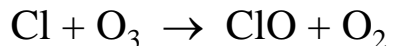
Airborne Antarctic Ozone Expedition: Punta Arenas, Chile, 1987



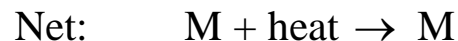
Anderson et al., *Science*, 1991

Polar Ozone Loss Cycles

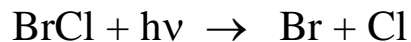
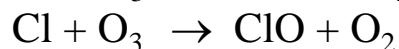
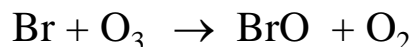
Cycle (1a):



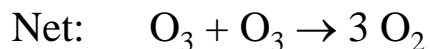
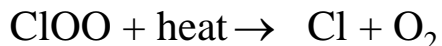
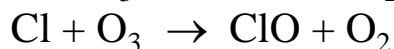
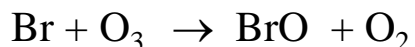
Cycle (1b):



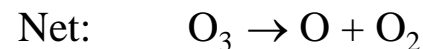
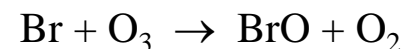
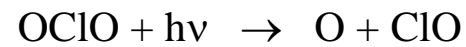
Cycle (2a):



Cycle (2b):



Cycle (2c):



Cycle (1) accounts for ~60% of polar ozone loss; Cycle (2) accounts for nearly all of the rest

Rate constants and products for these reactions worked out by many scientists:

Molina and Molina, JPC, 1987

Sander, Friedl, and Yung, *Science*, 1989

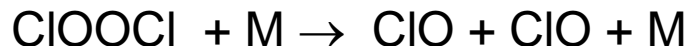
Moore, Okumura *et al.*, *Phys. Chem. A*, 1999

Bloss, Nickolaisen, Sander *et al.*, JPC, 2001

Thermal Decomposition

30.5 kcal/mole

2 × 24.3 kcal/mole



$\Delta H = 18.1$ kcal/mole

Lecture 11, Slide 21

$$\frac{k_{\text{THERMAL}}}{k_{\text{FORMATION}}} = e^{(G_{\text{REACTANTS}} - G_{\text{PRODUCTS}}) / RT} = K^{\text{EQUILIBRIUM}}$$

JPL Data Evaluation gives values of $K^{\text{EQUILIBRIUM}}$ and $k_{\text{FORMATION}}$

$$K^{\text{EQ}} = 1.27 \times 10^{-27} e^{(8744/T)} \text{ cm}^{-3}$$

In equilibrium:

$$k^{\text{THERMAL}} [\text{ClOOCI}] = k^{\text{FORMATION}} [\text{ClO}] [\text{ClO}]$$

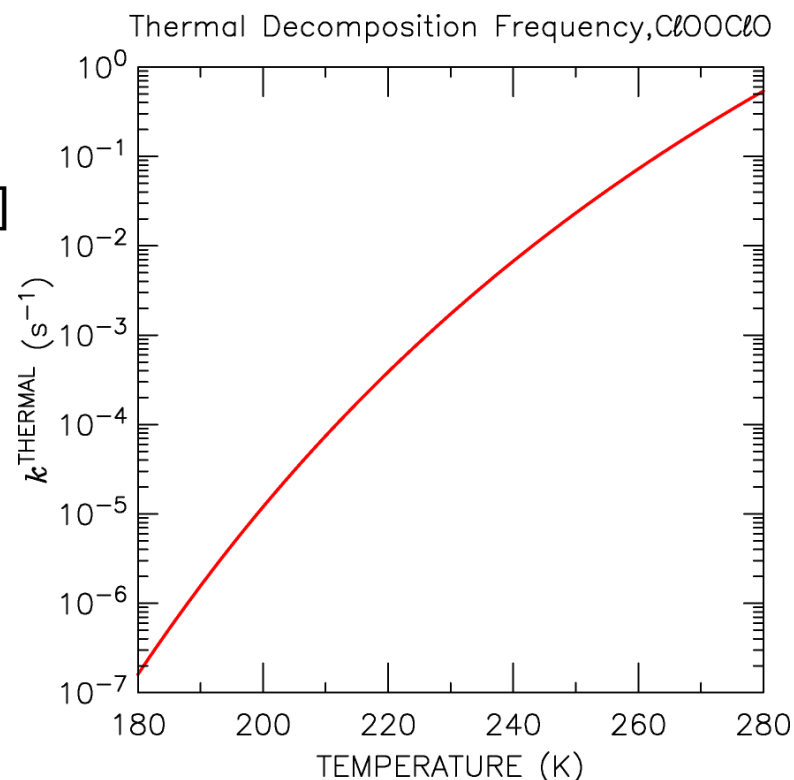
$$\text{where } k^{\text{THERMAL}} = k^{\text{FORMATION}} \times K^{\text{EQ}}$$

- Energetically, system favors ClOOCI
- Entropically, system favors ClO & ClO

at low T, ClOOCI stable: energy wins !

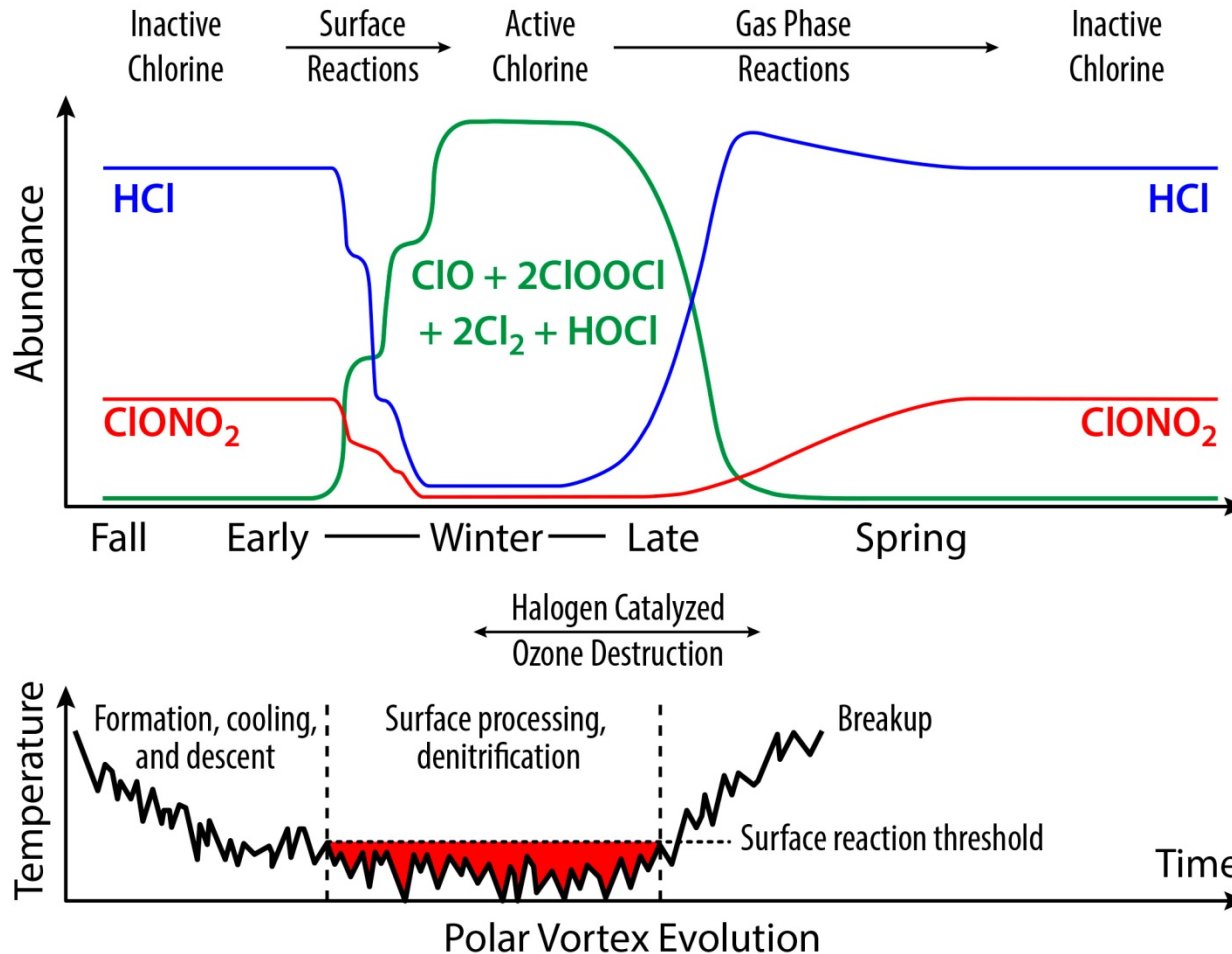
at high T, ClOOCI unstable: entropy rules !

Equilibrium constants given in **Section 3**
of the JPL Data Evaluation.



