Stratospheric Chemistry: Polar Ozone Depletion

AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2015

Today:

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

Problem Set #4 has been posted: builds on J value calculation from P Set #3 and lecture material presented today

Lecture 15

2 April 2015

Polar Ozone Depletion

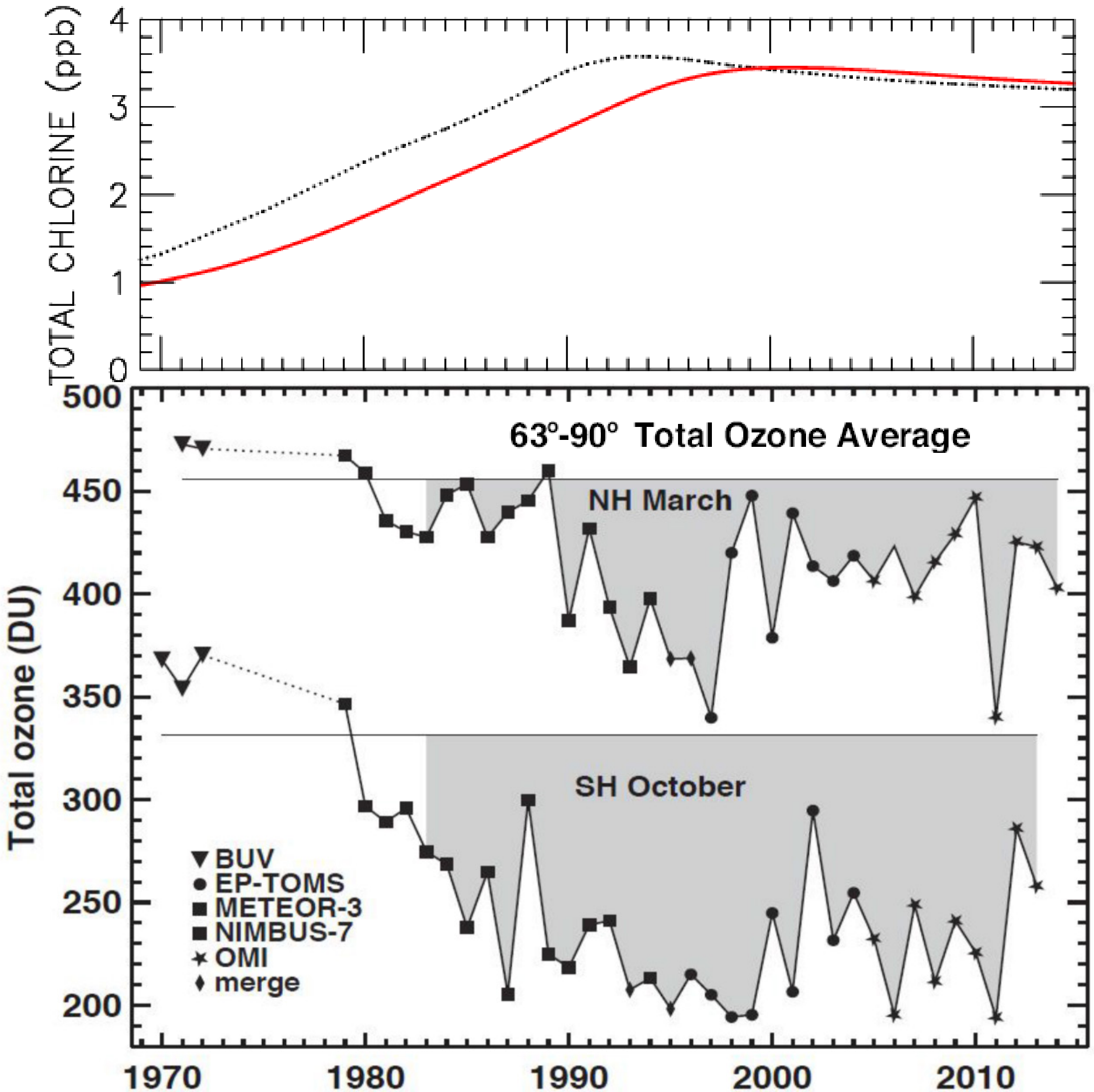
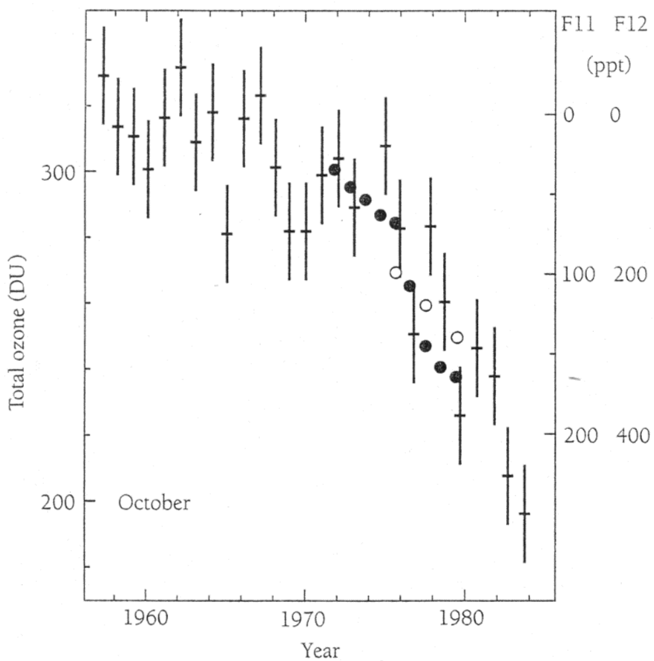


Figure 3-4, WMO/UNEP (2014)

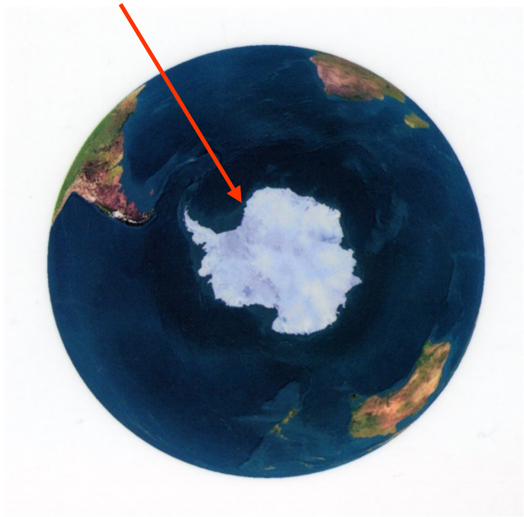
Polar Ozone Depletion

Discovery of the ozone hole:

Halley Bay (76°S)
October Mean



HALLEY BAY

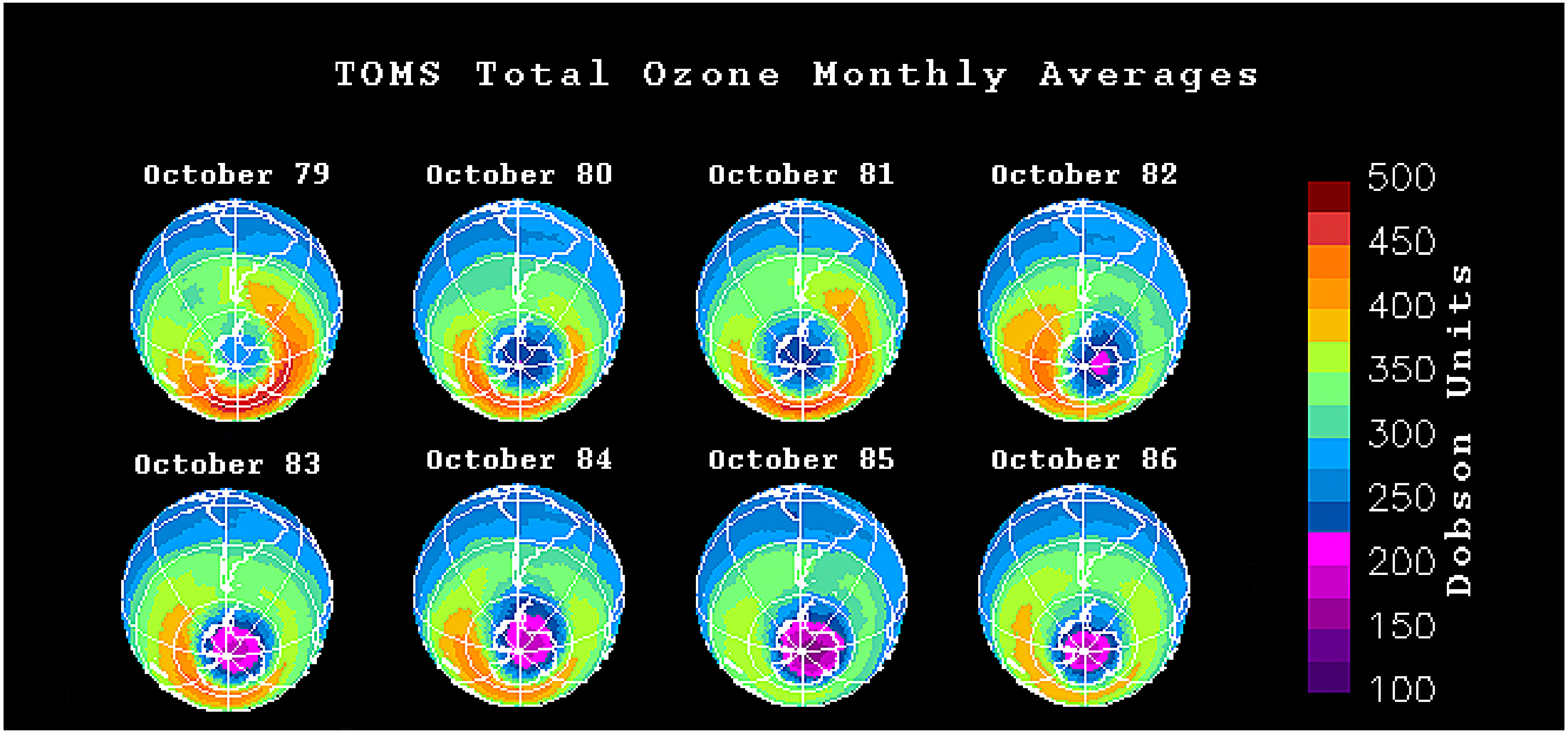


Southern Hemisphere

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:



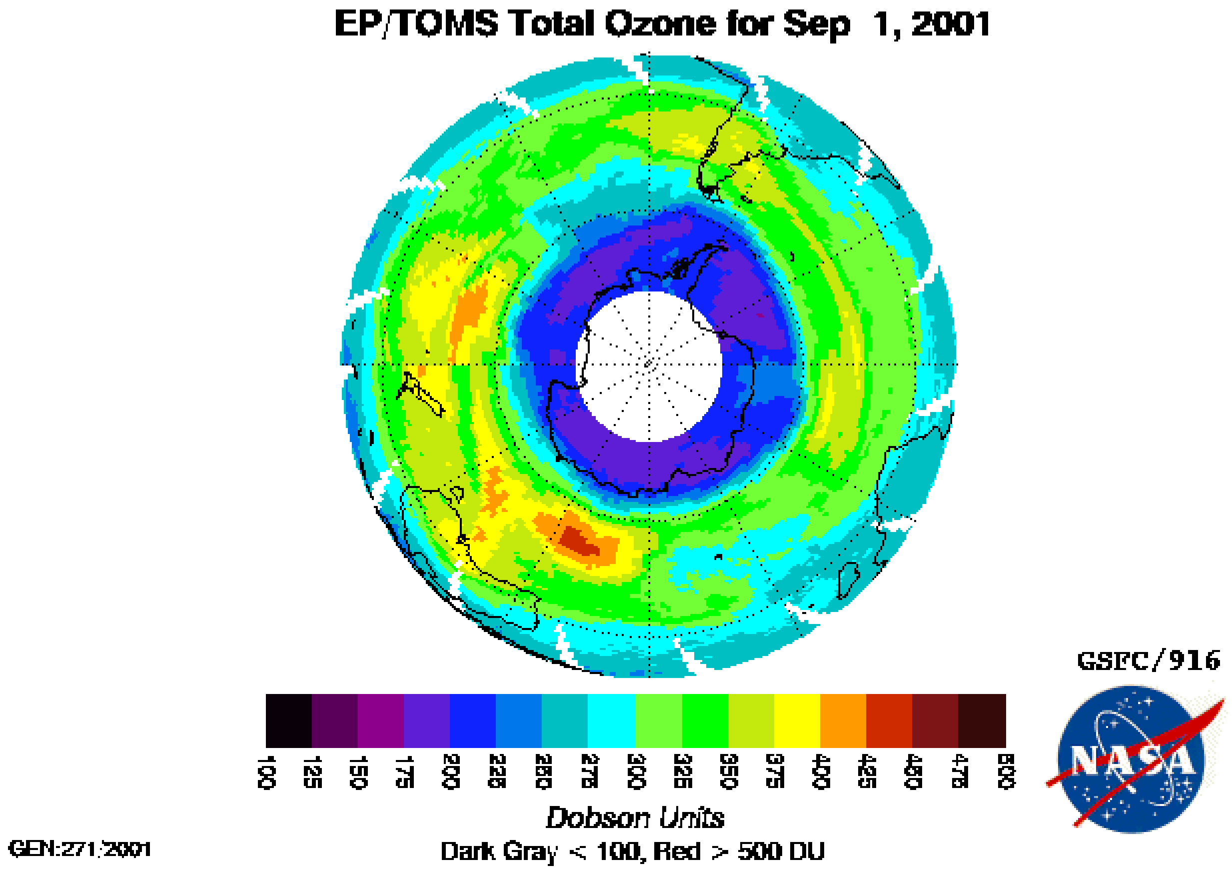
Stolarski *et al.*, *Nature*, 322, 808, 1986.

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



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 ($ClO + ClO + M \rightarrow ClOOCl + M$; $BrO + ClO \rightarrow Br + Cl + O_2$)
    [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 $ClNO_3$)
    [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].