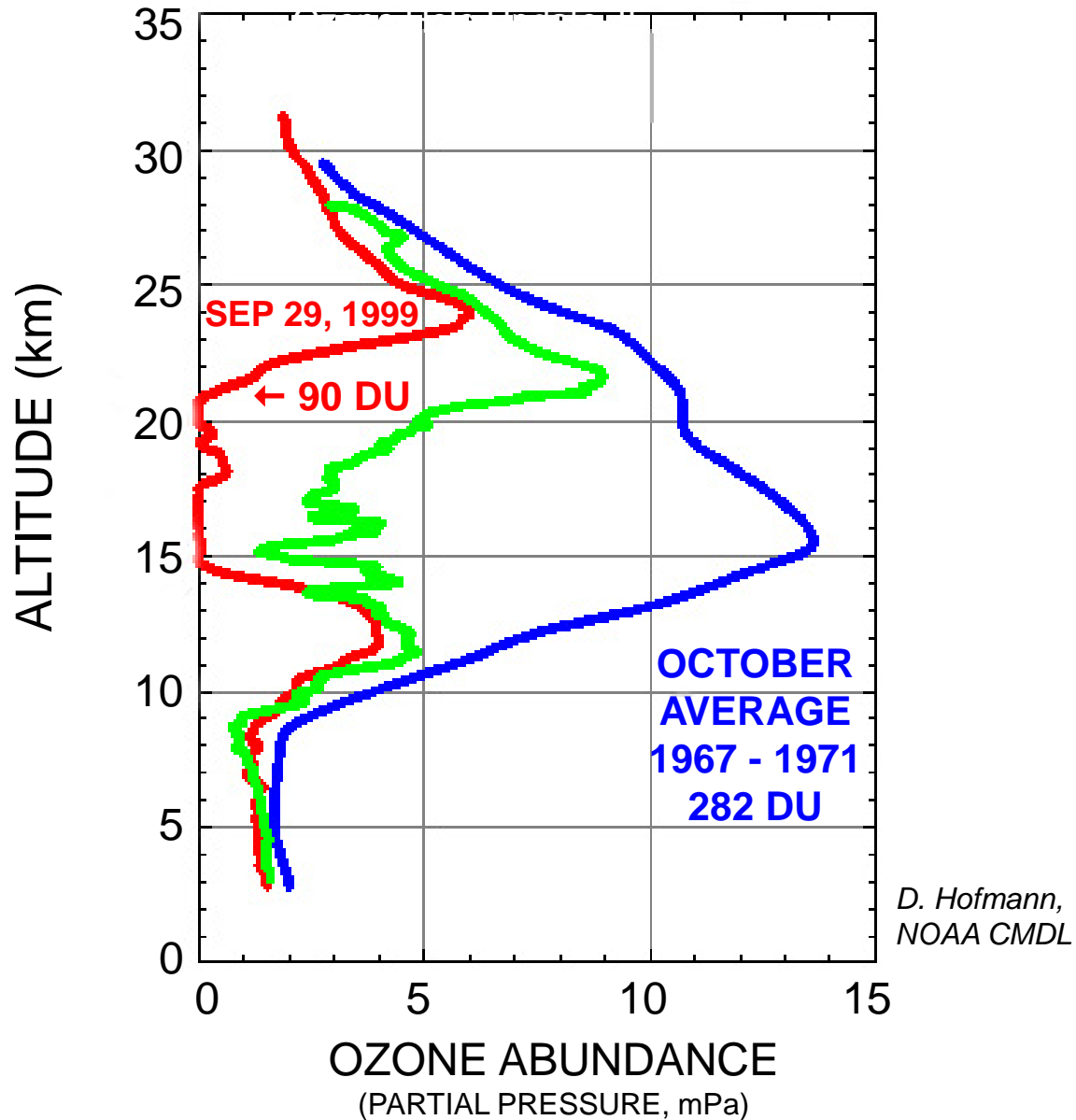
Polar Halogens, Seasonal Evolution

Inorganic Chlorine in the Polar Stratosphere

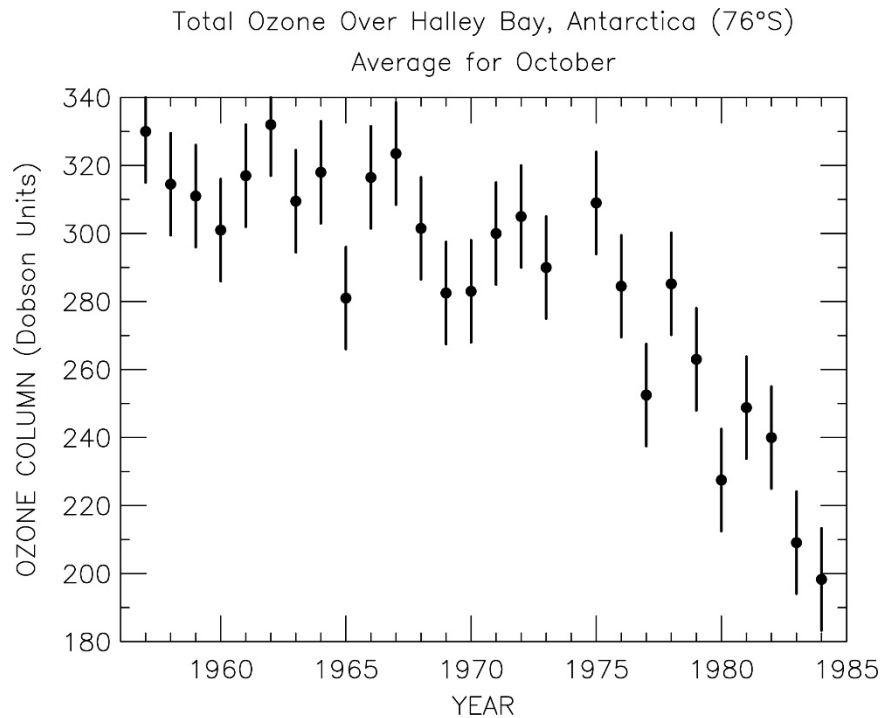


From Wilmoth, Salawitch & Canty, Stratospheric Ozone Depletion and Recovery, in press, 2017,

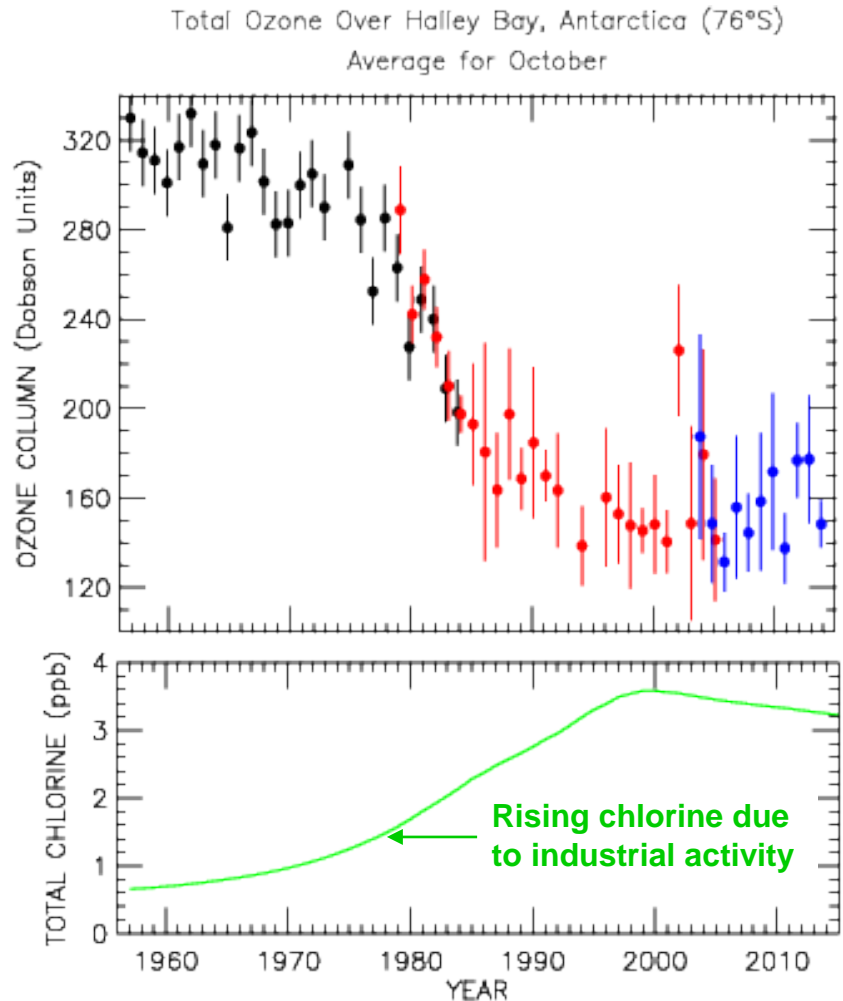
OZONE PROFILES, SOUTH POLE: UPDATE



Update



After Farman et al., Large losses of total ozone in Antarctica reveal Seasonal ClO_x/NO_x interaction, Nature, 315, 207, 1985.



- **Models provide good overall simulation of Antarctic O₃ loss**
- **Scientific understanding of polar O₃ depletion led to international ban on CFCs**

Arctic Overview

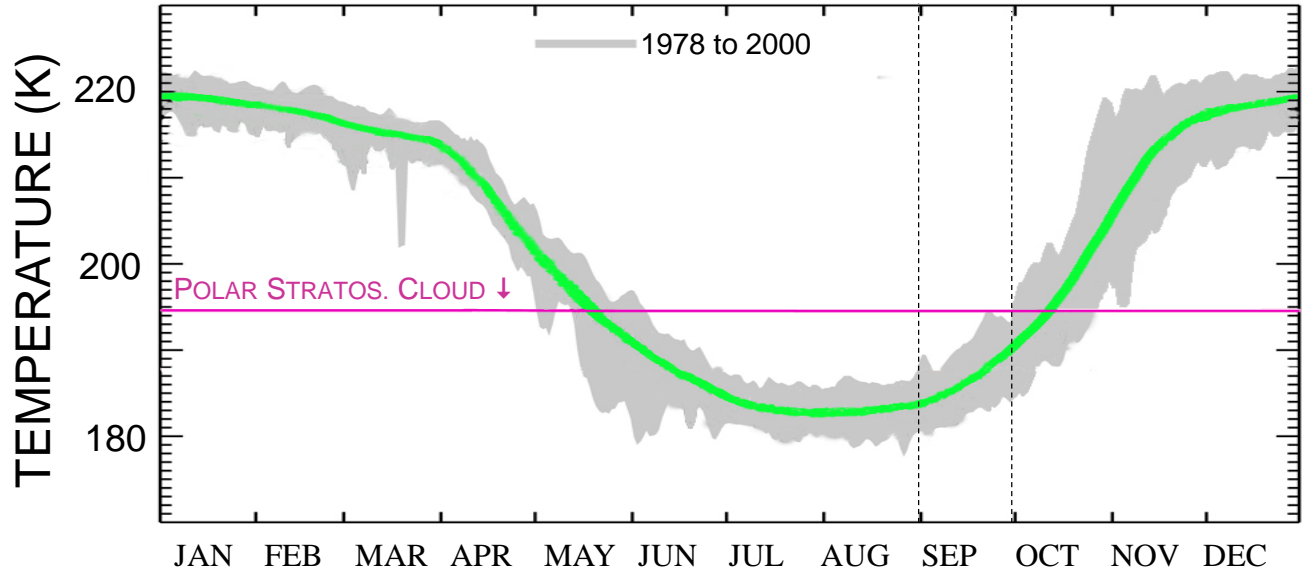
Arctic vortex (polar stratosphere):

- Always warmer than typical Antarctic winter
- Tremendous year to year variability in temperature
- Chemical ozone loss occurs only during cold winters
- Enough HNO_3 usually remains so that ClO recovers to ClONO_2 :
faster ClO de-activation (less ozone depletion) compared to Antarctic

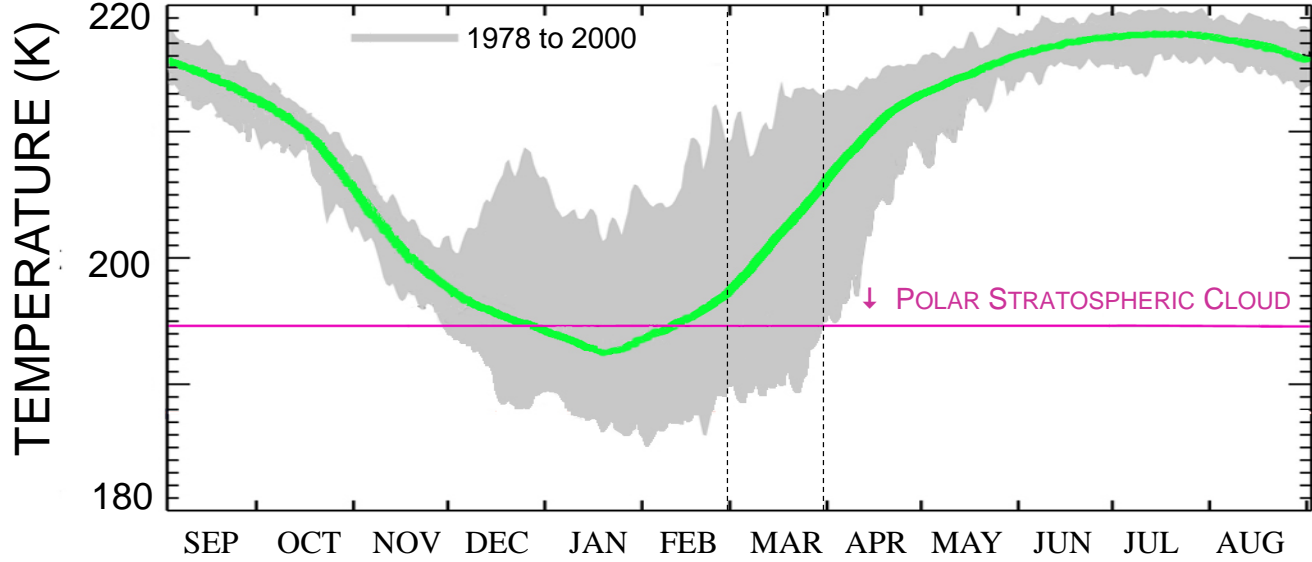
All of this is due to hemispheric differences in atmospheric dynamics:

- More vigorous circulation in NH due to much more land-sea contrast, which triggers poleward transport of heat by atmospheric motions
(Antarctic ice sheet suppresses poleward transport of heat by atmosphere)
- Stronger circulation in NH leads to more disturbed vortex (warmer, less PSCs)

ANTARCTIC POLAR VORTEX, MINIMUM TEMPERATURE, 20 km

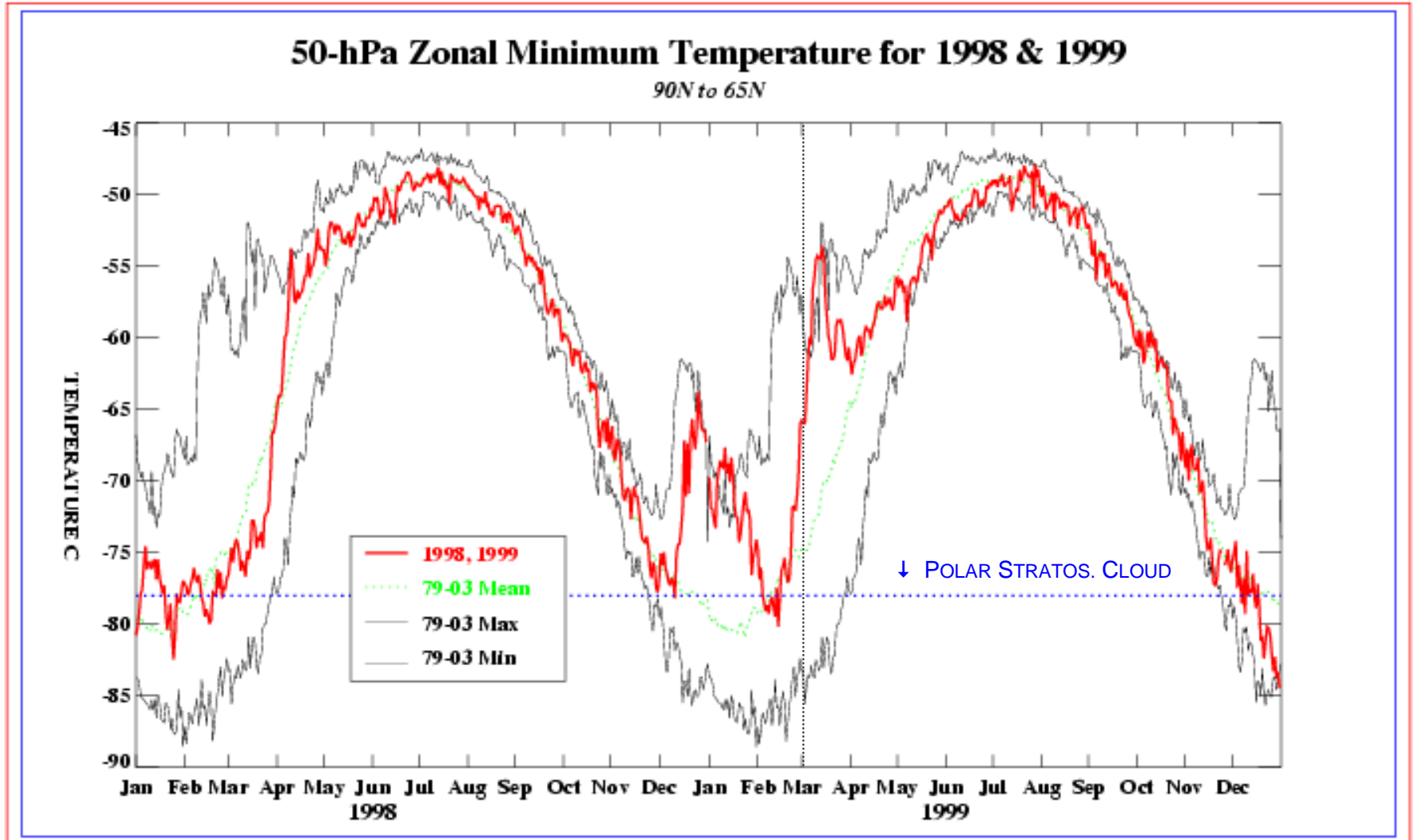


ARCTIC POLAR VORTEX, MINIMUM TEMPERATURE, 20 km



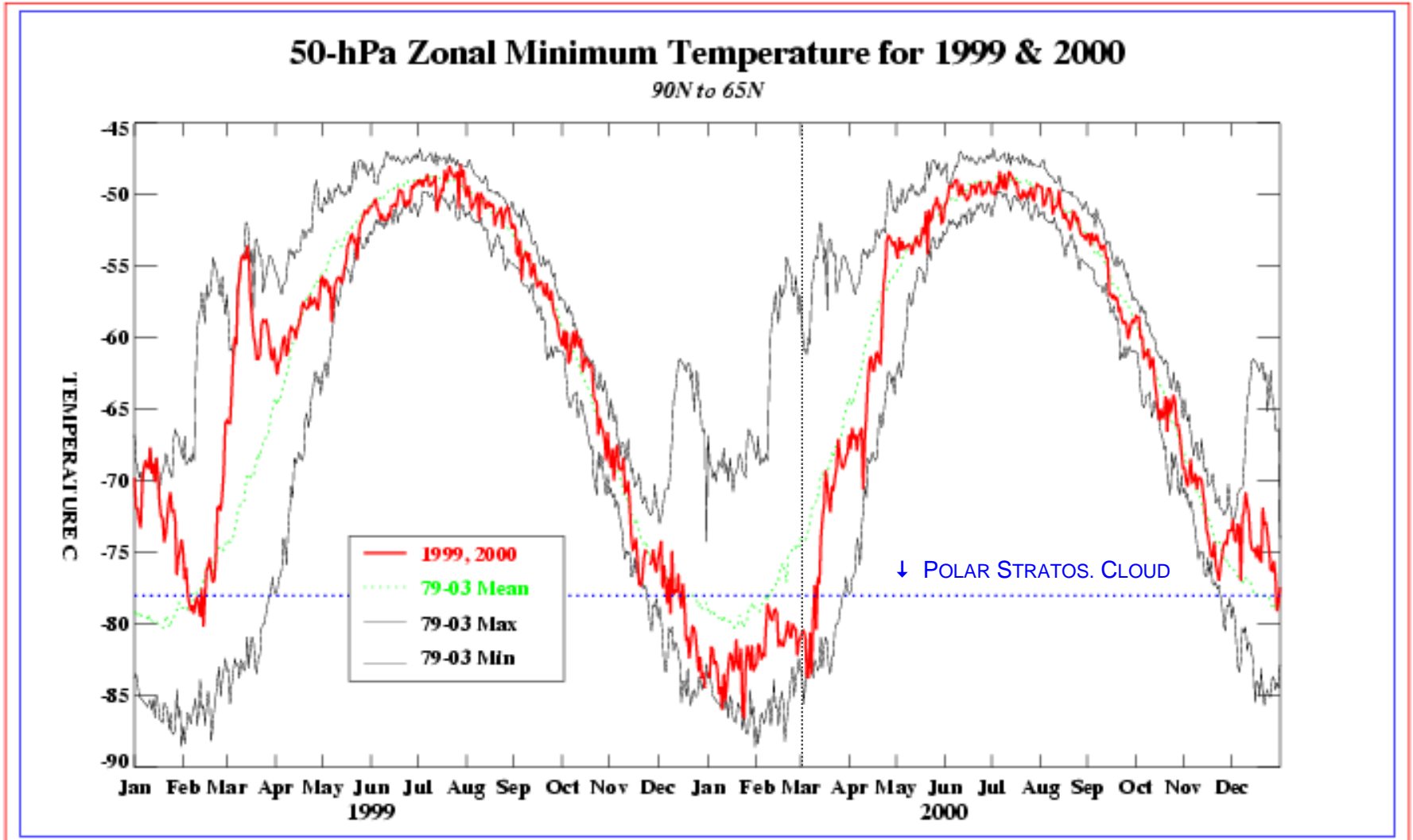
Data Courtesy P. Newman,
NASA/GSFC

Arctic Temperature, 1998 & 1999



http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_1999.gif

Arctic Temperature, 1999 & 2000

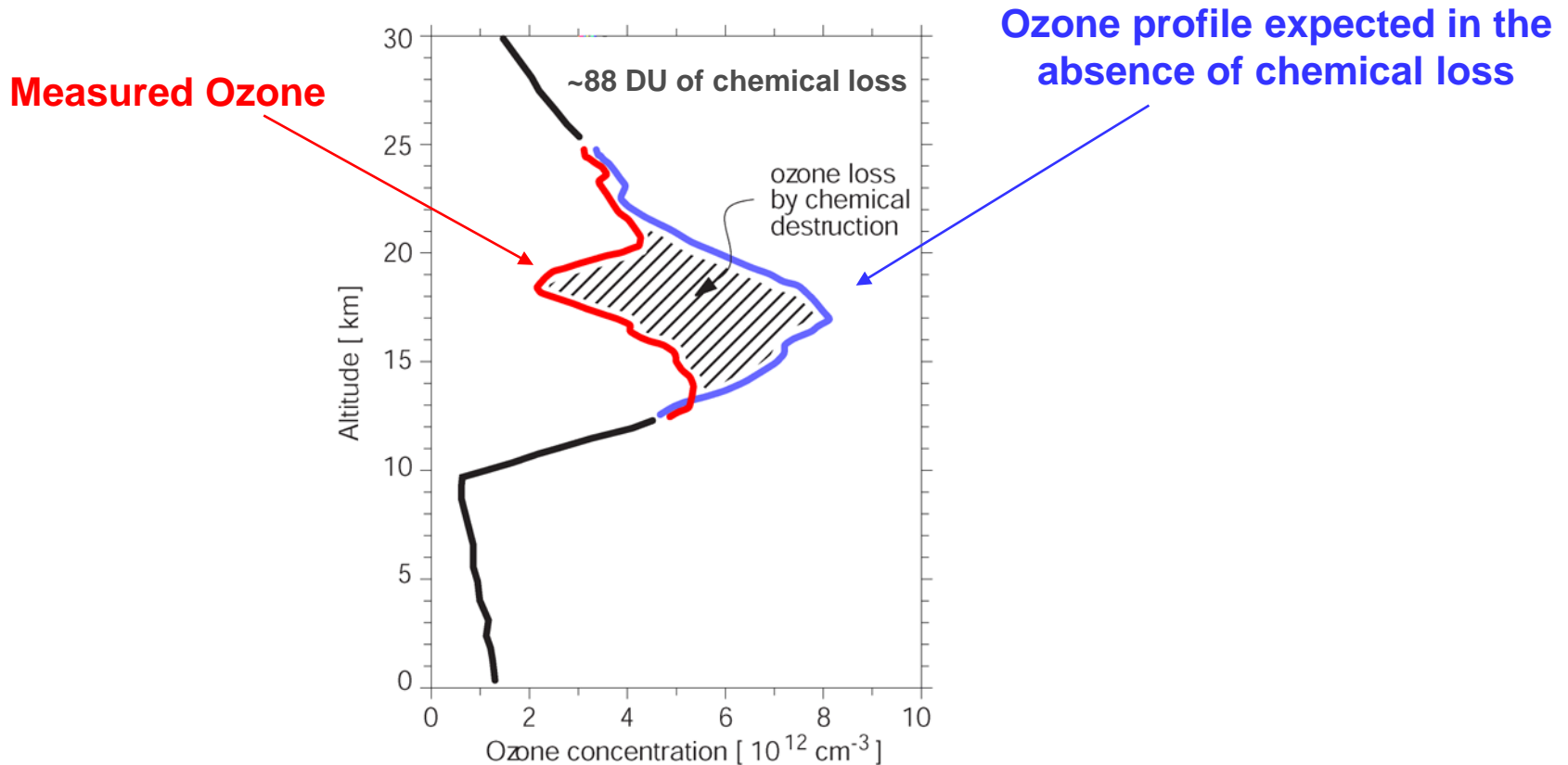


http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2000.gif

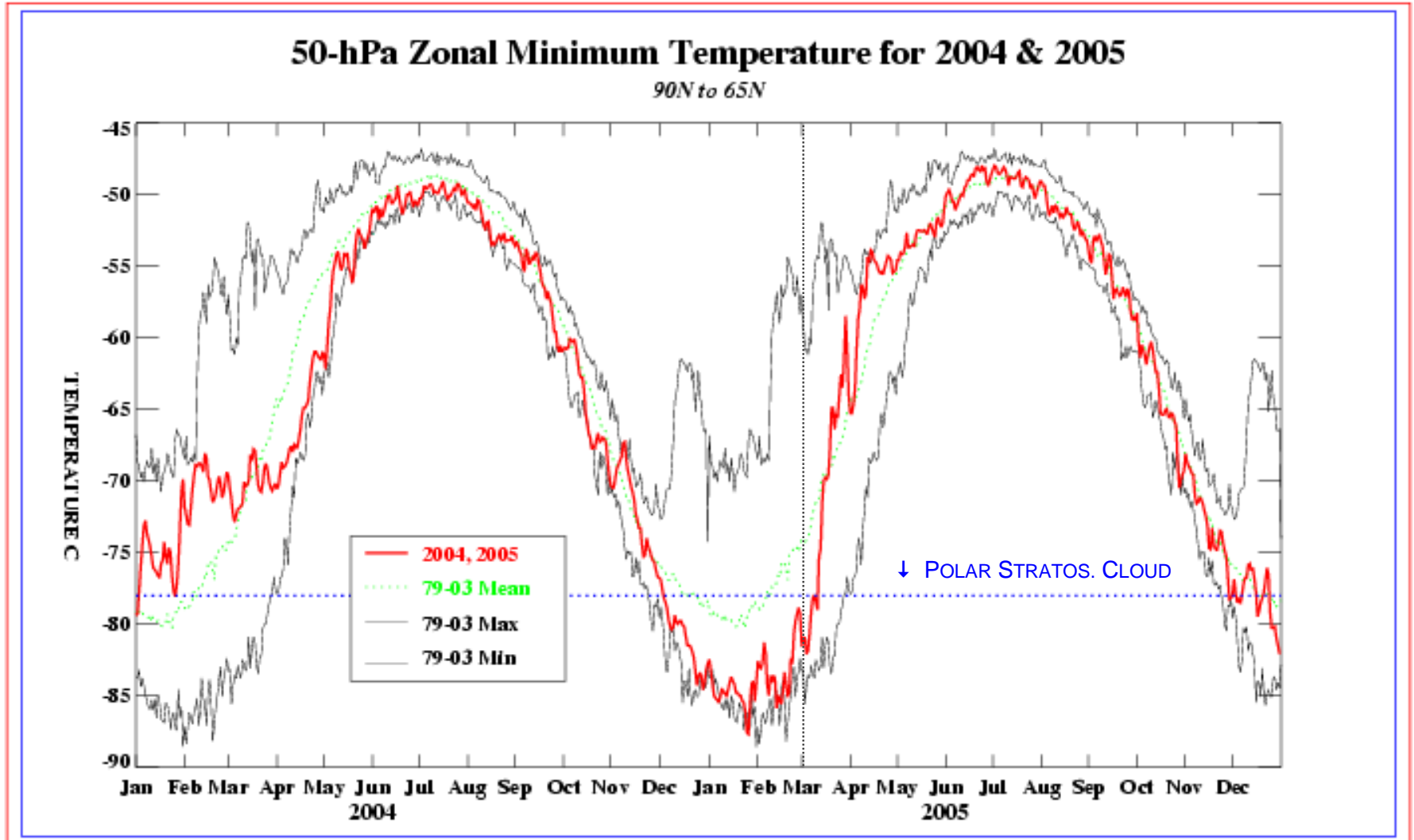
ARCTIC WINTER OF 1999/2000

- **COLD** (MANY DAYS BELOW PSC THRESHOLD)
- **ELEVATED ClO** THROUGHOUT WINTER
- **SIGNIFICANT OZONE DEPLETION**

Arctic Ozone Loss in Winter 1999/2000

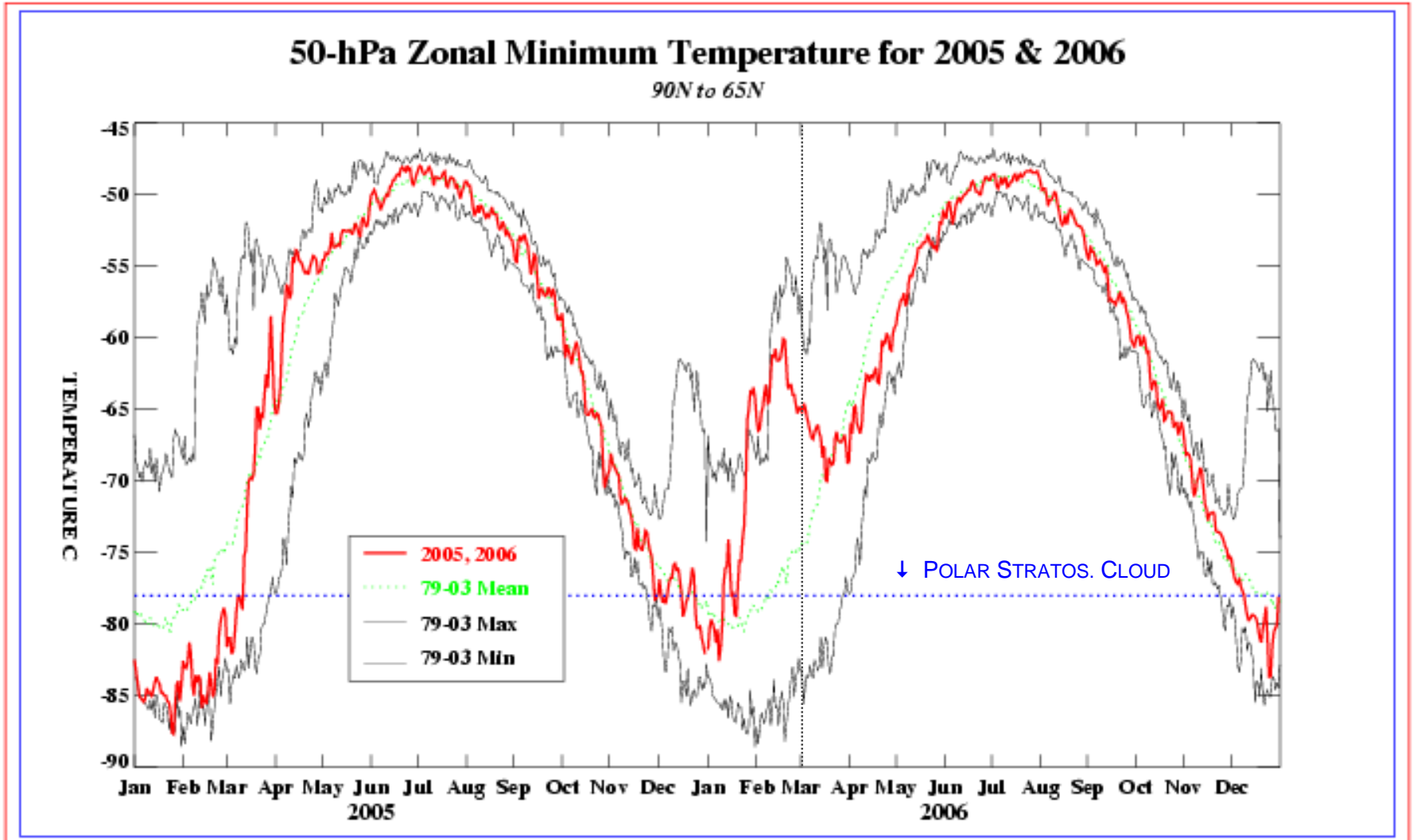