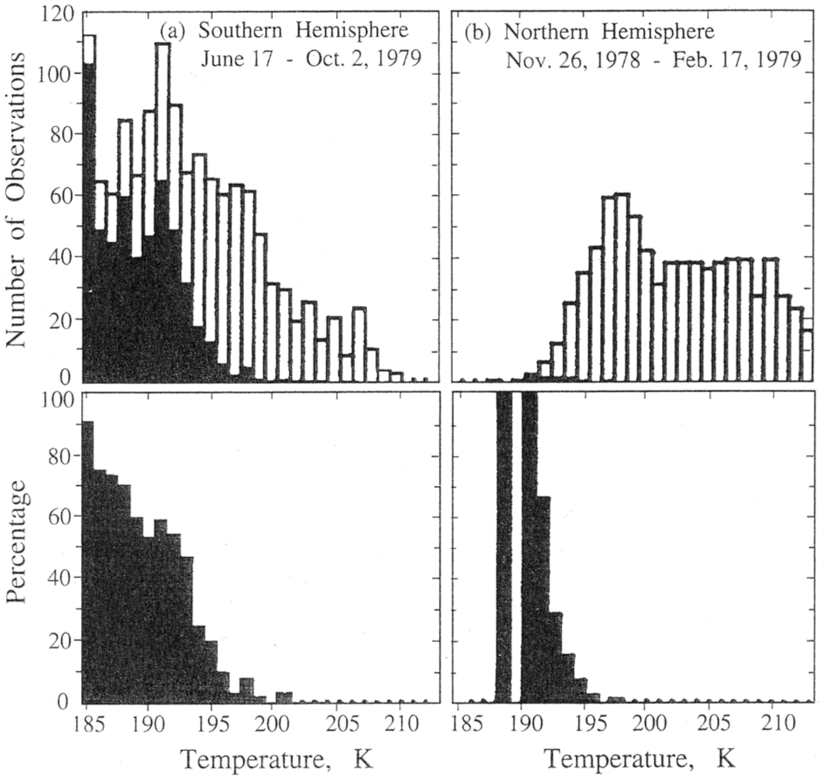


FIGURE 4.20 The top panels show a histogram of the total number of vertical temperature profiles having a given minimum temperature for the Antarctic and Arctic winters. The darkened bars represent observations of PSCs. The lower panel shows the frequency of PSC observations as a percentage of the total 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

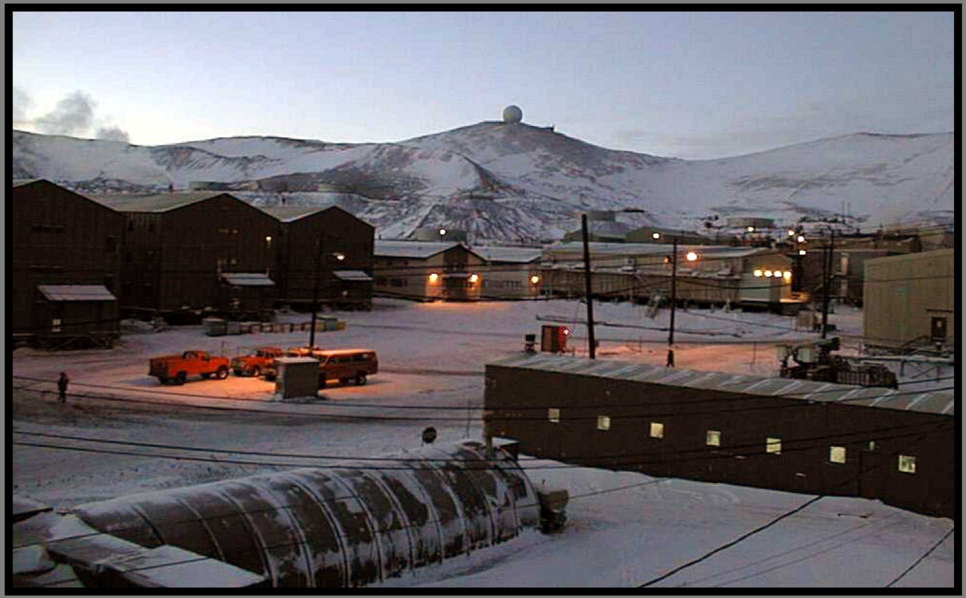
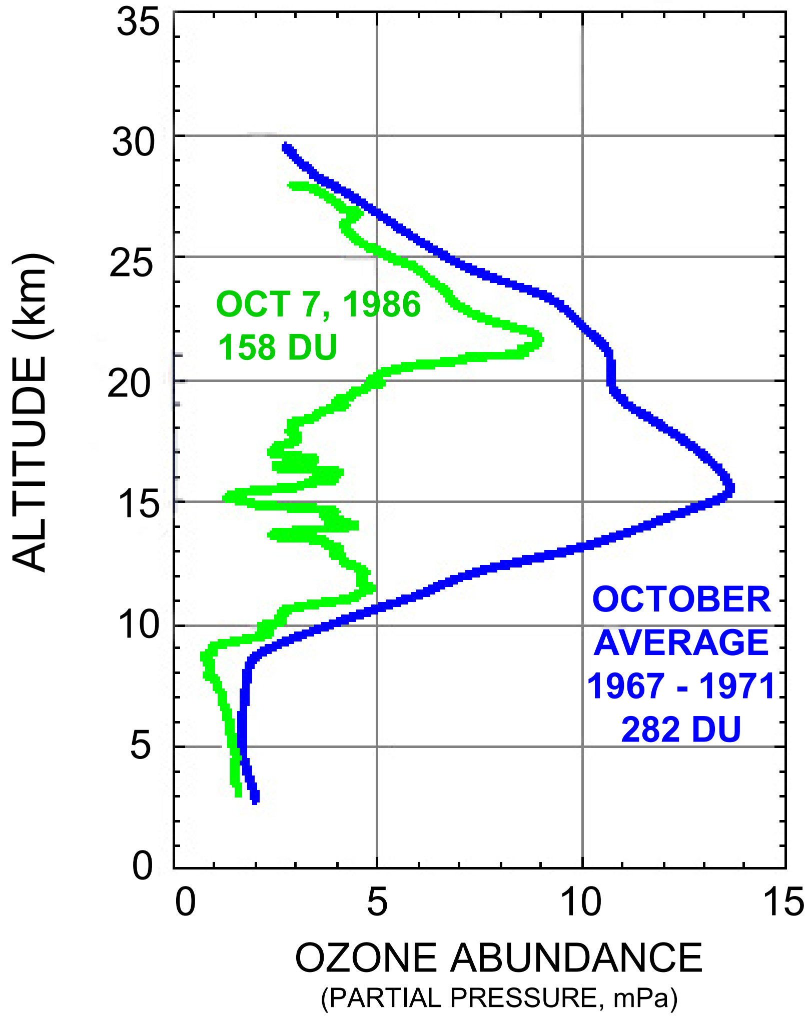


Photo © Geoff Toon

National Ozone Expedition: McMurdo Station, 1986

Balloon-borne ozonesondes showed:

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



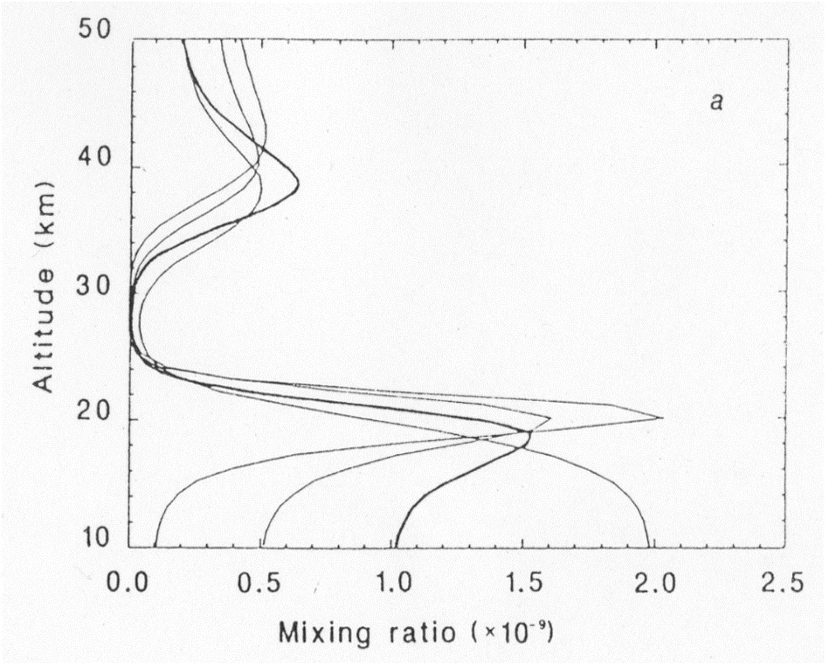
Hofmann et al., *Nature, 326*, 59, 1987.

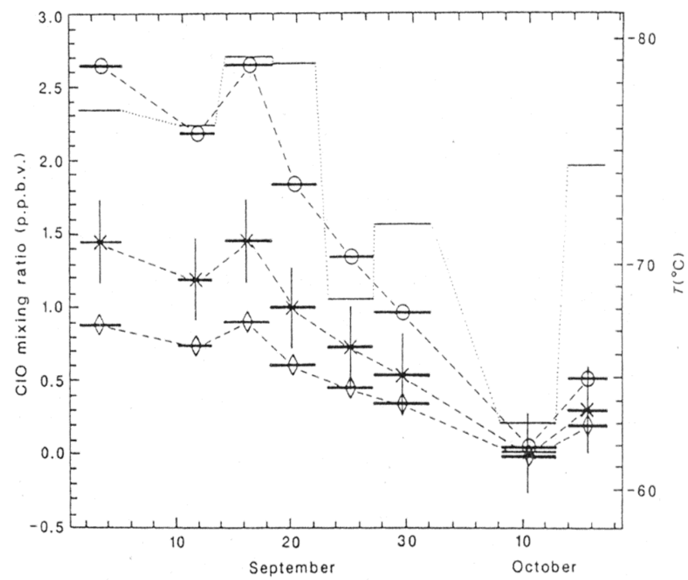
National Ozone Expedition: McMurdo Station, 1986

Ground based measurements revealed:

- Presence of ~1 ppb of ClO over Antarctica
- Decreasing column HNO_3 throughout springtime and suppressed column HCl and $ClNO_3$, consistent with existence of large amounts of ClO

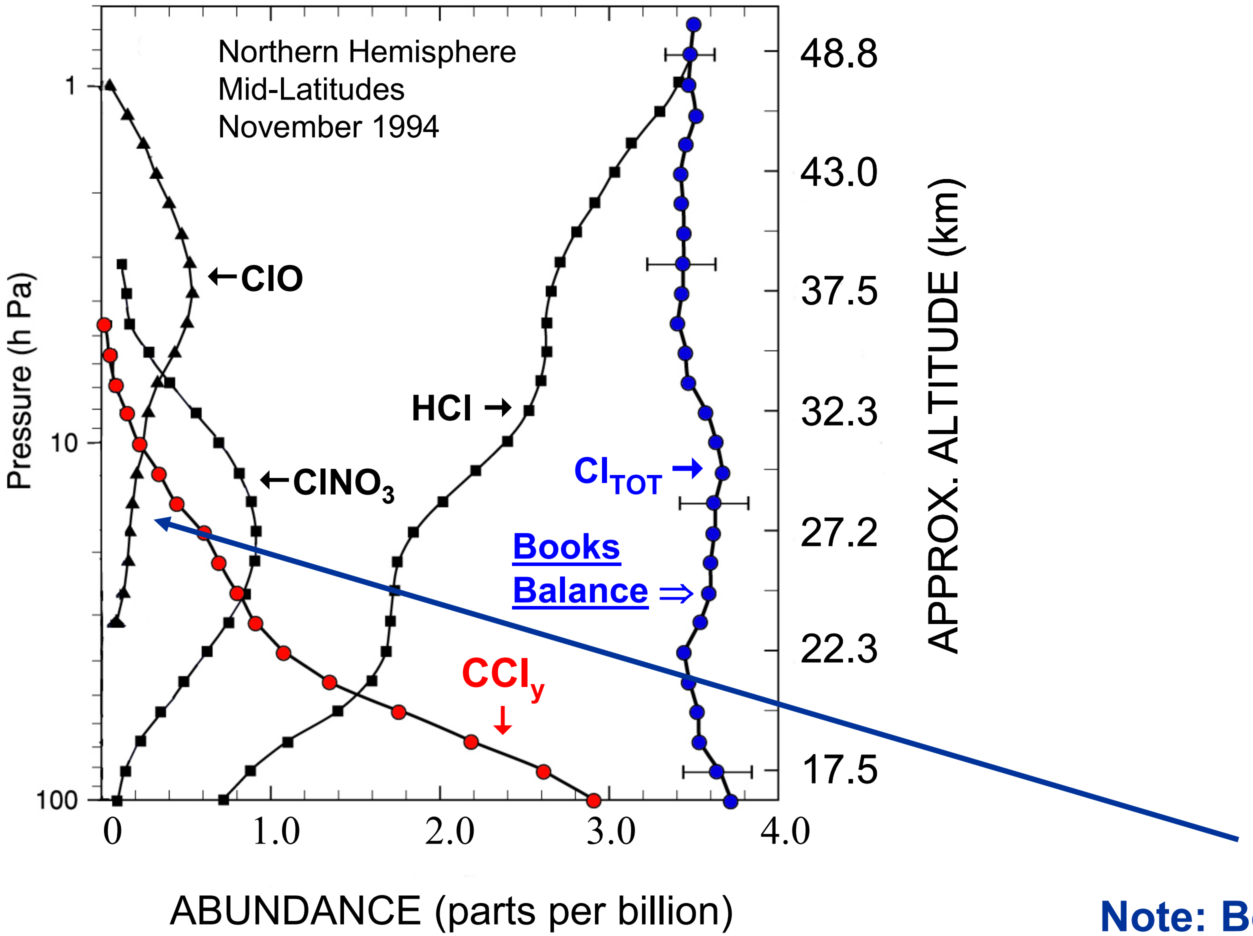
  [Farmer et al., *Nature*, 1987]





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



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

Note: Below ~30 km, $ClO \ll ClNO_3$ and HCl

Lecture 14, Slide 21

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?

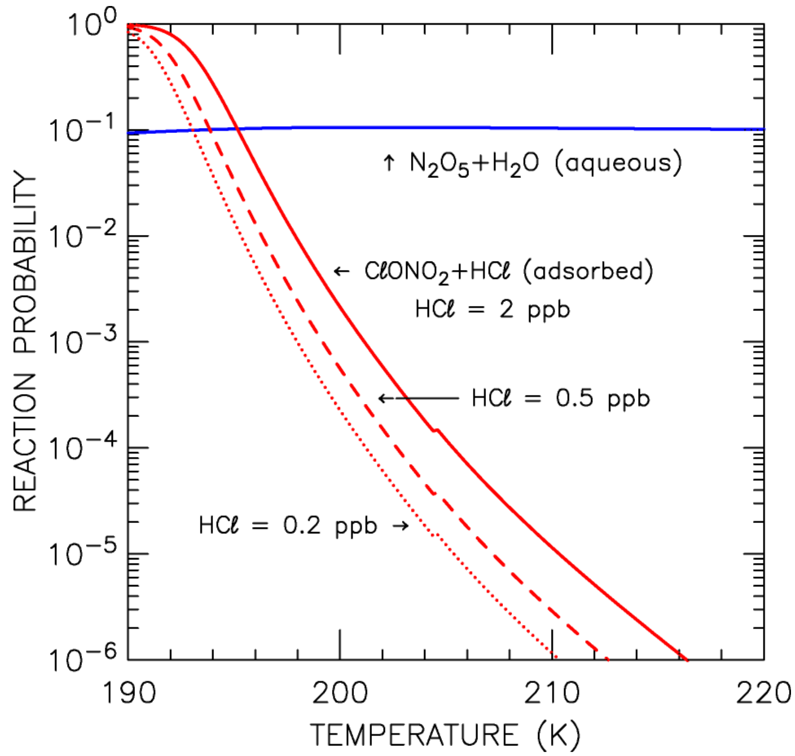
d) What is the effect of these particles on the chemical composition of the polar stratosphere
Scientists have shown that chemical reactions occurring on the surface of these particles convert species such as and (that do not depleted ozone) and that do not cause harm to the ozone layer in the dark of 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.

Lecture 11, Slide 19

Polar Ozone Loss

- Cold Temperatures → Polar Stratospheric Clouds (**PSCs**)
- Reactions on PSC surfaces lead to elevated **ClO**

$HCl + ClNO_3 \rightarrow Cl_2$ (gas) + HNO_3 (solid)

$ClNO_3 + H_2O \rightarrow HOCl + HNO_3$

Cl_2 + SUNLIGHT + $O_3 \rightarrow ClO$

HOCl + SUNLIGHT + $O_3 \rightarrow ClO$

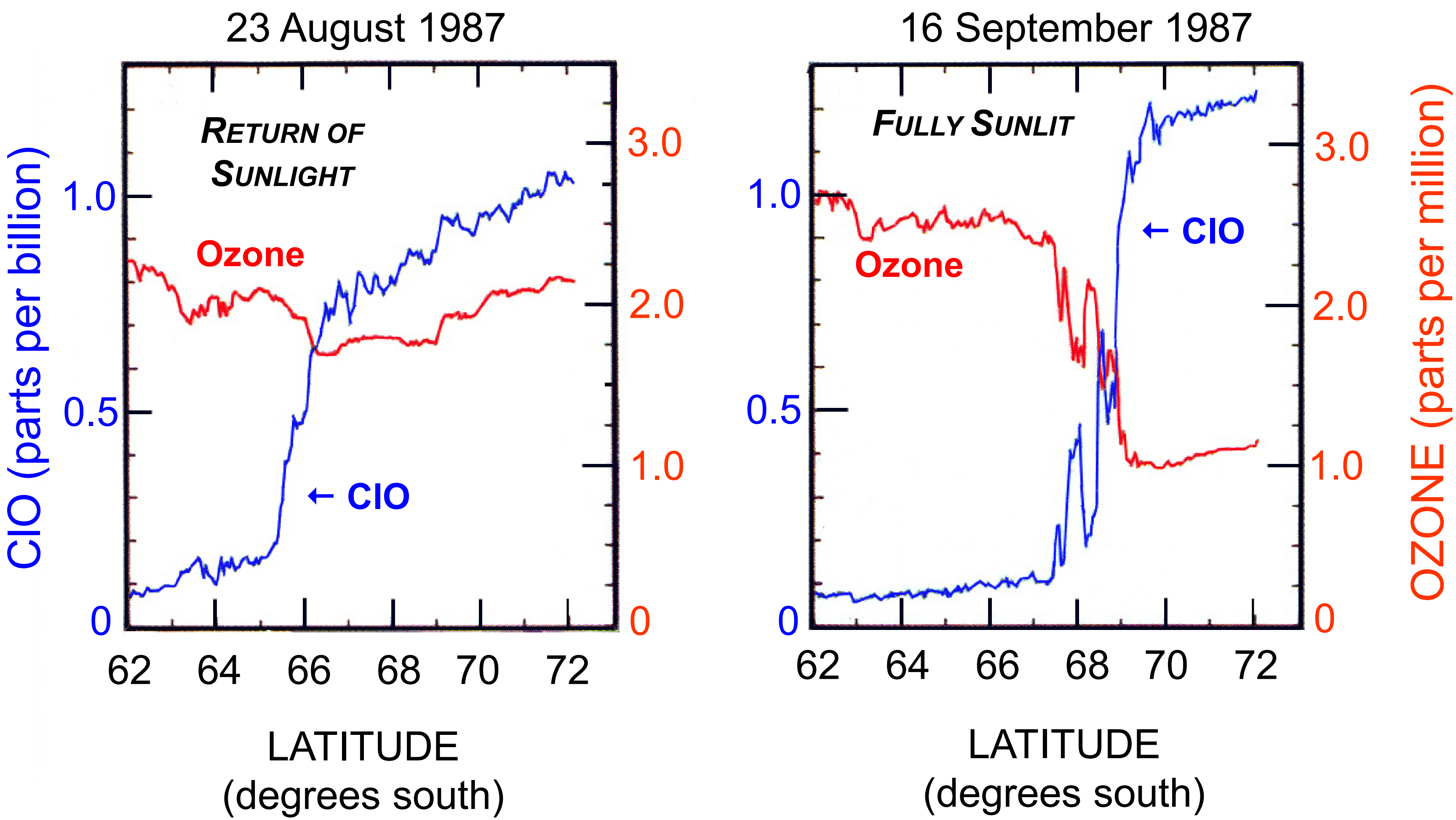
HNO_3 SEDIMENTS (PSCs fall due to gravity)

- Elevated **ClO** + Sunlight destroys O_3
- BrO : Reaction Partner For ClO ⇒ Additional O_3 Loss


N817NA


809
NASA

Airborne Antarctic Ozone Expedition: Punta Arenas, Chile,1987



Anderson et al., *Science*, 1991

Polar Ozone Loss Cycles

Cycle (1a):

$$ClO + ClO + M \rightarrow ClOOCl + M$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClOOCl + h\nu \rightarrow ClOO + Cl$$
$$ClOO + heat \rightarrow Cl + O_2$$
$$\text{Net:} \quad O_3 + O_3 \rightarrow 3\ O_2$$

Cycle (1b):

$$ClO + ClO + M \rightarrow ClOOCl + M$$
$$ClOOCl + heat \rightarrow ClO + ClO$$
$$\text{Net:} \quad M + heat \rightarrow M$$

Cycle (2a):

$$BrO + ClO \rightarrow BrCl + O_2$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$BrCl + h\nu \rightarrow Br + Cl$$
$$\text{Net:} \quad O_3 + O_3 \rightarrow 3\ O_2$$

Cycle (2b):

$$BrO + ClO \rightarrow ClOO + Br$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClOO + heat \rightarrow Cl + O_2$$
$$\text{Net:} \quad O_3 + O_3 \rightarrow 3\ O_2$$

Cycle (2c):

$$BrO + ClO \rightarrow OClO + Br$$
$$OClO + h\nu \rightarrow O + ClO$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$\text{Net:} \quad O_3 \rightarrow O + O_2$$

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

ClOOCl + M → ClO + ClO + M   ΔH = 18.1 kcal/mole

Lecture 11, Slide 21

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

JPL Data Evaluation gives values of $K^{\mathrm{EQUILBRIUM}}$ and $k_{\mathrm{FORMATION}}$

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

In equilibrium:

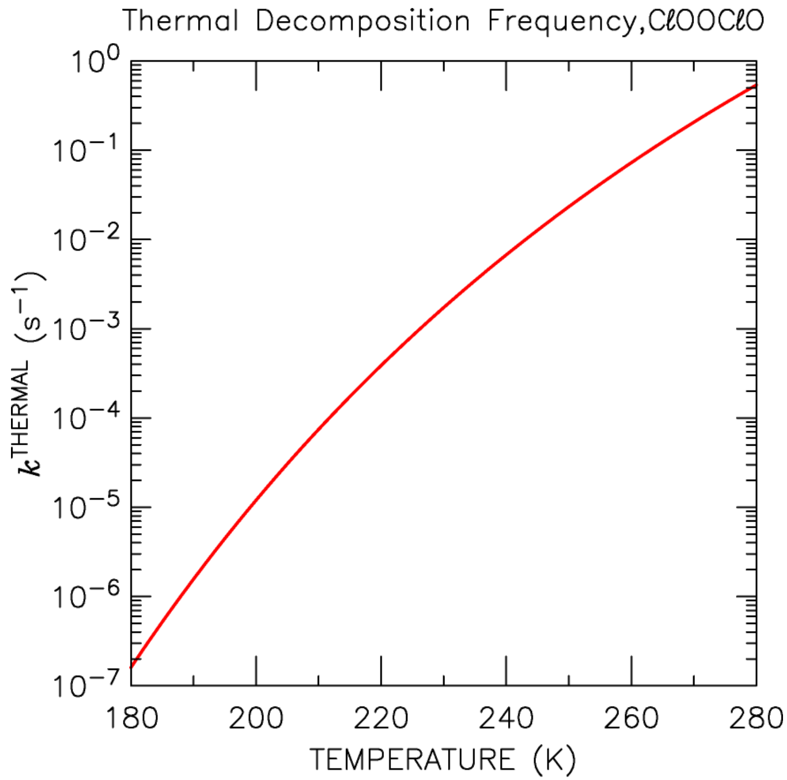
$$k^{\mathrm{THERMAL}}\,[\mathrm{ClOOCl}] = k^{\mathrm{FORMATION}}\,[\mathrm{ClO}]\,[\mathrm{ClO}]$$

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

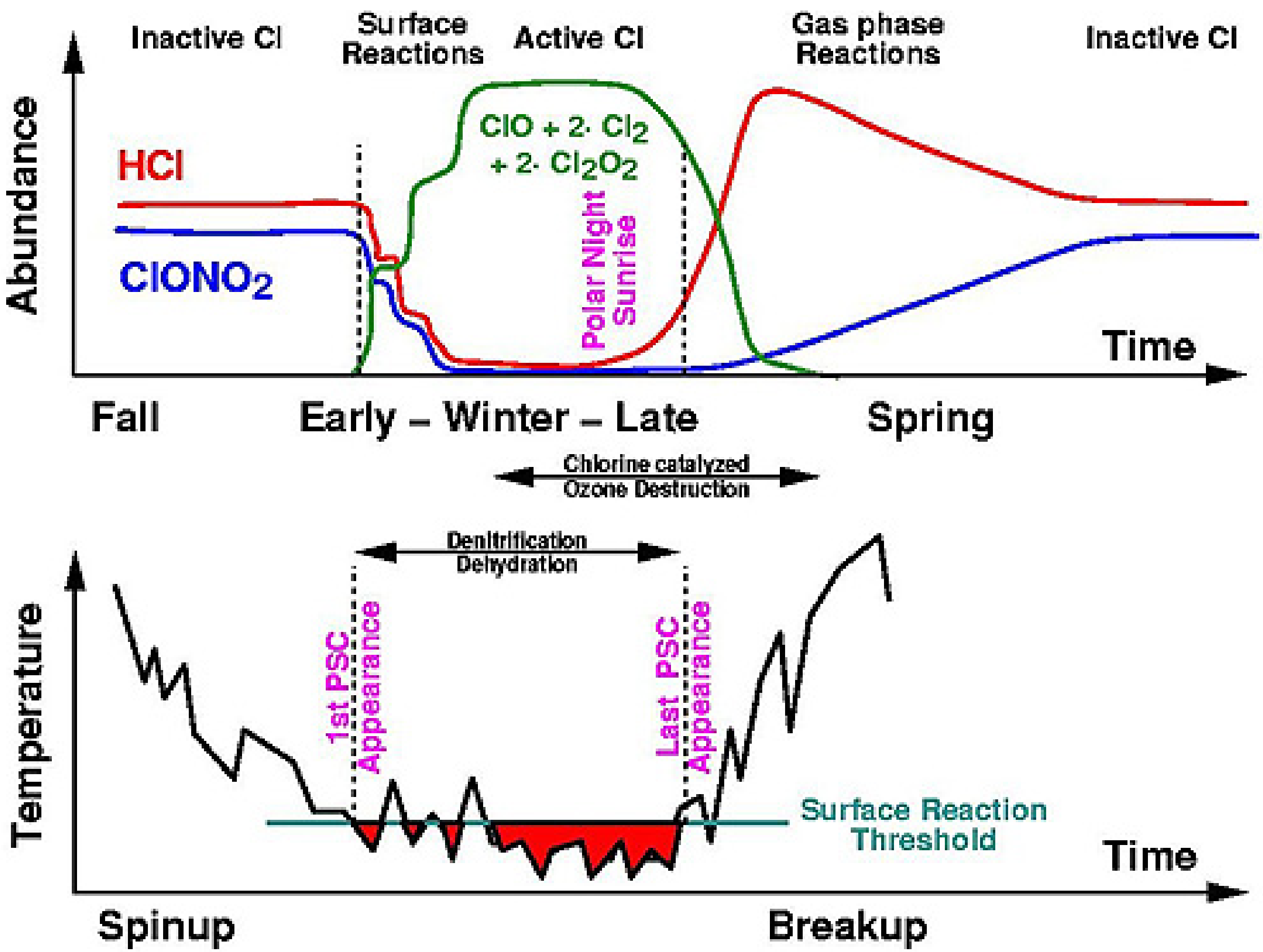
- **Energetically, system favors ClOOCl**
- **Entropically, system favors ClO & ClO**

at low T, ClOOCl stable: energy wins !
at high T, ClOOCl unstable: entropy rules !