Arctic Temperature, 2004 & 2005



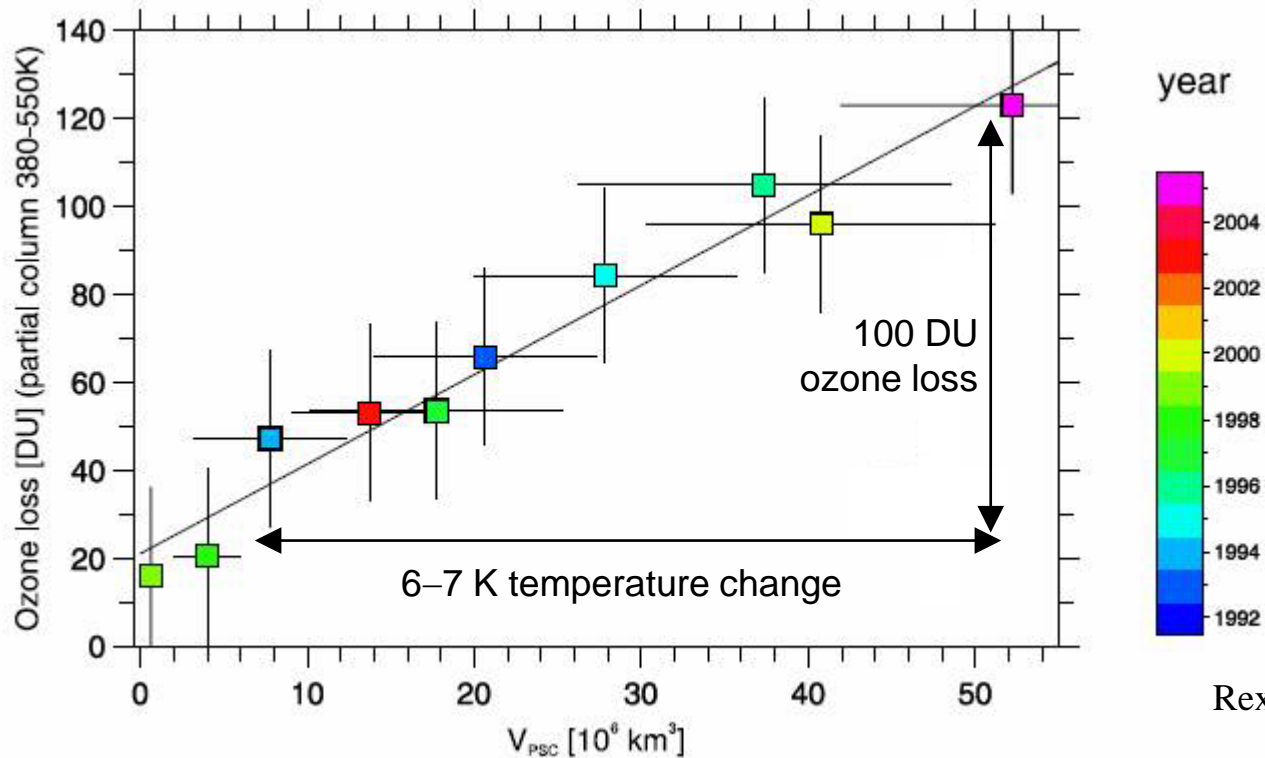
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2005.gif

Arctic Temperature, 2005 & 2006



http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2006.gif

Arctic Ozone Loss and Climate Change



Rex et al., GRL, 2006

- Surprisingly simple relationship between chemical loss of column ozone and volume of air exposed to PSC temperatures for entire *Arctic* winter (V_{PSC})
- This relation leads to estimate of ~15 DU additional loss of ozone per degree Kelvin cooling of the *Arctic* stratosphere

The Stratosphere **Cools** as the Surface **Warms** !

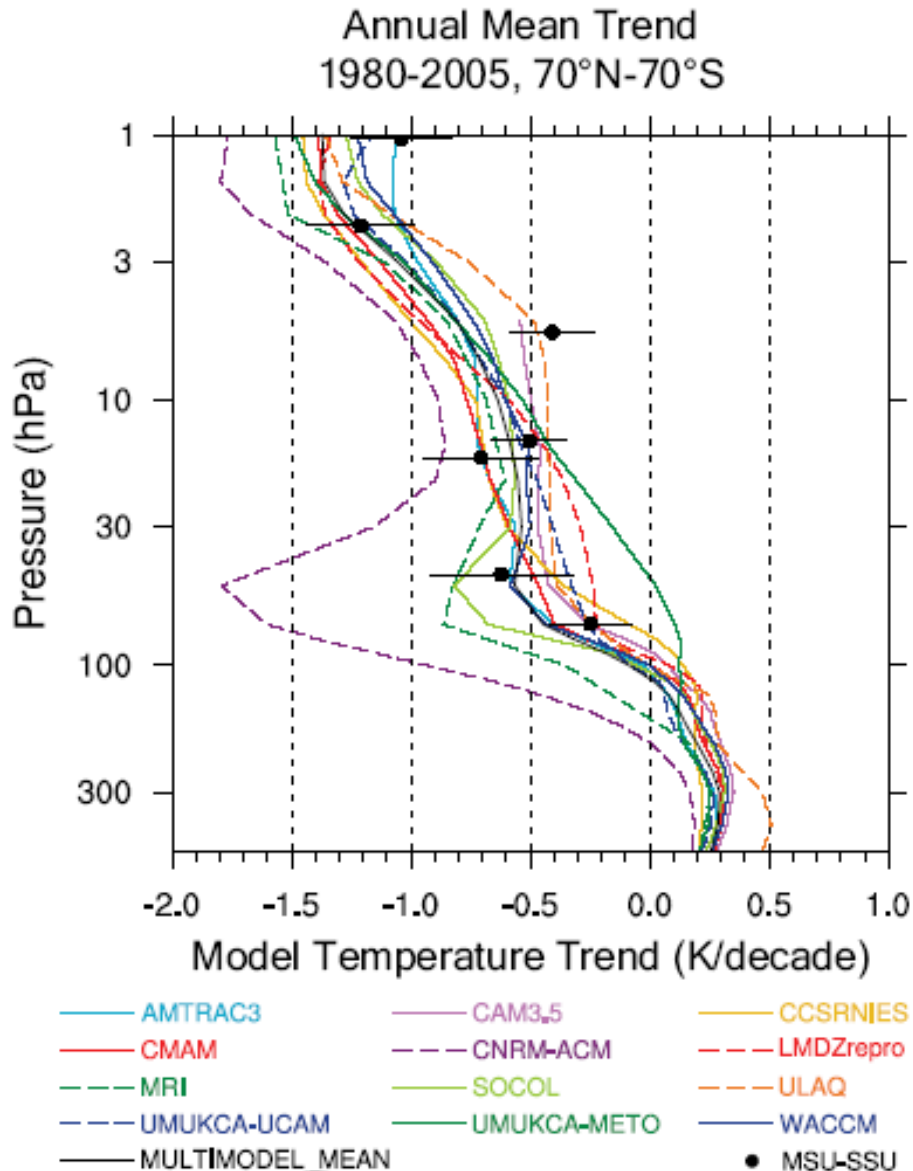


Figure 4-11, WMO/UNEP (2011)