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

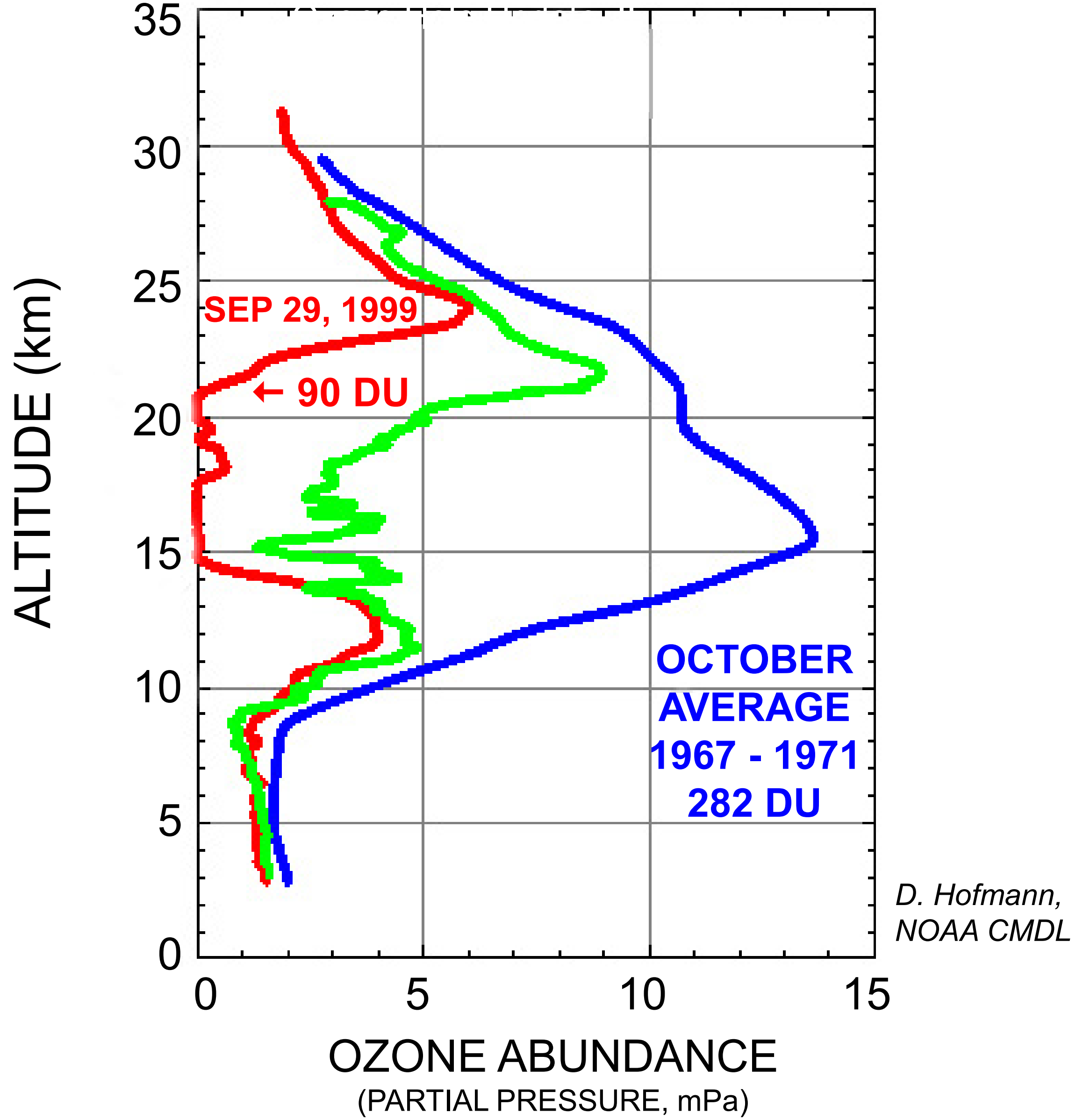


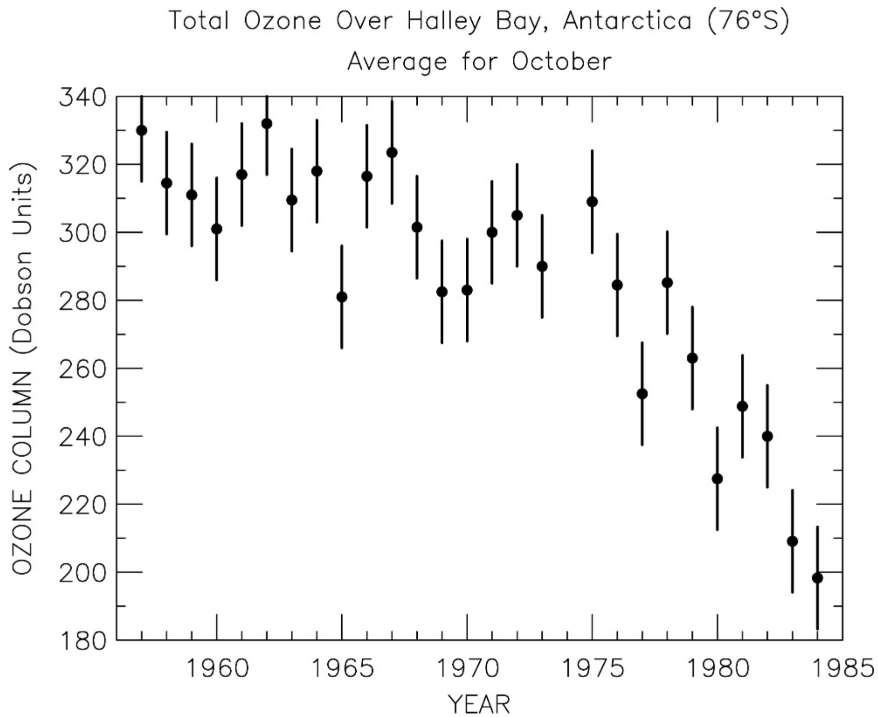
Polar Halogens, Seasonal Evolution



From http://www.ccpo.odu.edu/~lizsmith/SEES/ozone/class/Chap_11

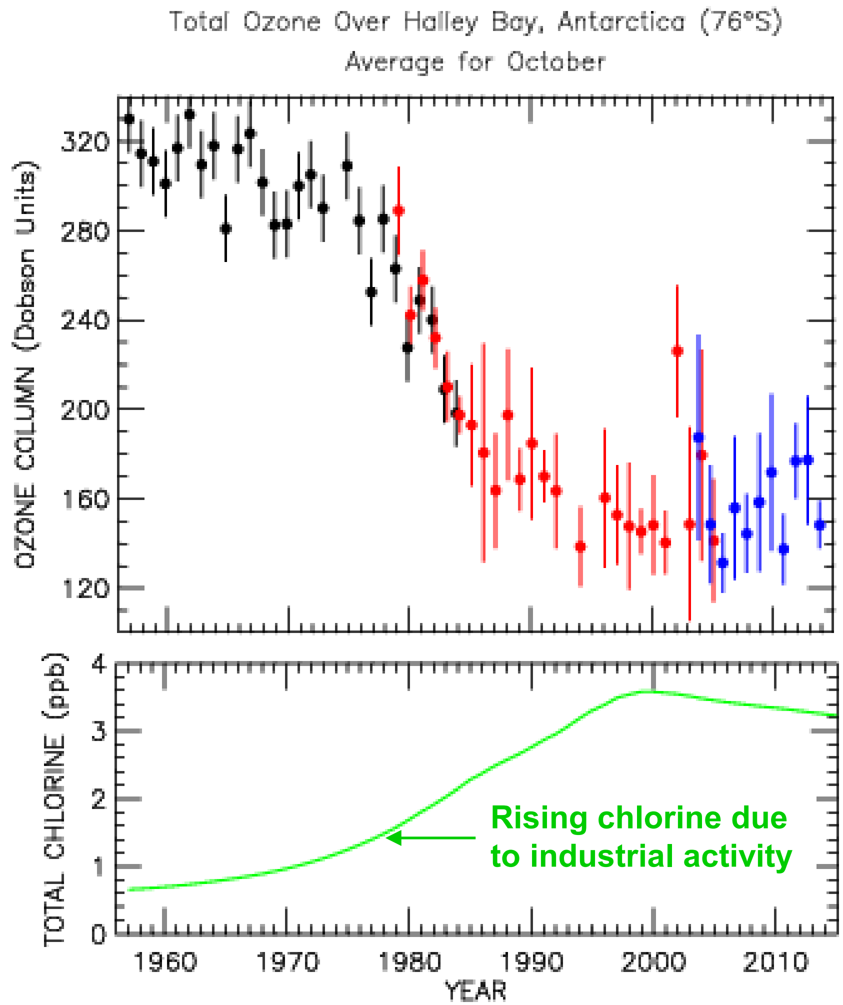
Ozone Profiles, South Pole: Update





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

Update



- **Models provide good overall simulation of Antarctic O_3 loss**
- **Scientific understanding of polar O_3 depletion led to international ban on CFCs**

Lecture 2, Slide 17

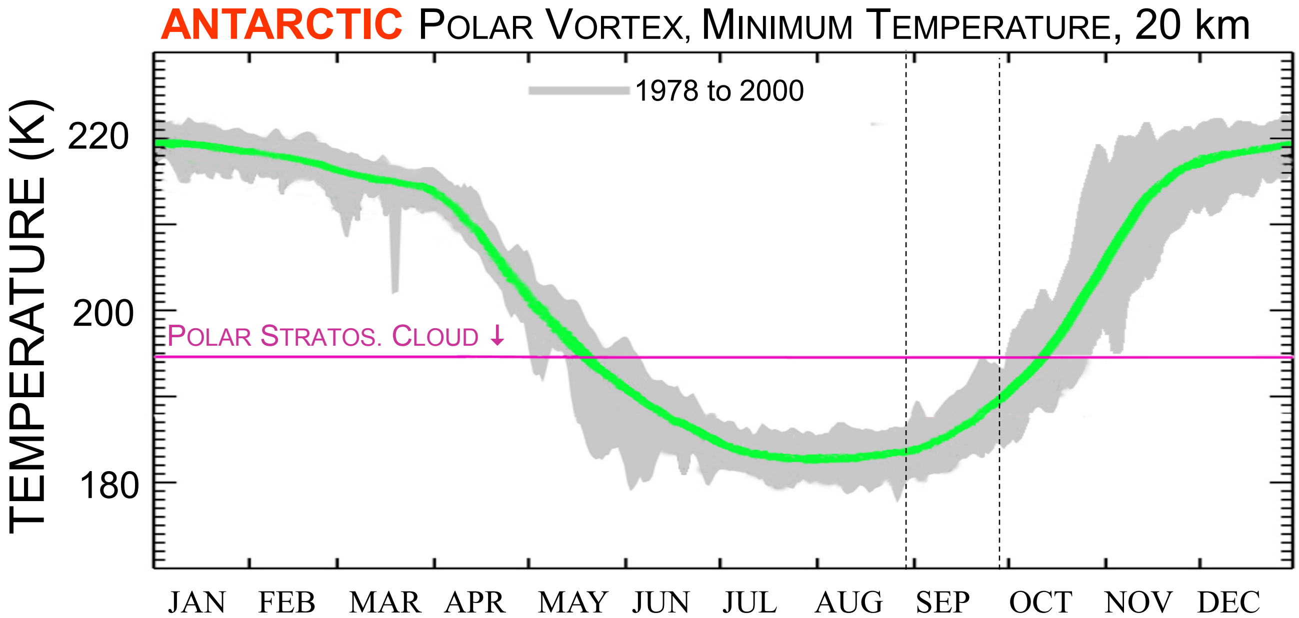
Arctic Overview

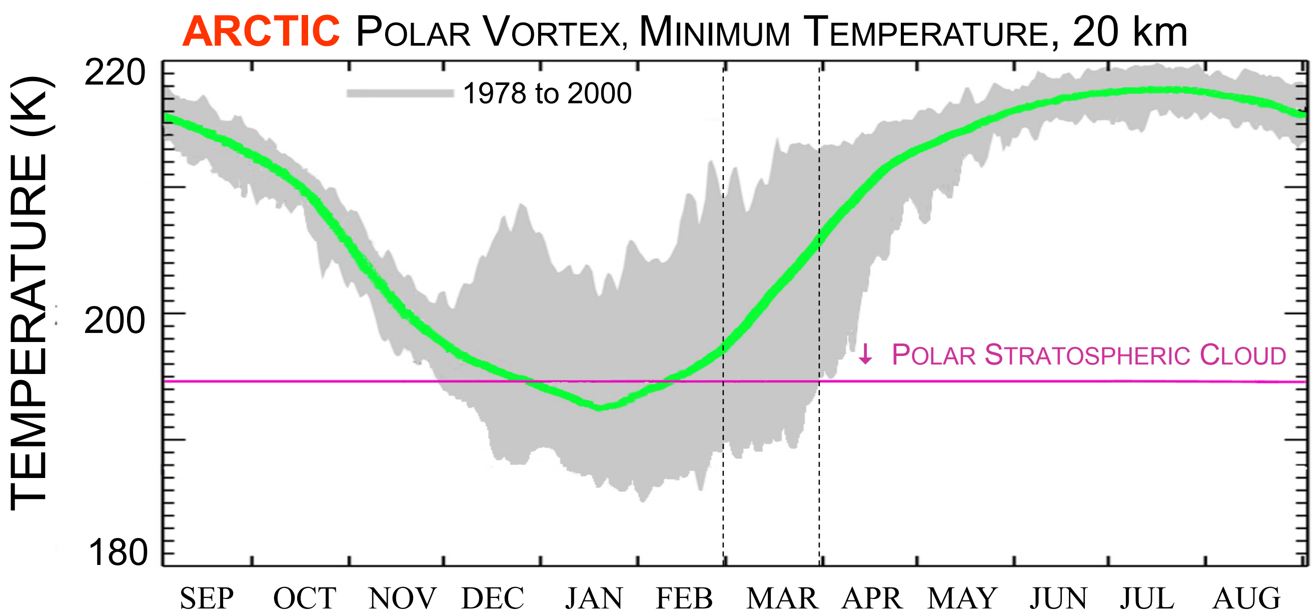
Arctic vortex (polar stratosphere):

- 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 $ClNO_3$:
  faster ClO de-activation (less ozone depletion) compared to Antarctic

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

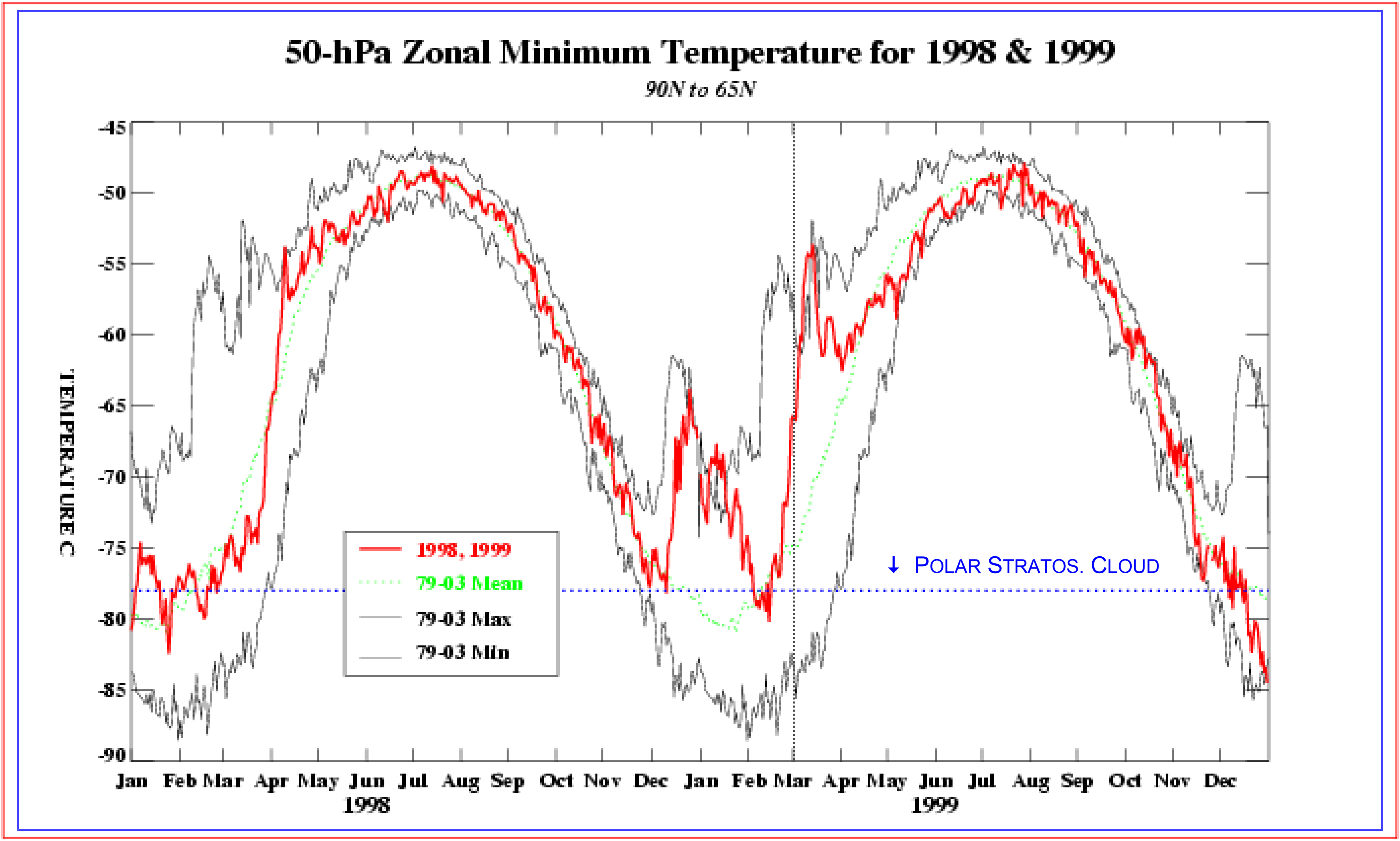
- More vigorous circulation in NH due to much more land-sea contrast, which
  triggers poleward transport of heat by atmospheric motions
  (Antarctic ice sheet suppresses poleward transport of heat by atmosphere)
- Stronger circulation in NH leads to more disturbed vortex (warmer, less PSCs)





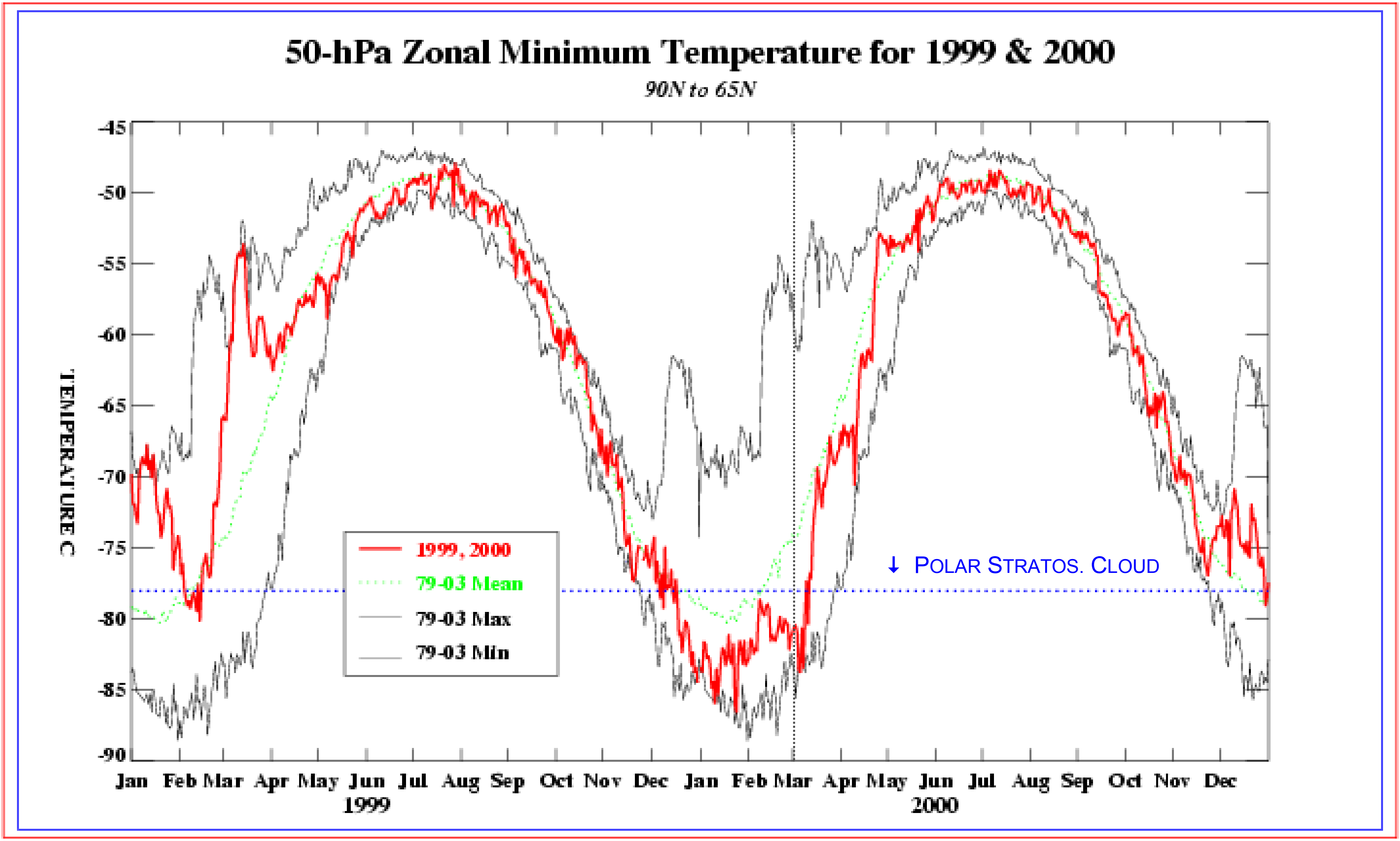
Data Courtesy P. Newman, NASA/GSFC

Arctic Temperature, 1998 &1999



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

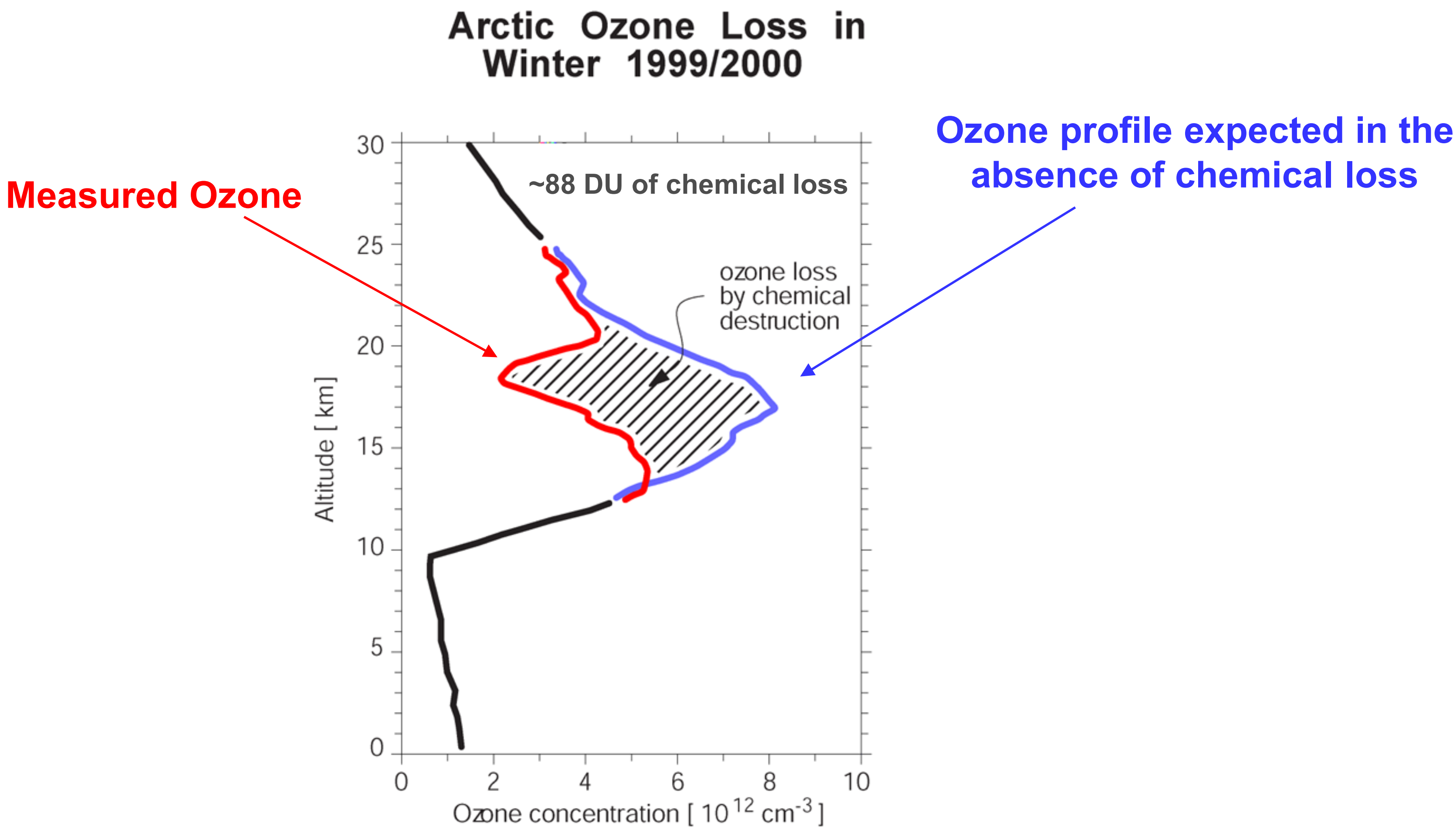
Arctic Temperature, 1999 &2000



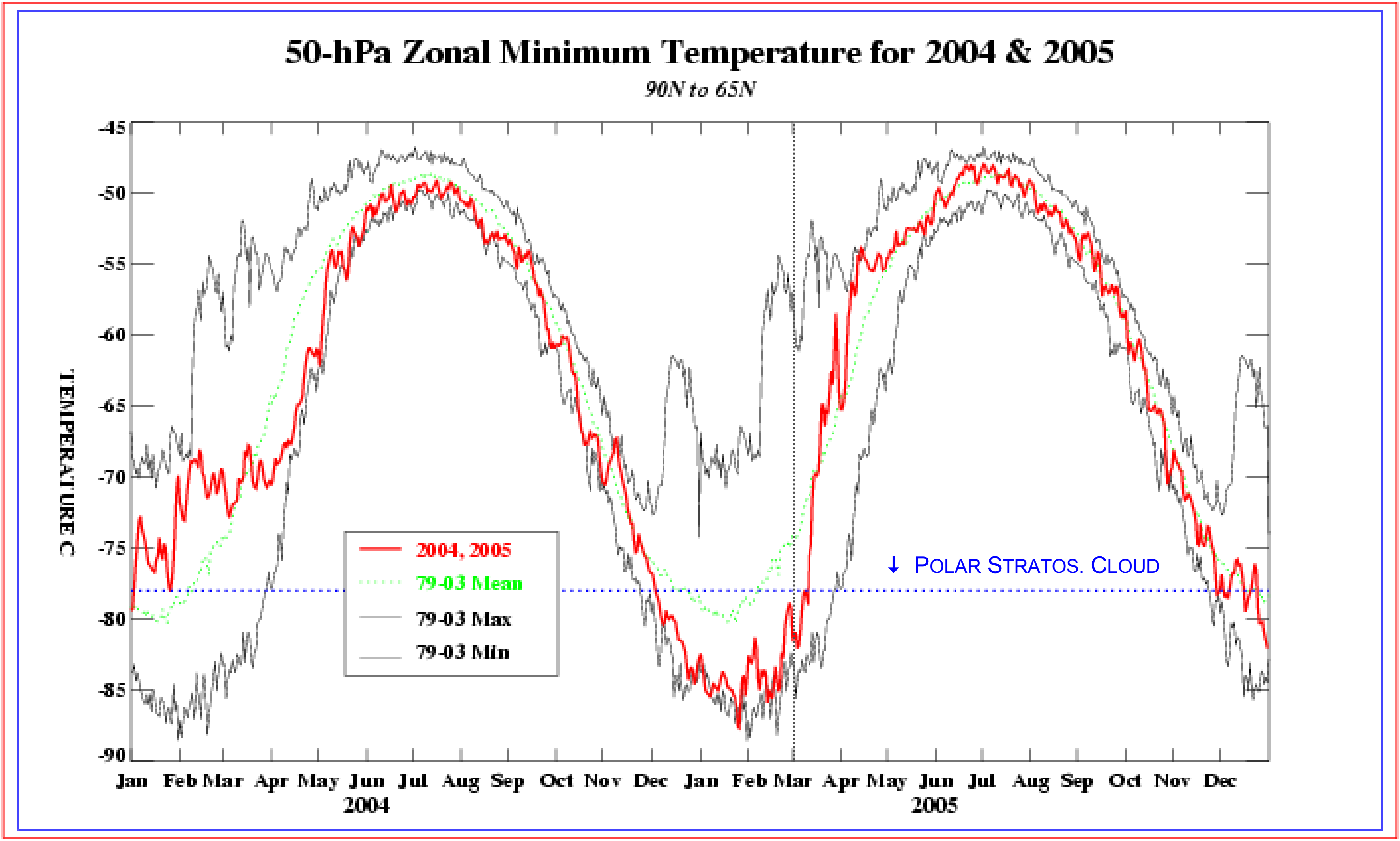
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2000.gif

Arctic Winter of 1999/2000

- **Cold** (many days below PSC threshold)
- Elevated **ClO** throughout winter
- Significant **Ozone Depletion**