Arctic Ozone Loss and Climate Change

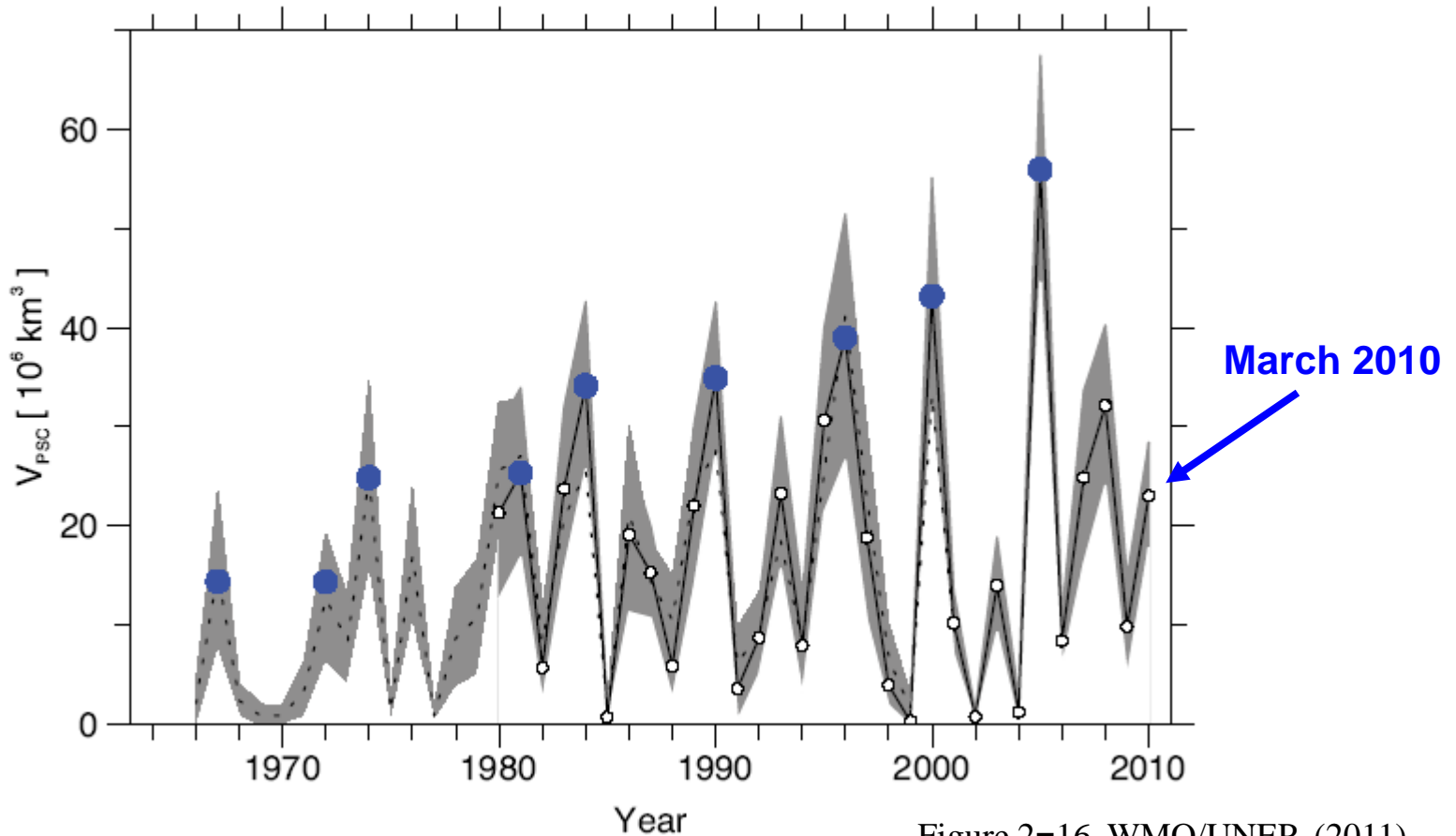
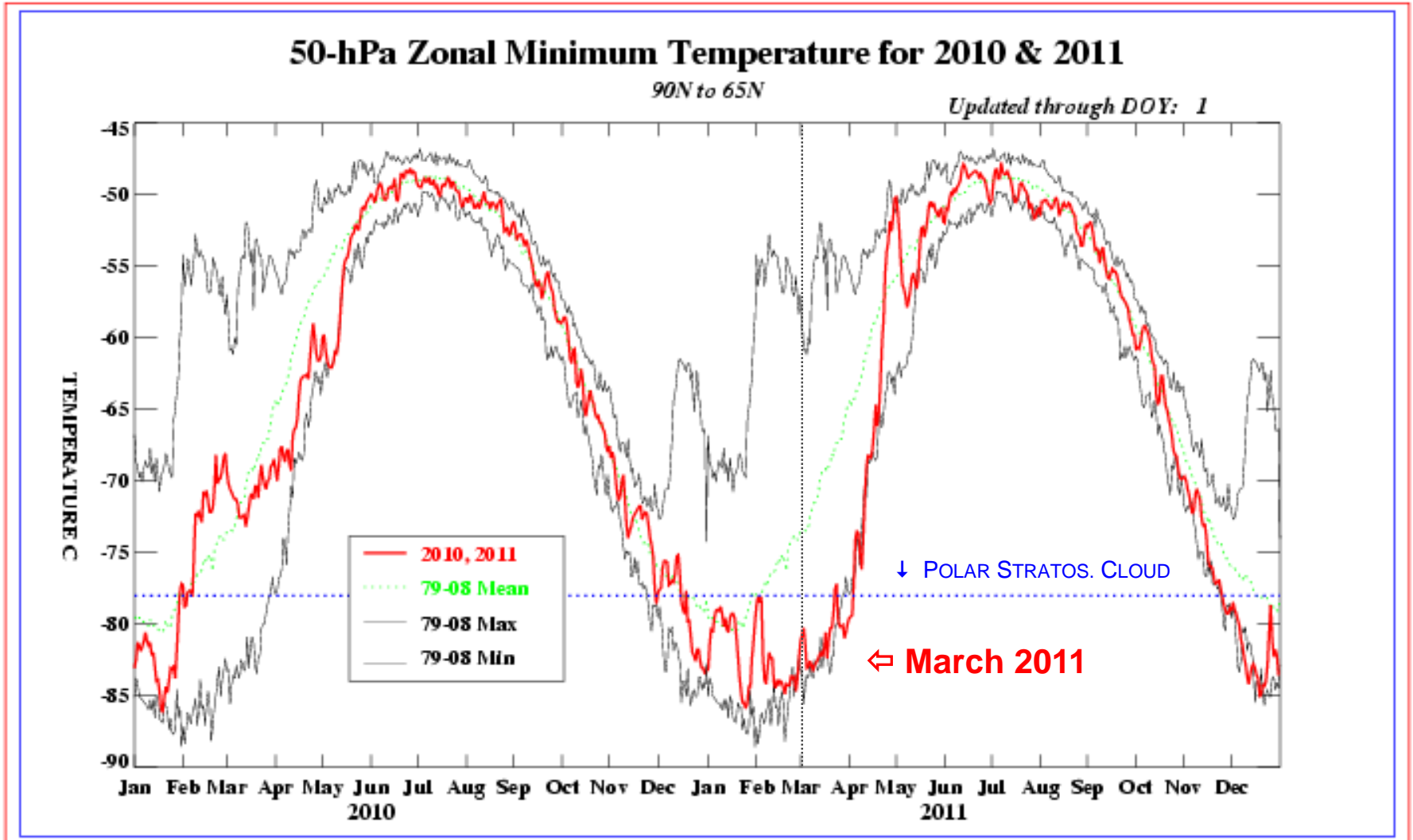


Figure 2-16, WMO/UNEP (2011)
Updated from Rex et al., GRL, 2006
URL in Supplemental Reading

- Lots of year to year variability in V_{PSC}
- Peak levels appear to be rising ... suggesting “coldest winters getting colder“

Arctic Temperature

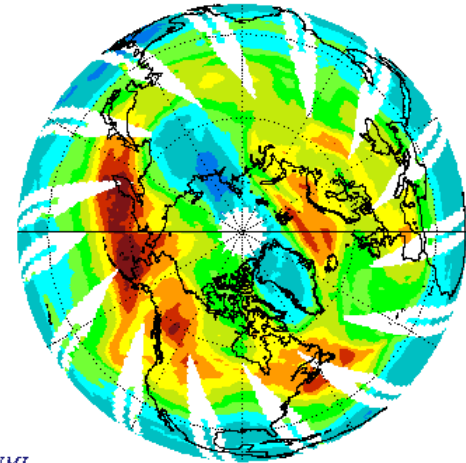
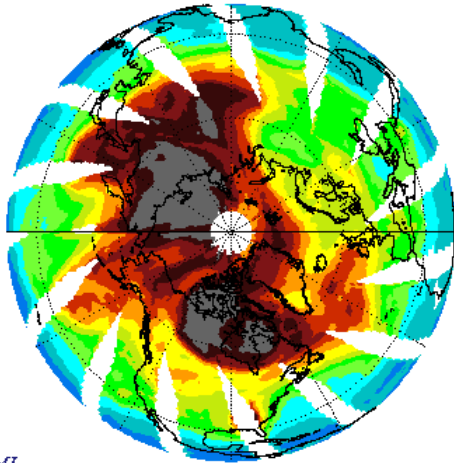


http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2011.gif

OMI Total Ozone for Mar 22, 2010

22 March

OMI Total Ozone for Mar 22, 2011



NIVR-FMI-NASA-KNMI



Dark Gray < 100 and > 500 DU

GSFC



NIVR-FMI-NASA-KNMI



Dark Gray < 100 and > 500 DU

GSFC

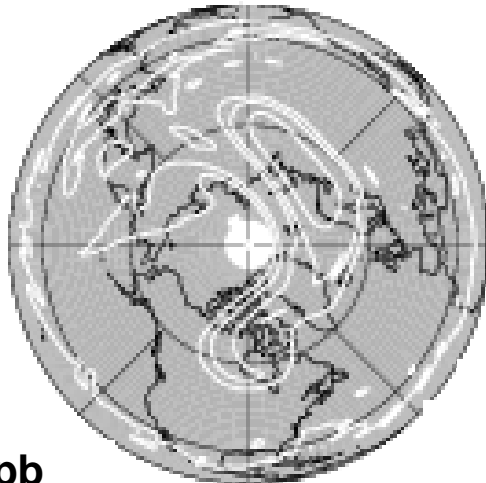


NASA Aura MLS CIO
490 K pot'l temp
~18 km

22 March

← 2010

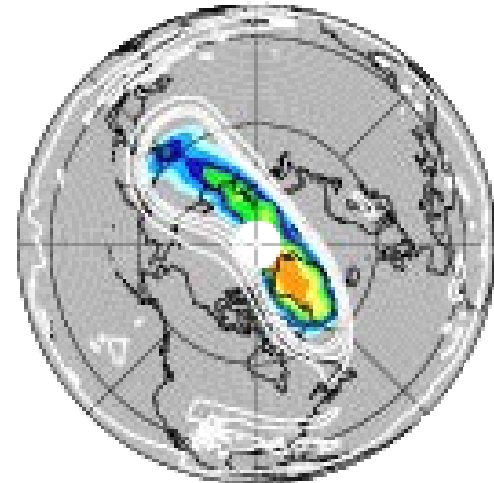
2011 →



ppb



0.30 0.60 0.90 1.20 1.50 1.80

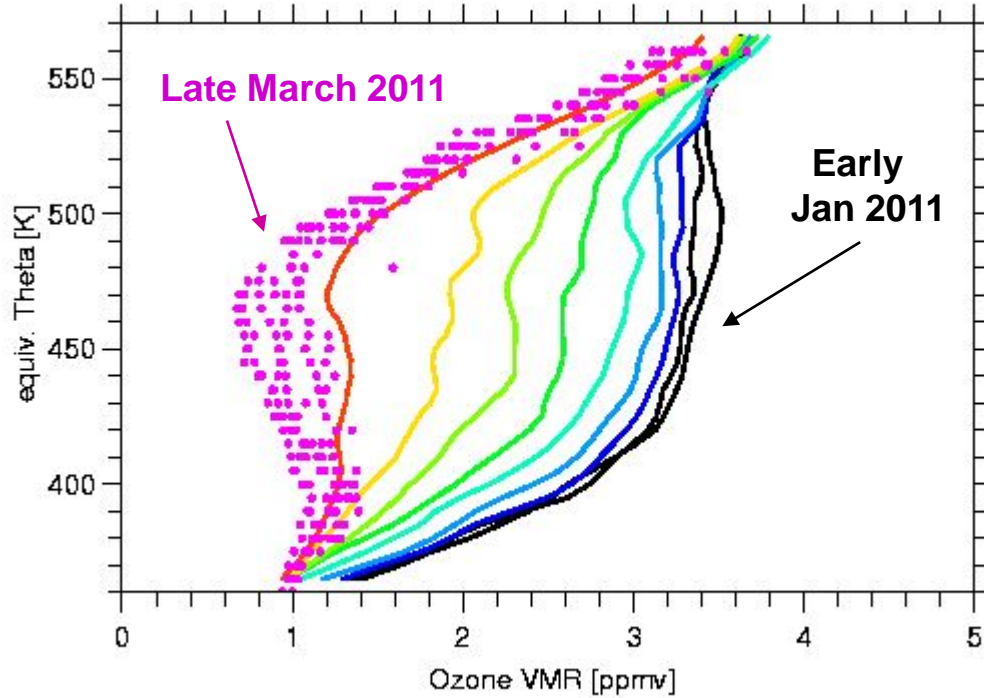


ppb

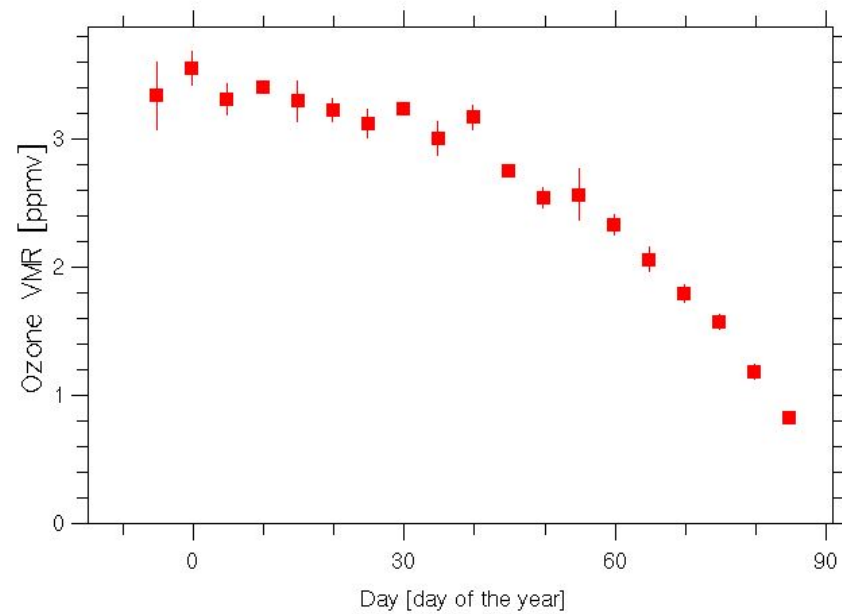


0.30 0.60 0.90 1.20 1.50 1.80

Arctic Ozone 2011



Ozone Mixing Ratio, 2011
475 K Potl Temp Surface



Unprecedented Arctic ozone loss in 2011

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Chemical ozone destruction occurs over both polar regions in local winter–spring. In the Antarctic, essentially complete removal of lower–stratospheric ozone currently results in an ozone hole every year, whereas in the Arctic, ozone loss is highly variable and has until now been much more limited. Here we demonstrate that chemical ozone destruction over the Arctic in early 2011 was—for the first time in the observational record—comparable to that in the Antarctic ozone hole. Unusually long-lasting cold conditions in the Arctic lower stratosphere led to persistent enhancement in ozone–destroying forms of chlorine and to unprecedented ozone loss, which exceeded 80 per cent over 18–20 kilometres altitude. Our results show that Arctic ozone holes are possible even with temperatures much milder than those in the Antarctic. We cannot at present predict when such severe Arctic ozone depletion may be matched or exceeded.

Since the emergence of the Antarctic ‘ozone hole’ in the 1980s¹ and elucidation of the chemical mechanisms^{2–5} and meteorological conditions⁶ involved in its formation, the likelihood of extreme ozone depletion over the Arctic has been debated. Similar processes are at work in the polar lower stratosphere in both hemispheres, but differences in the evolution of the winter polar vortex and associated polar temperatures have in the past led to vastly disparate degrees of spring-time ozone destruction in the Arctic and Antarctic. We show that chemical ozone loss in spring 2011 far exceeded any previously observed over the Arctic. For the first time, sufficient loss occurred to reasonably be described as an Arctic ozone hole.

Arctic Ozone 2011

Alfred Wegner Research Institute, 14 March 2011 press release:

http://www.awi.de/en/news/press_releases/detail/item/arctic_on_the_verge_of_record_ozone_loss

NASA 30 March 2011 release:

<http://earthobservatory.nasa.gov/IOTD/view.php?id=49874>

Early press coverage:

<http://www.livescience.com/13238-arctic-ozone-loss-cfcs-global-warming.html>

http://blogs.nature.com/news/thegreatbeyond/2011/03/spectre_of_an_arctic_ozone_hole.html

http://www.science20.com/news_articles/ozone_layer_loss_arctic_may_be_record_dont_panic-77157

<http://news.nationalgeographic.com/news/2011/03/110321-ozone-layer-hole-arctic-north-pole-science-environment-uv-sunscreen/>

Later press coverage following publication of Manney et al.:

http://www.antarctica.ac.uk/about_bas/news/news_story.php?id=1484

<http://www.livescience.com/14073-arctic-ozone-hole-uk.html>

Points of contention:

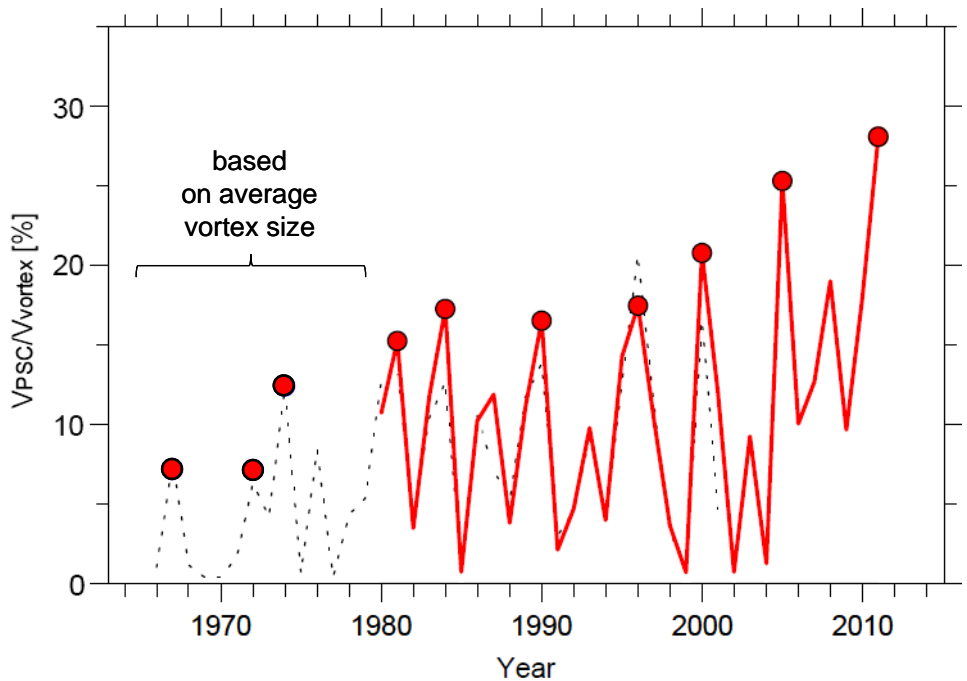
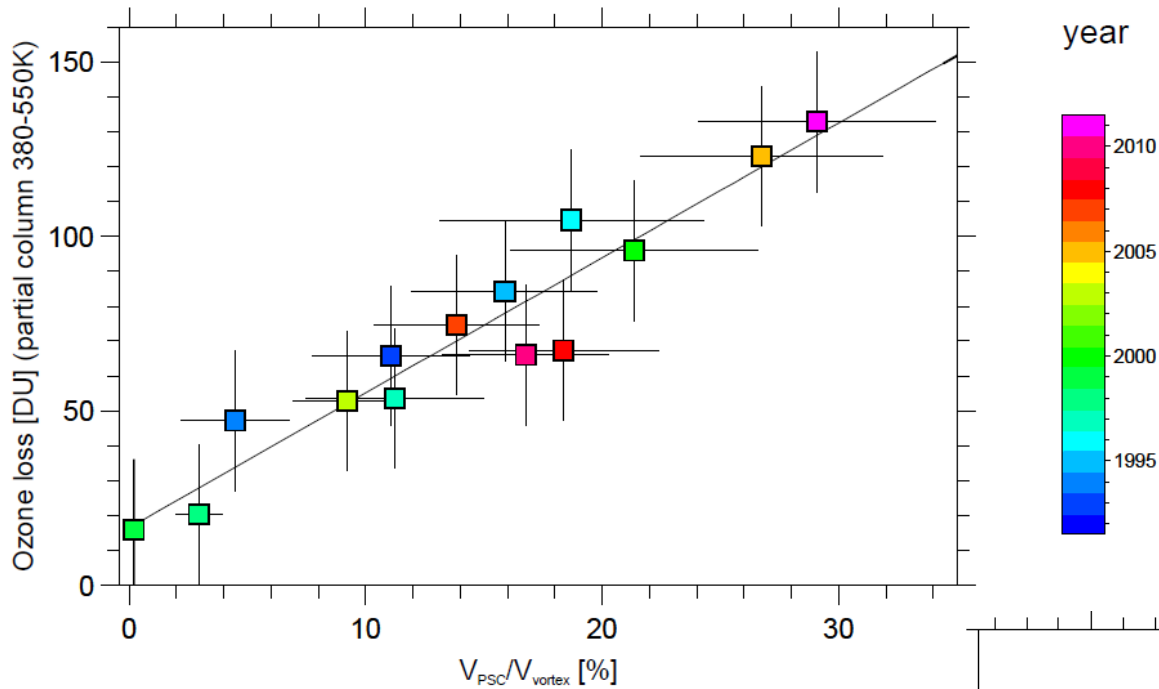
a) Was 2011 really an “Arctic Ozone hole”?

⇒ many in the community strongly resist use of these words to describe Arctic Ozone 2011, despite what is written in Manney et al.