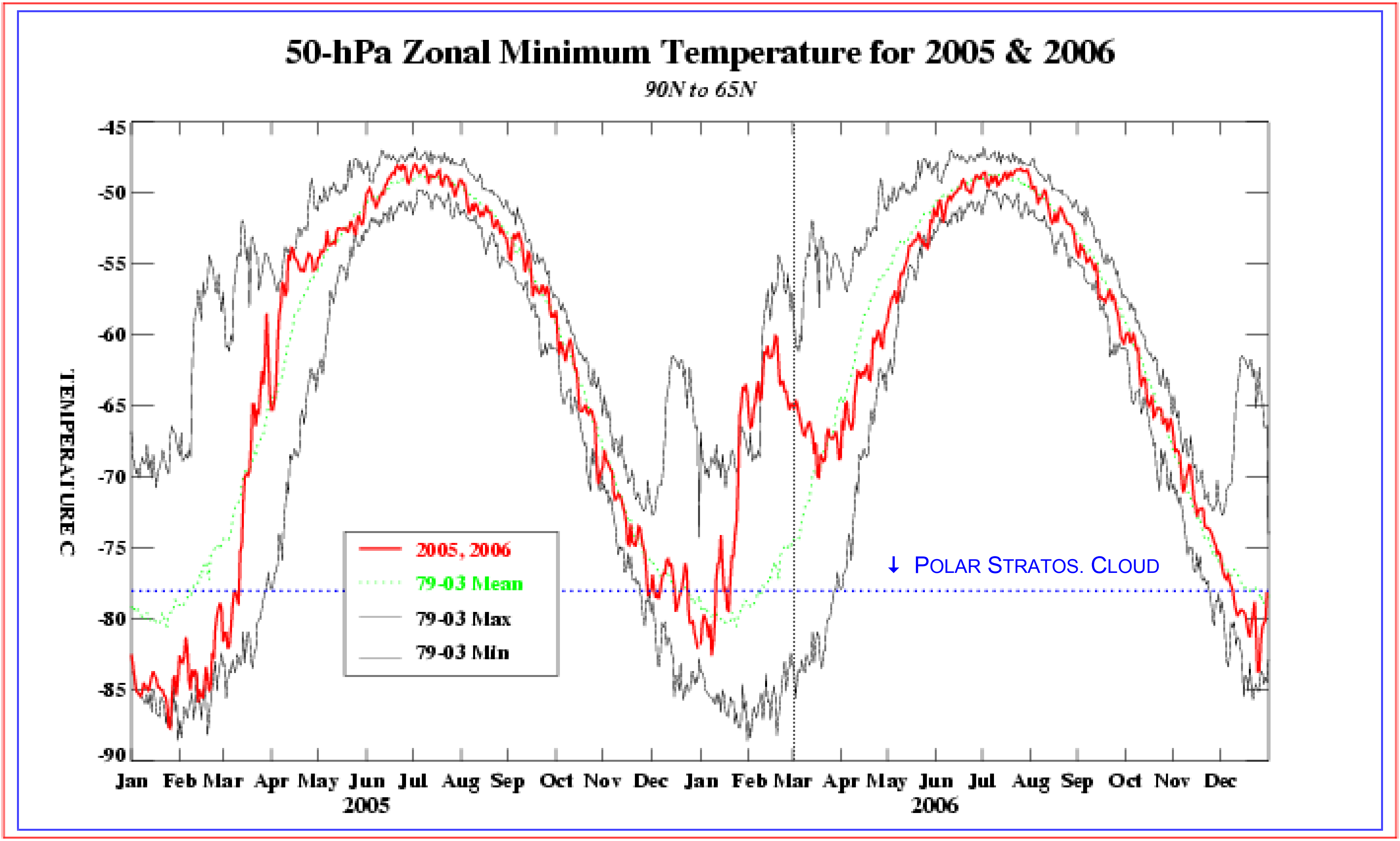


Arctic Temperature, 2004 &2005



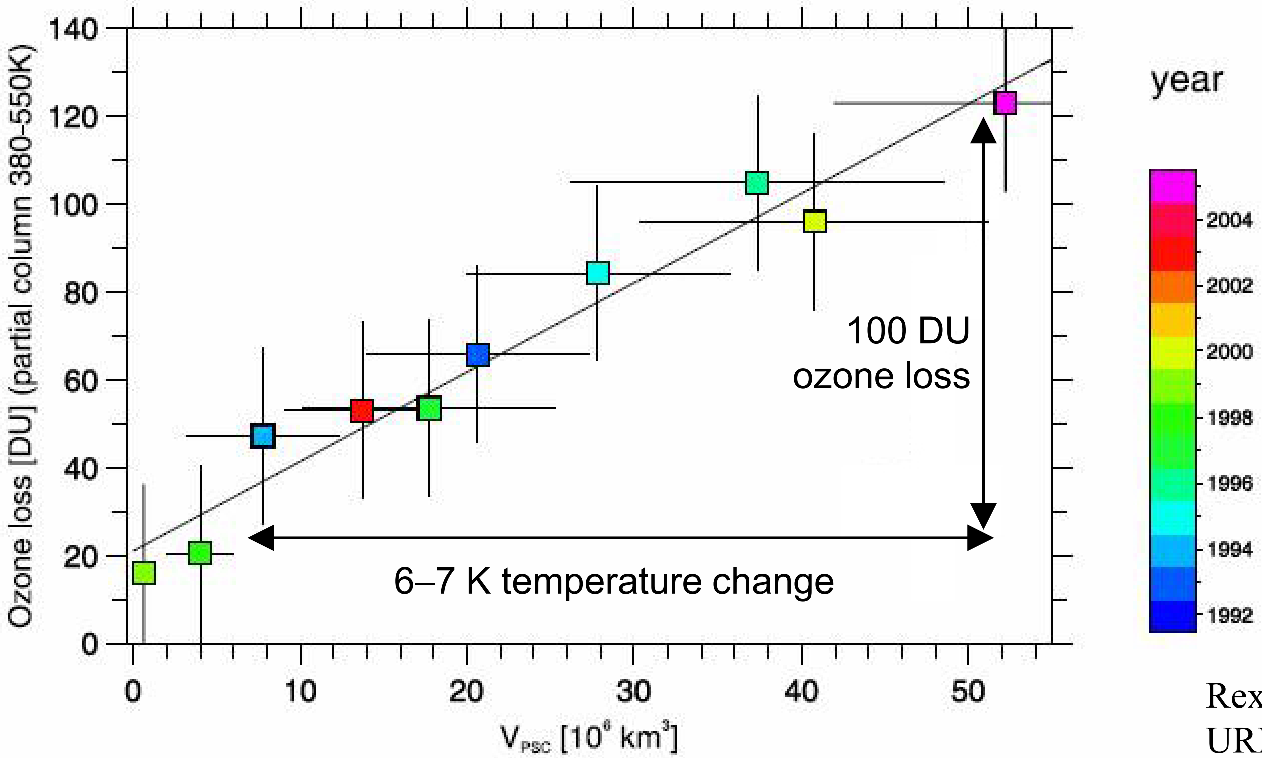
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2005.gif

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
URL in Supplemental Reading

- **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 !

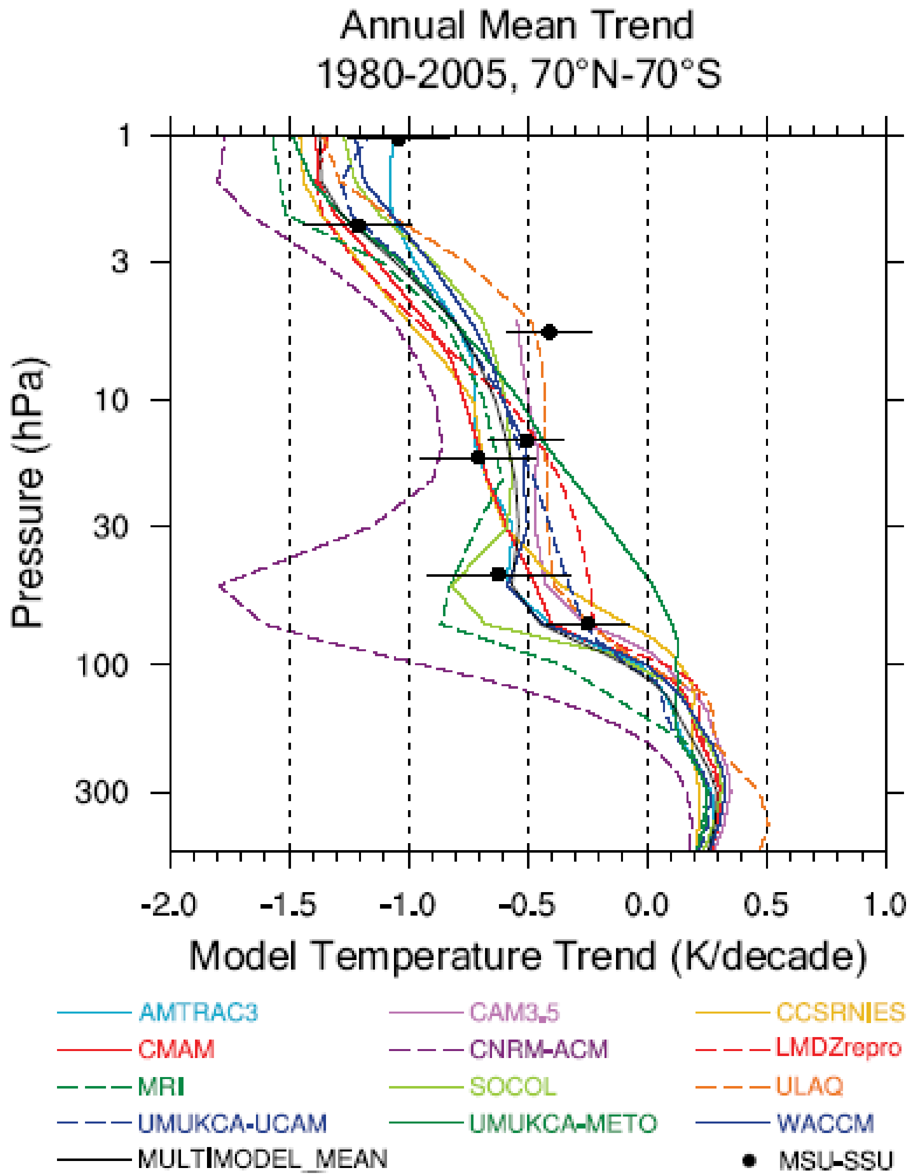


Figure 4−11, WMO/UNEP (2011)

Arctic Ozone Loss and Climate Change

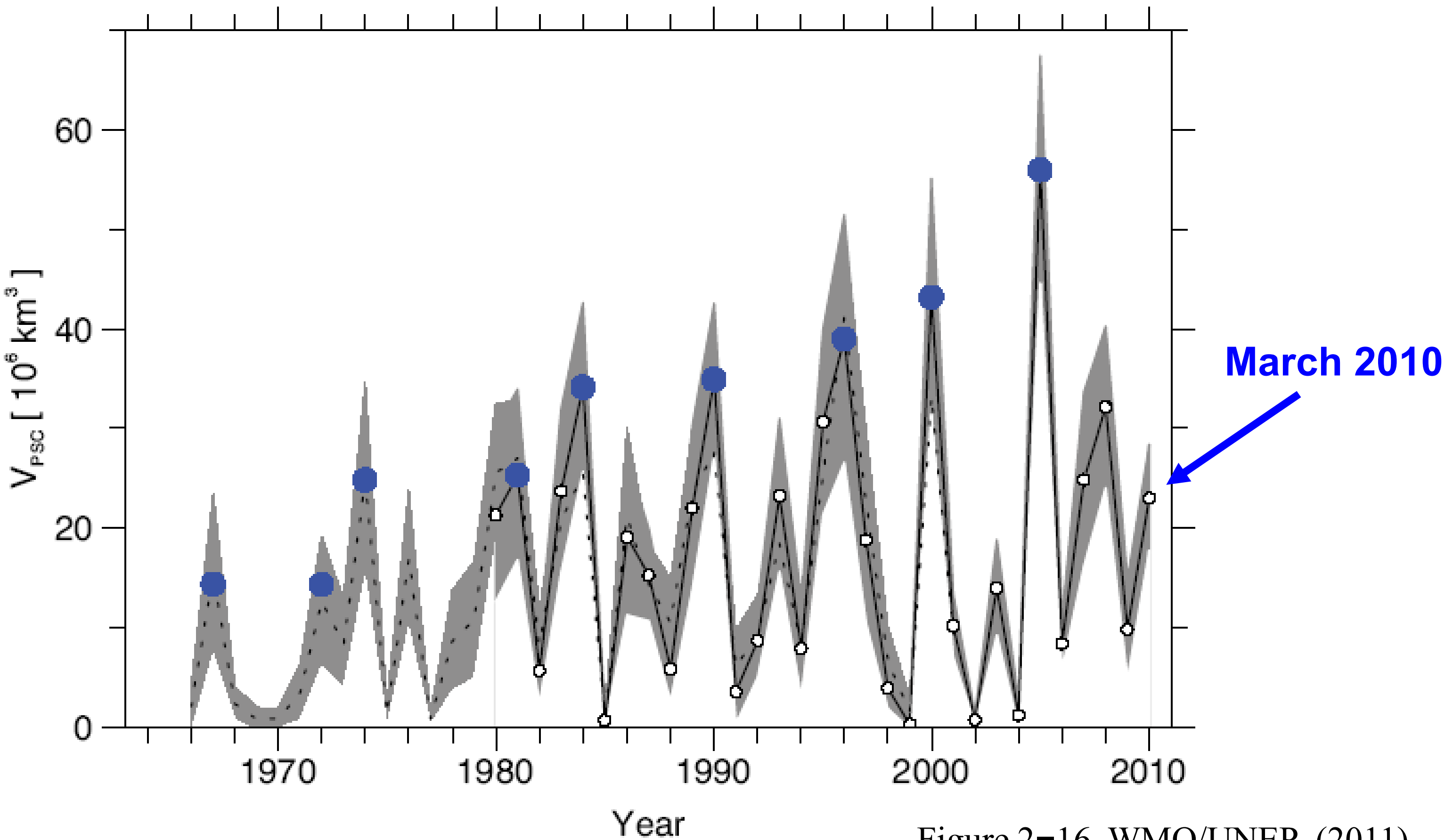
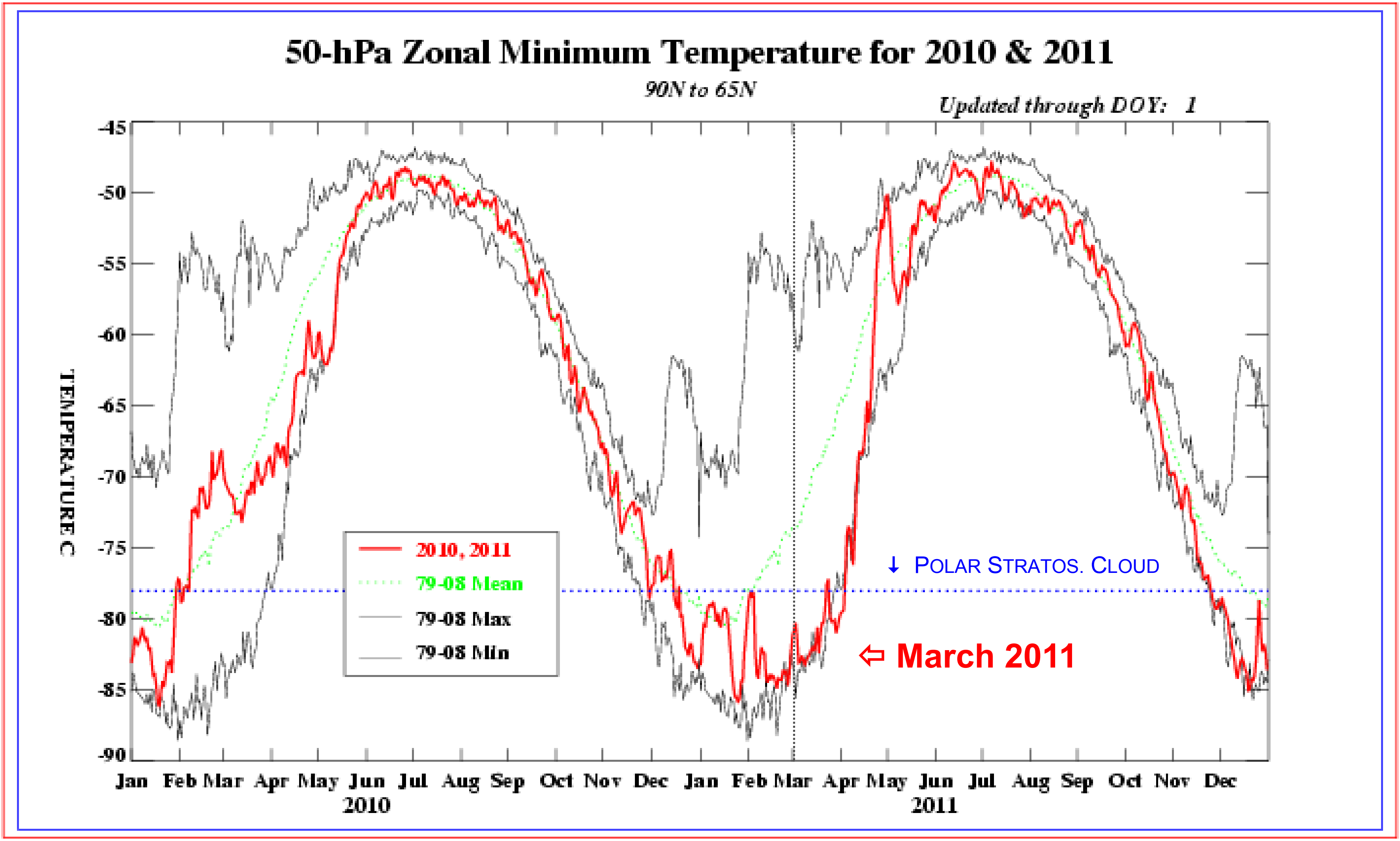