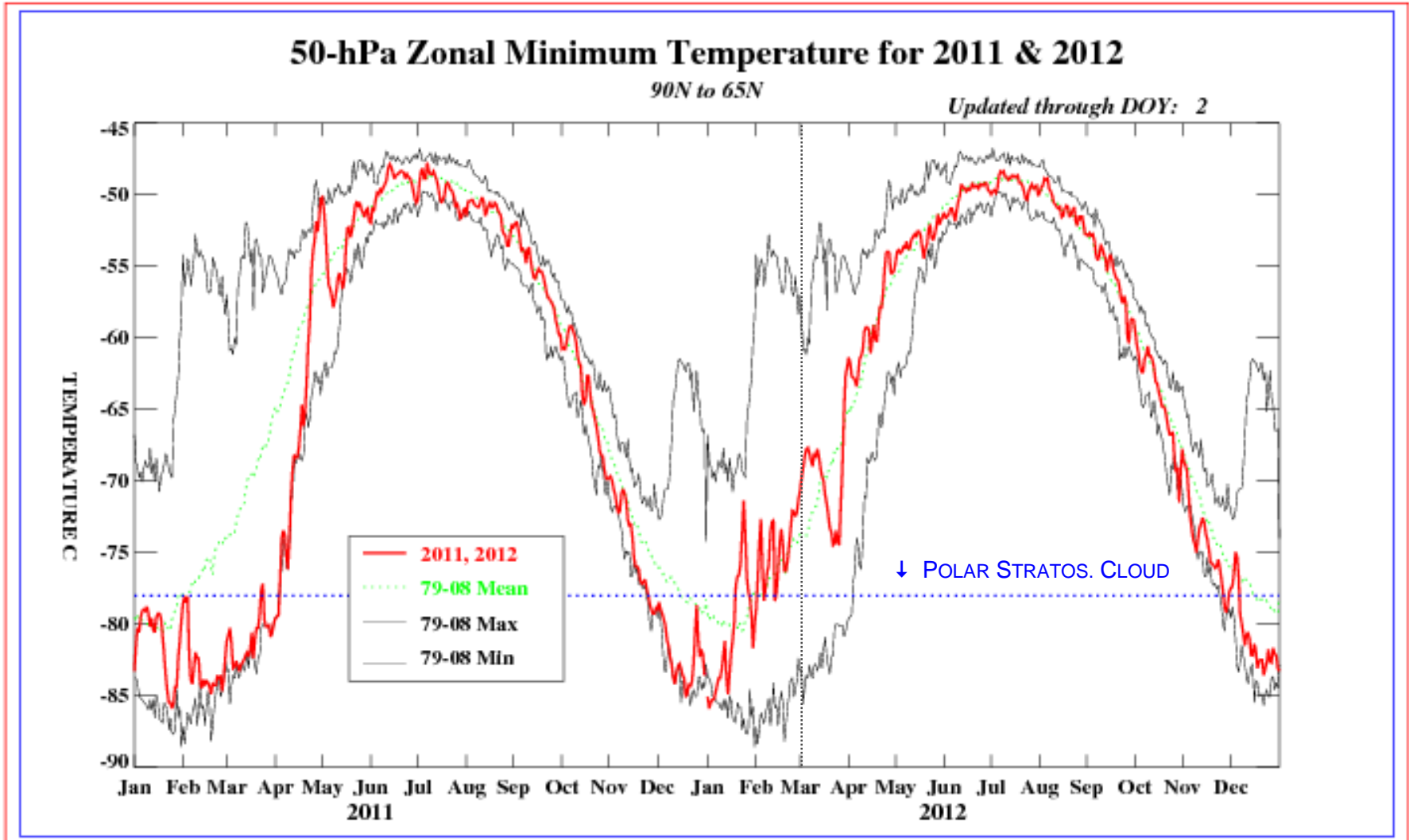
b) are GHGs responsible for the “coldest winters getting colder”?

⇒ vitally important active research

Arctic Ozone 2011 in Context of Prior Years

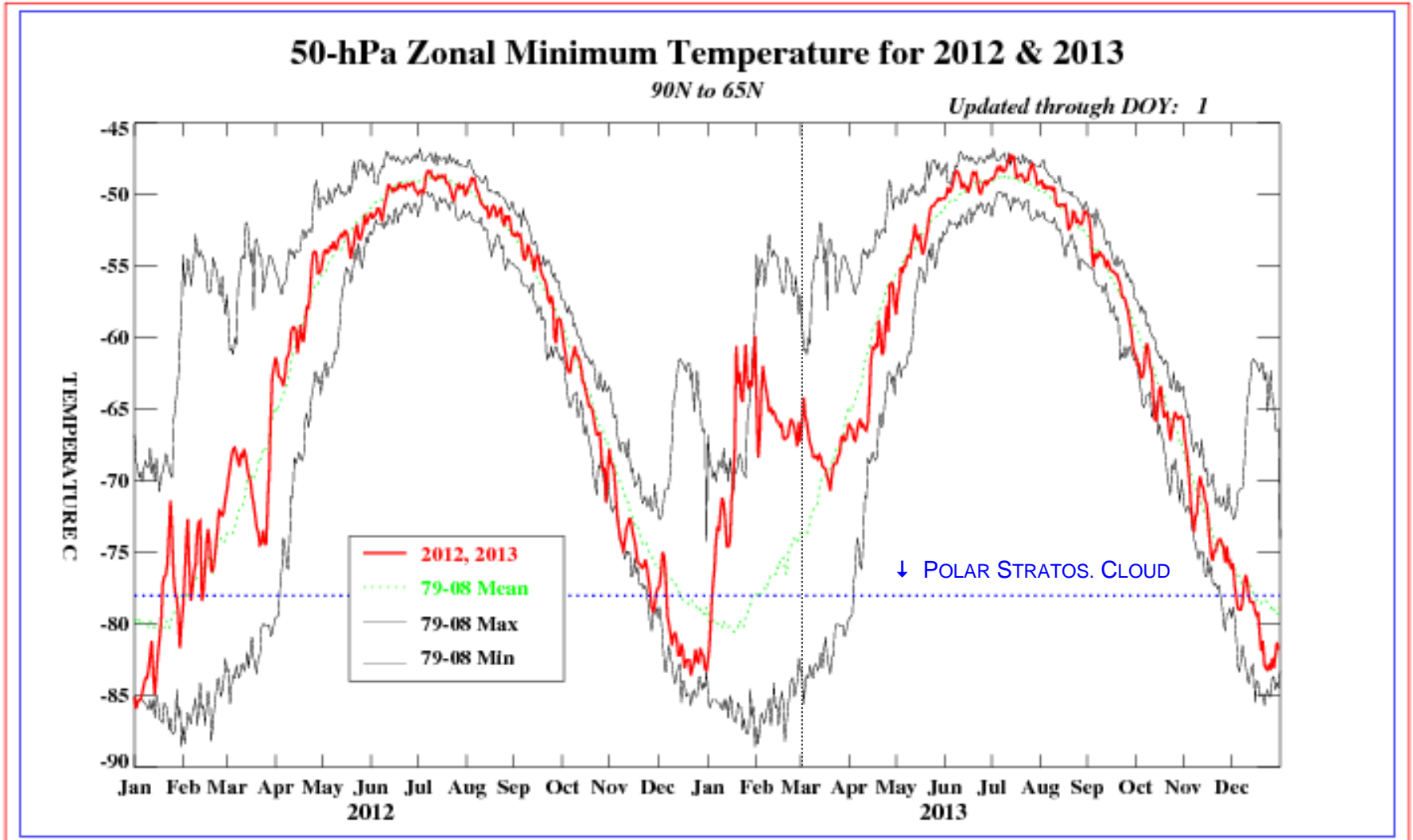


Arctic Temperature: Mar 2012



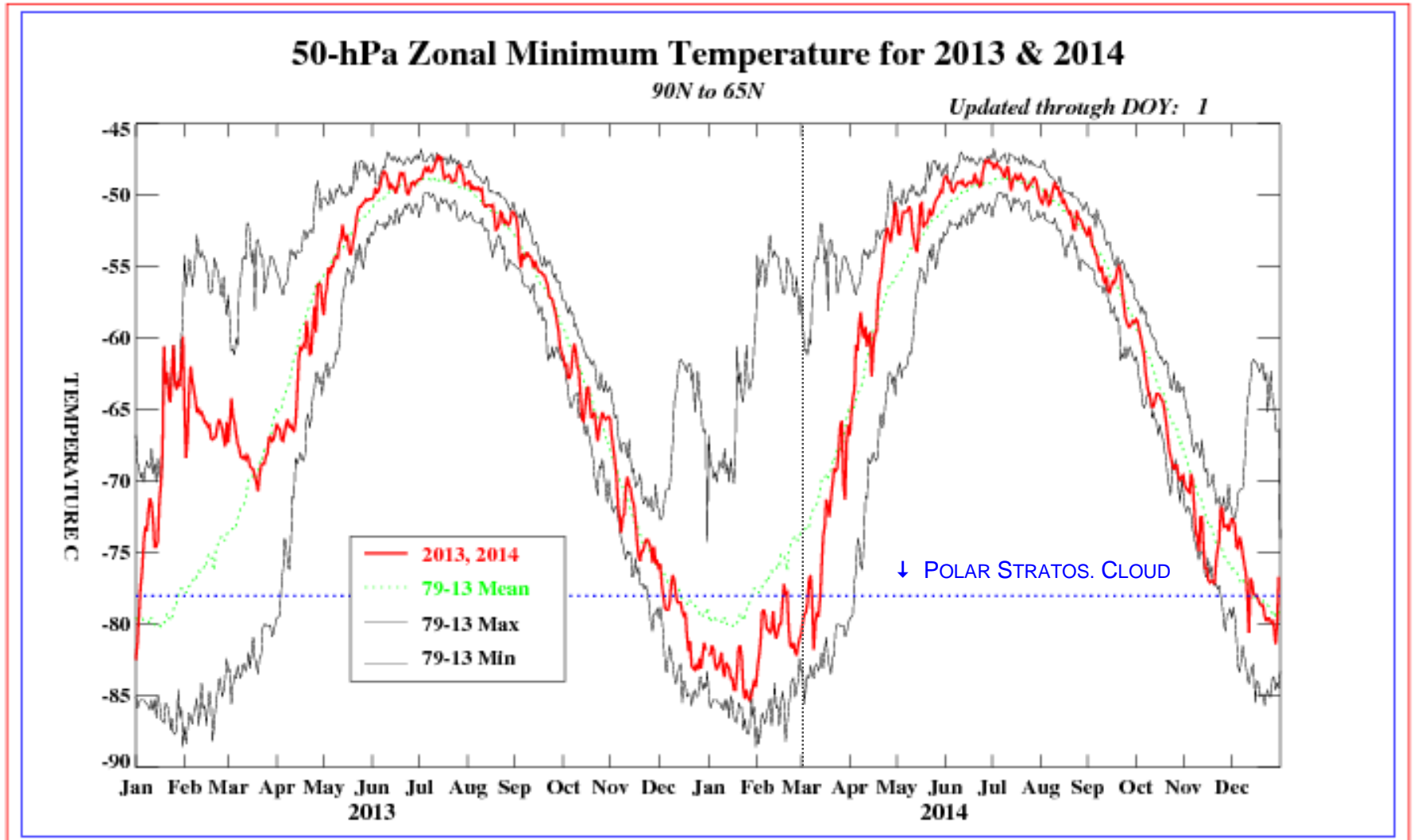
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Arctic Temperature: Mar 2013



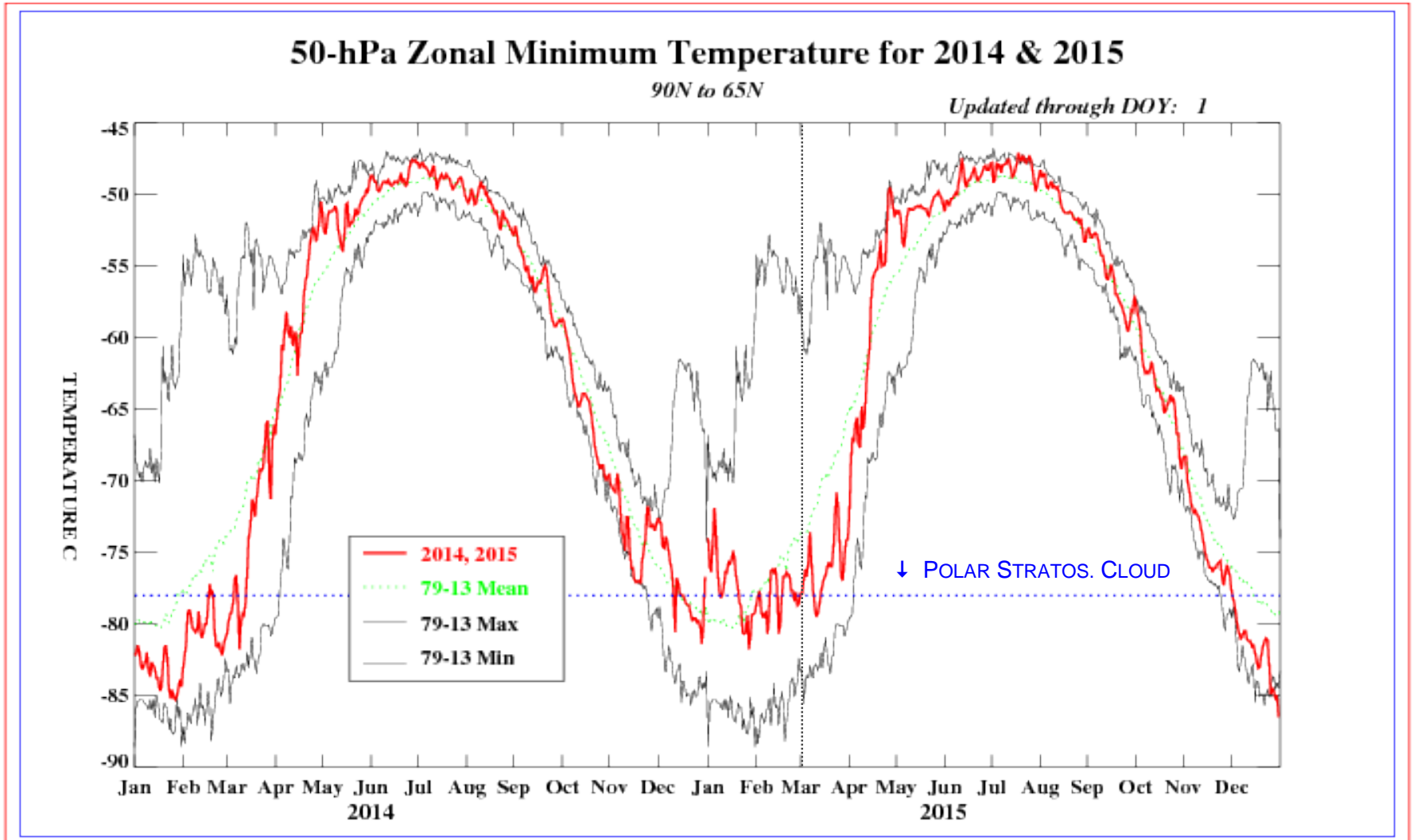
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2013.gif

Arctic Temperature: Mar 2014



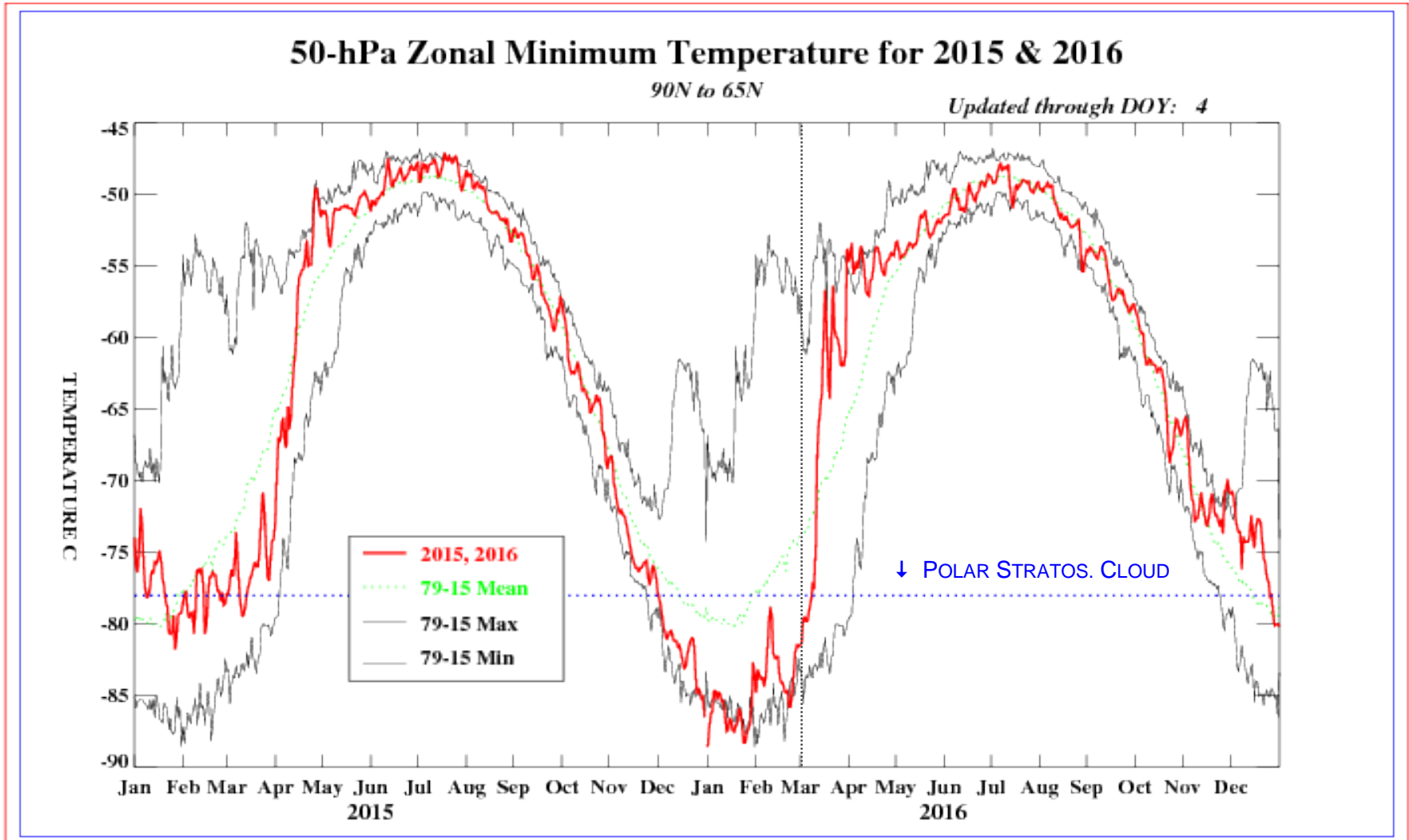
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Arctic Temperature: Mar 2015



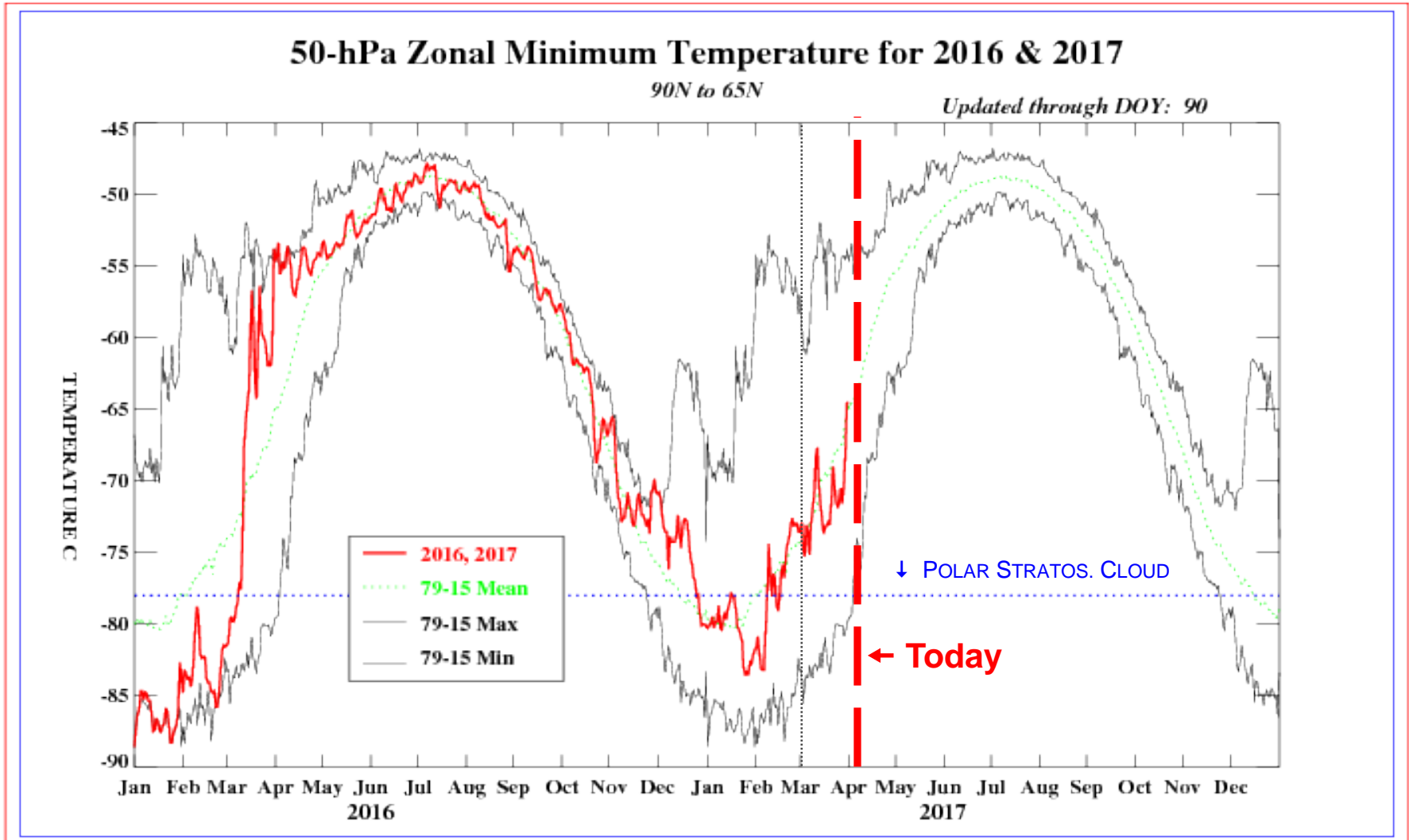
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Arctic Temperature: Mar 2016



http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2016.gif

Arctic Temperature: Mar 2017

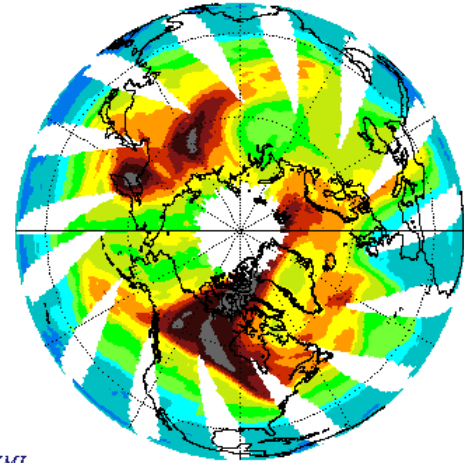
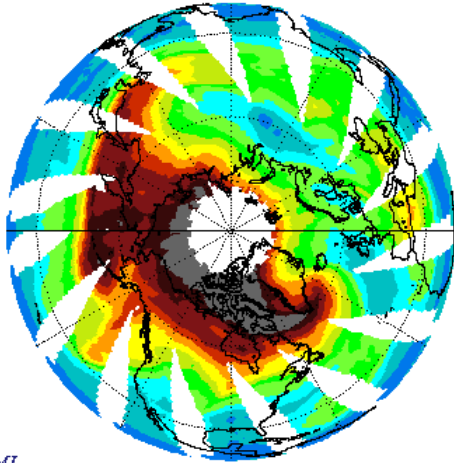


<http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbnhlo.png>

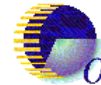
OMI Total Ozone for **Mar 10, 2016**

10 March

OMI Total Ozone for **Mar 10, 2017**



NIVR-FMI-NASA-KNMI

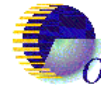


Dobson Units
Dark Gray < 100 and > 500 DU

GSFC



NIVR-FMI-NASA-KNMI



Dobson Units
Dark Gray < 100 and > 500 DU

GSFC



Images from <ftp://toms.gsfc.nasa.gov/pub/omi/images/npole>