Figure 2−16, WMO/UNEP (2011)
Updated from Rex et al., GRL, 2006
URL in Supplemental Reading

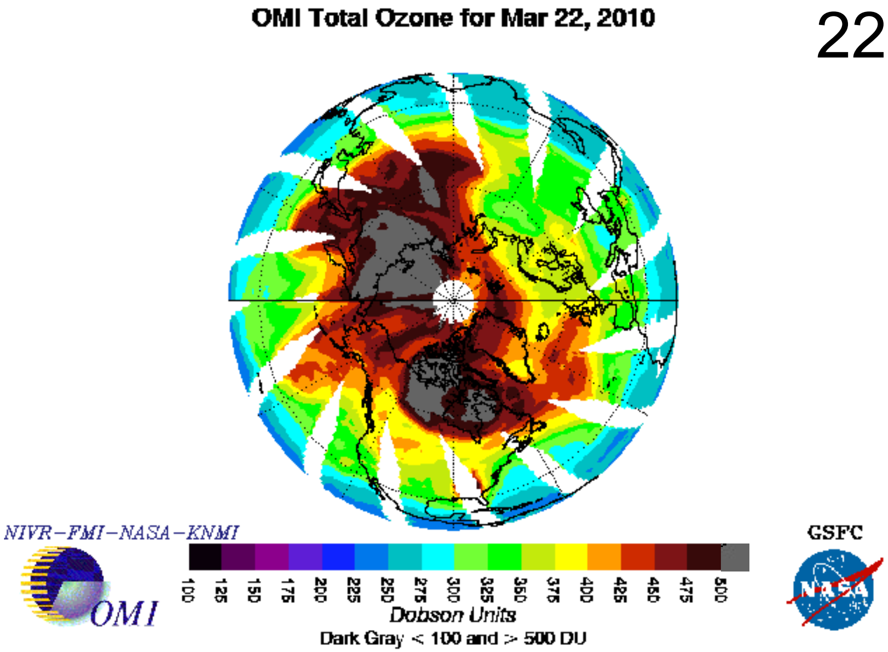
- **Lots of year to year variability in V_{PSC}**
- **Peak levels appear to be rising ... suggesting "coldest winters getting colder"**

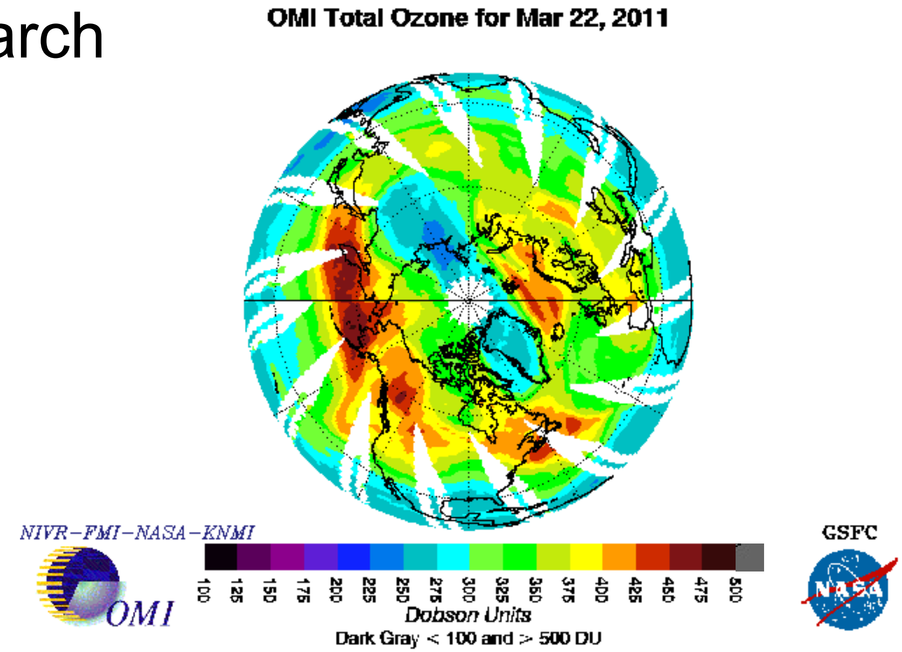
Arctic Temperature



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

22 March

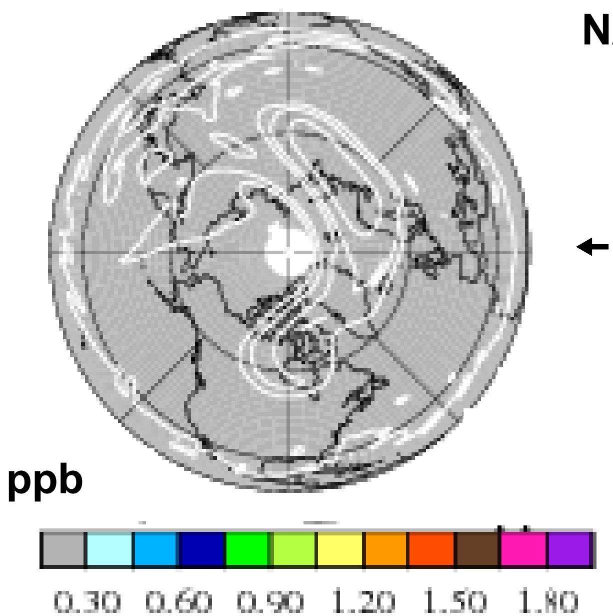


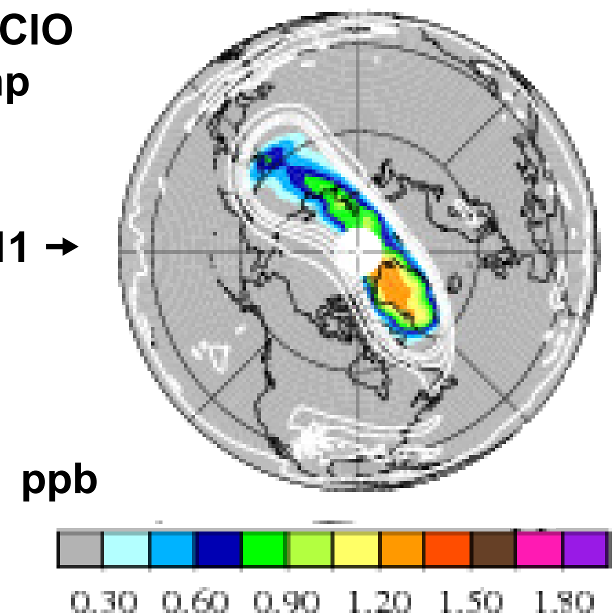


NASA Aura MLS ClO
490 K pot'l temp
~18 km

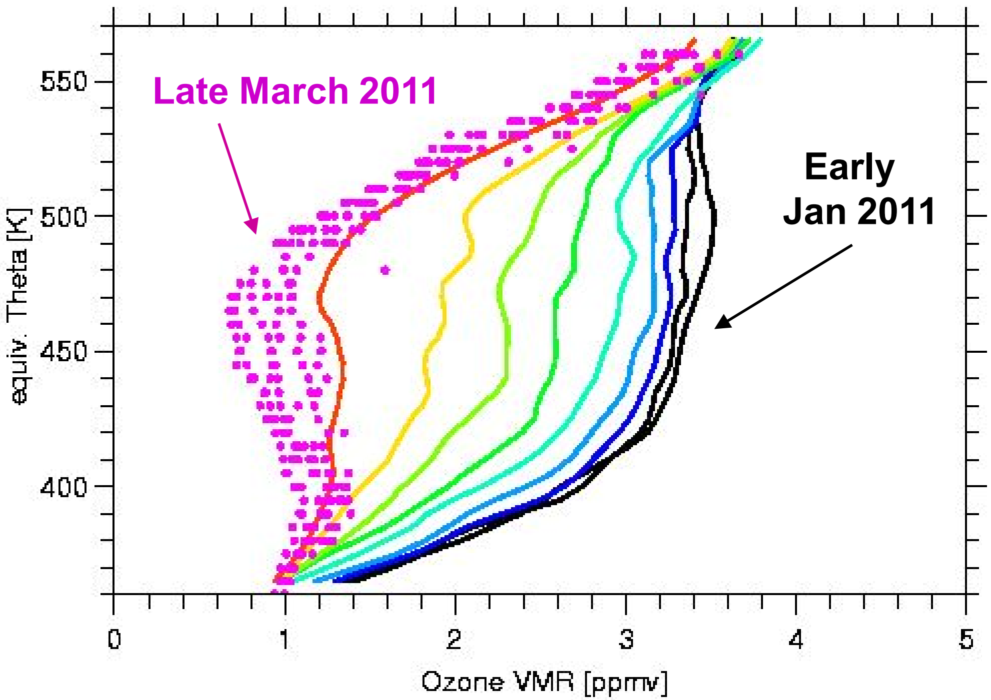
22 March

← 2010 2011 →

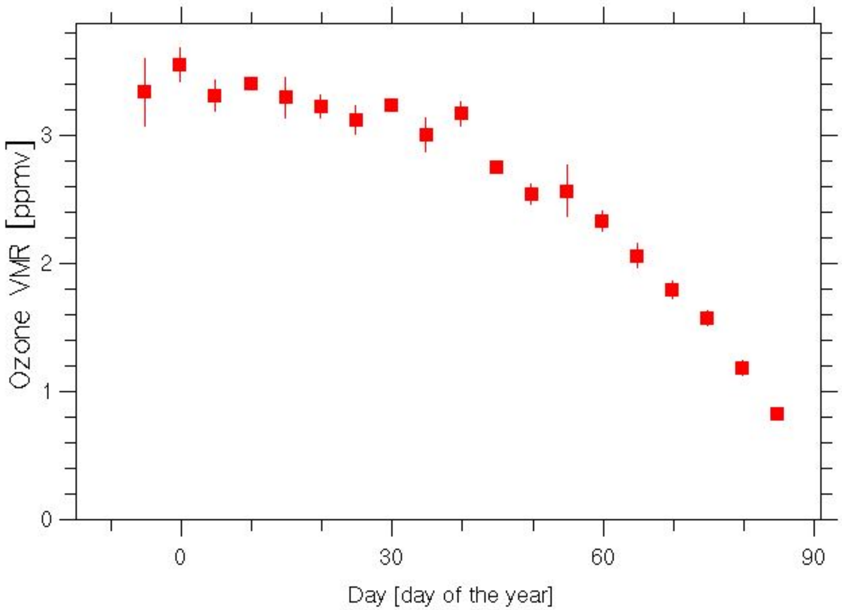




Arctic Ozone 2011



Ozone Mixing Ratio, 2011
475 K Potl Temp Surface



Manney *et al.*, *Nature*, 2011

Unprecedented Arctic ozone loss in 2011

Gloria L. Manney[1,2], Michelle L. Santee[1], Markus Rex[3], Nathaniel J. Livesey[1], Michael C. Pitts[4], Pepijn Veefkind[5,6], Eric R. Nash[7], Ingo Wohltmann[3], Ralph Lehmann[3], Lucien Froidevaux[1], Lamont R. Poole[8], Mark R. Schoeberl[9], David P. Haffner[7], Jonathan Davies[10], Valery Dorokhov[11], Hartwig Gernandt[3], Bryan Johnson[12], Rigel Kivi[13], Esko Kyrö[13], Niels Larsen[14], Pieternel F. Levelt[5,6,15], Alexander Makshtas[16], C. Thomas McElroy[10], Hideaki Nakajima[17], Maria Concepción Parrondo[18], David W. Tarasick[10], Peter von der Gathen[3], Kaley A. Walker[19] & Nikita S. Zinoviev[16]

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 1980s[1] and elucidation of the chemical mechanisms[2–5] and meteorological conditions[6] 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 springtime 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_hol.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:

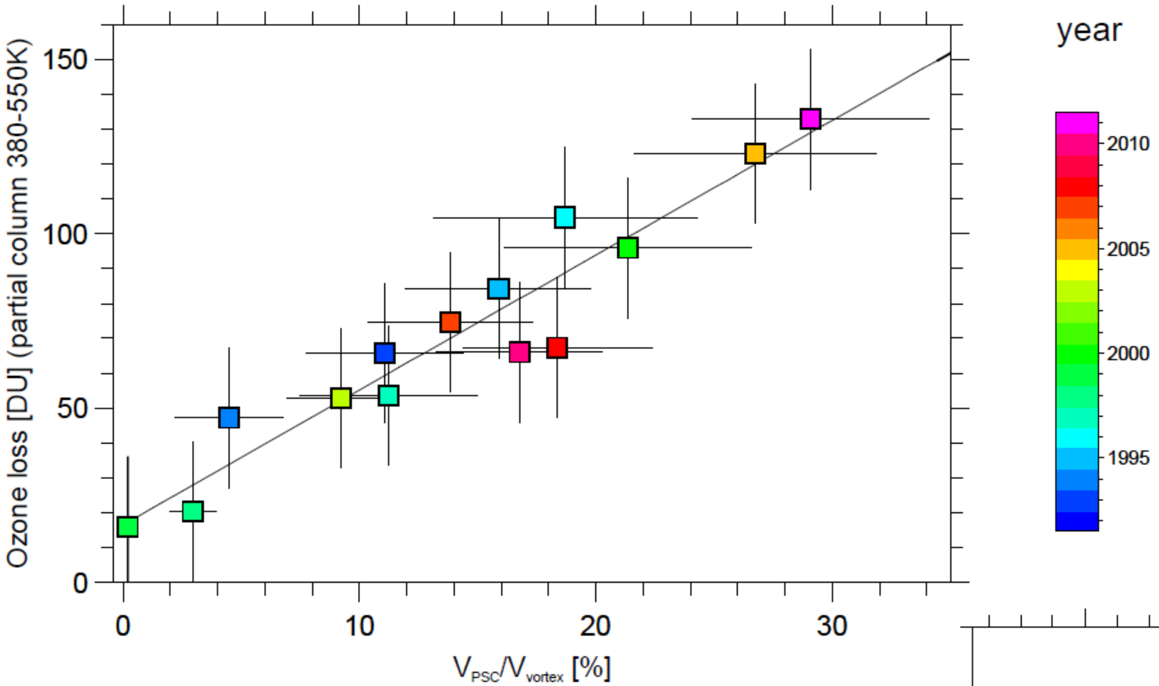
a) Was 2011 really an "Arctic Ozone hole"?

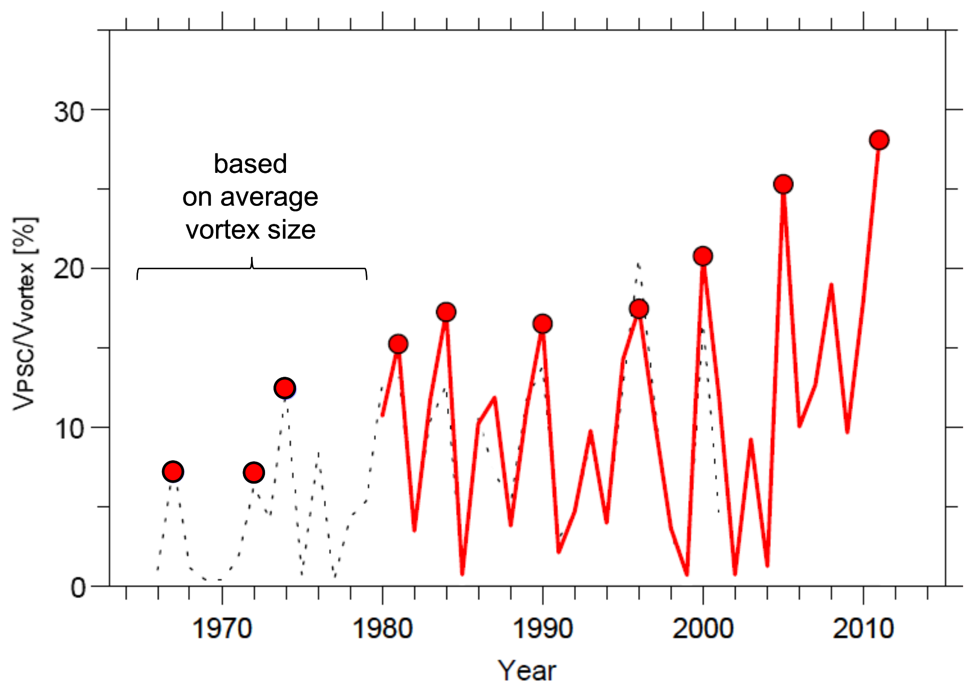
$\Rightarrow$ **many in the community strongly resist use of these words to describe Arctic Ozone 2011, despite what is written in Manney et al.**

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

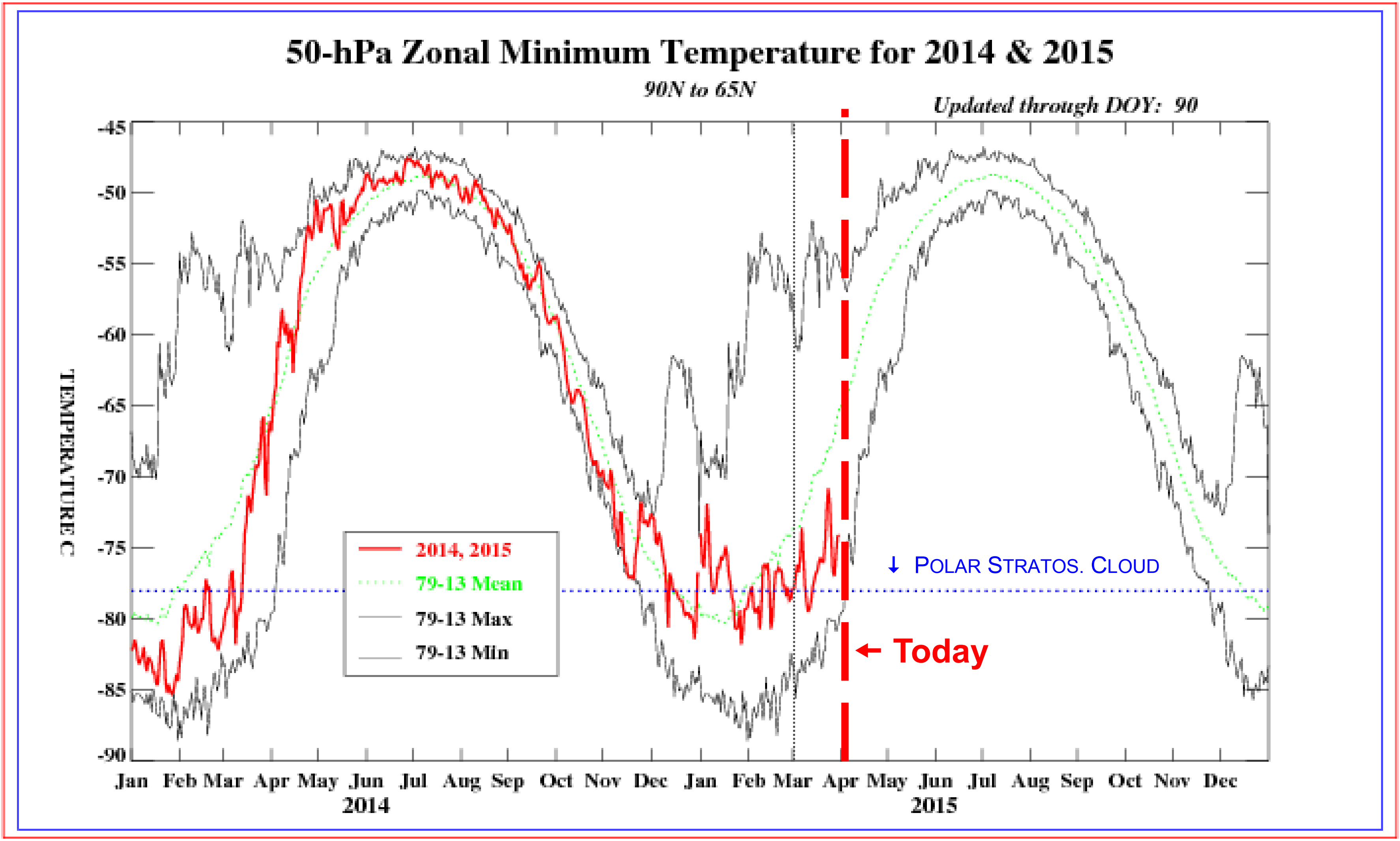
$\Rightarrow$ **vitally important active research**

Arctic Ozone 2011 in Context of Prior Years



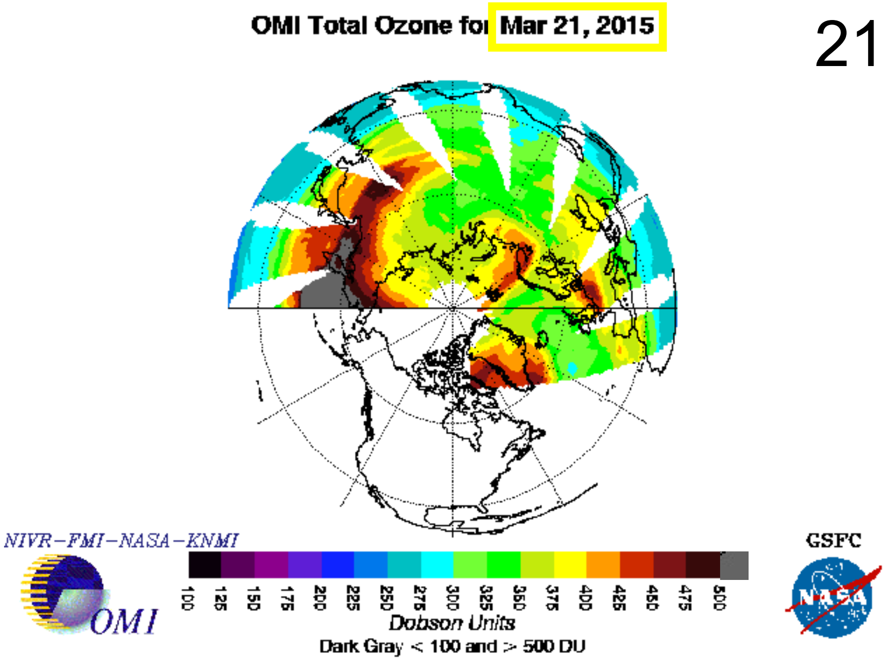


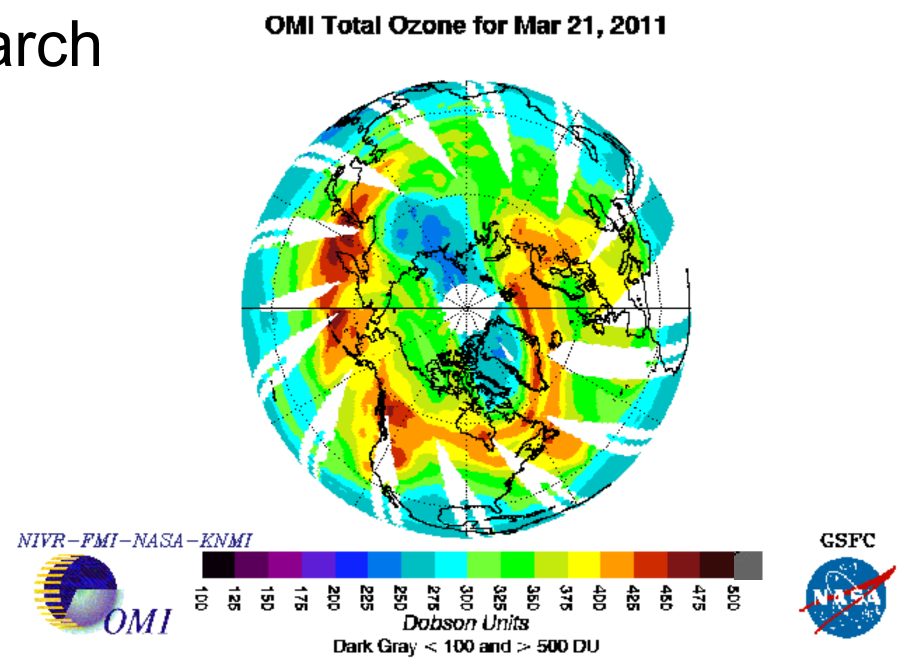
Arctic Temperature: Mar 2015



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

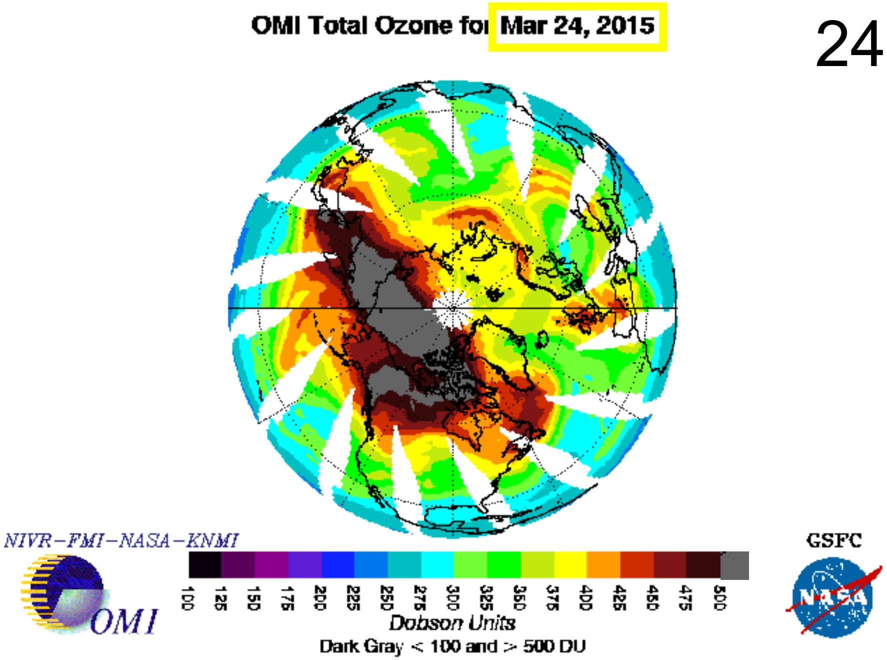
21 March

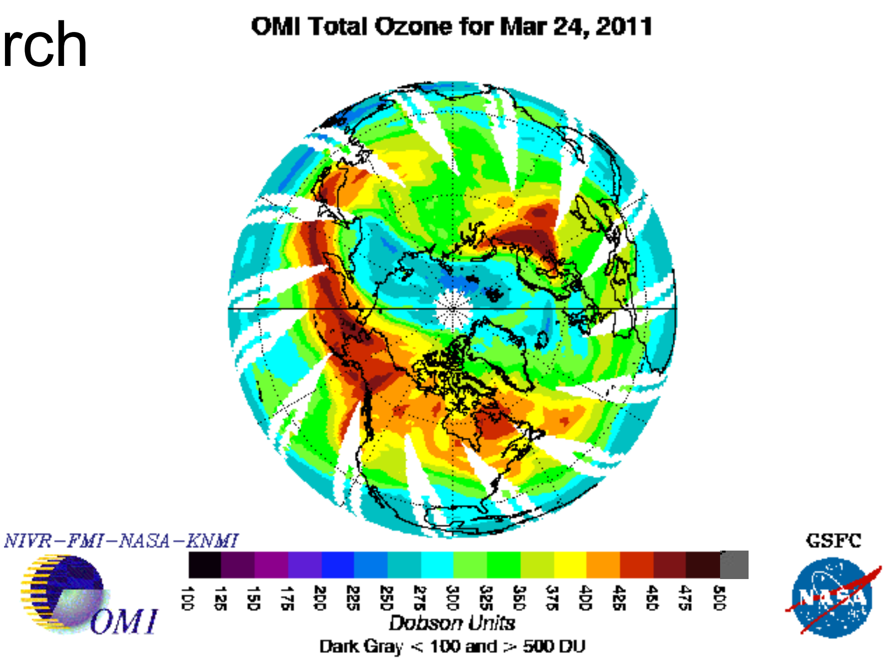




Images for 2015 from ftp://toms.gsfc.nasa.gov/pub/omi/images/npole/Y2015

24 March





Images for 2015 from ftp://toms.gsfc.nasa.gov/pub/omi/images/npole/Y2015