Stratospheric Chemistry: Polar Ozone Depletion

AOSC 433 / 633 & AOSC 633

Ross Salawitch & Walt Tribett

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2019

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 Tuesday
No Admission Ticket for Tuesday'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

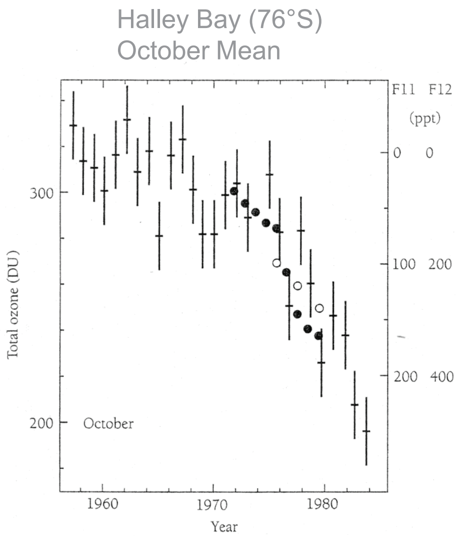
4 April 2019

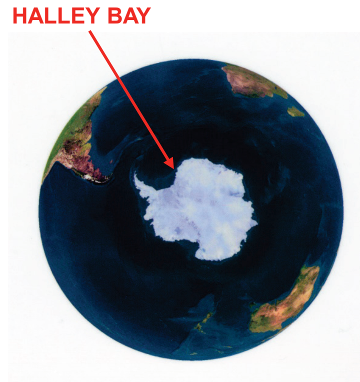
Student Projects

- **Mandatory for 633 students:** project grade will count towards final grade in an amount equal to each exam
- **Optional for 433 students:** can use project grade to replace a ***single*** problem set grade: advisable for anyone who failed to turn in a problem set or would otherwise like to replace the grade on a problem set
- Due Friday, 10 May 2019… you're welcome to complete sooner
- ~6 to 8 pages single spaced (not including reference list or figures) on a topic related to class (your choice …we're happy to discuss potential topics)
- Must be ***new work for this class*** but can be related to your dissertation or some other topic in which you've had prior interest
- ~welcome to attend
- Request all students who will complete a project to provide a **2 to 3 sentence description** at https://myelms.umd.edu/courses/1256337/quizzes/1270627 by **Tues, 9 April 2019**
- Happy to provide feedback on your project if given the opportunity

Polar Ozone Depletion

Discovery of the ozone hole:



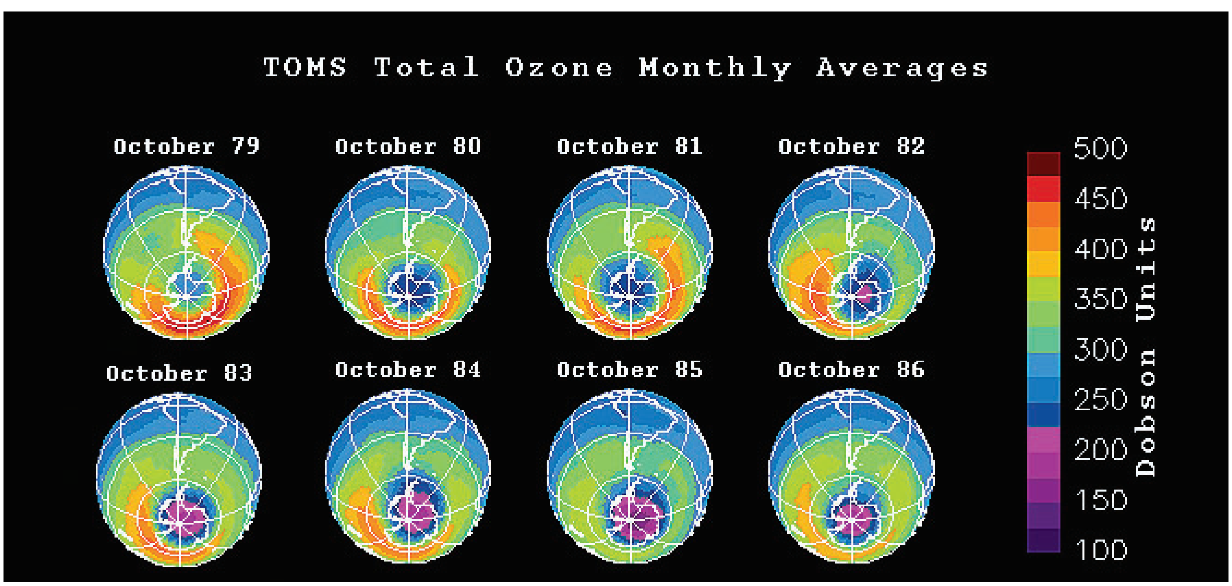


Southern Hemisphere

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:



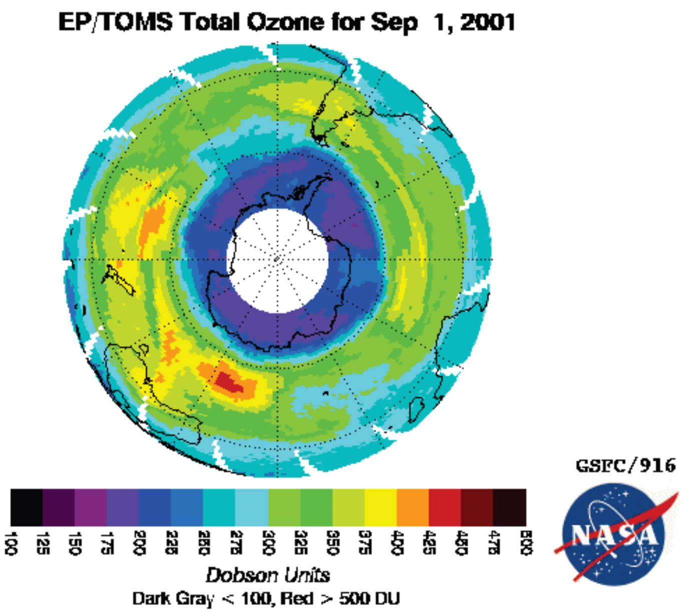
Stolarski *et al*., *Nature*, 322, 808, 1986.

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].

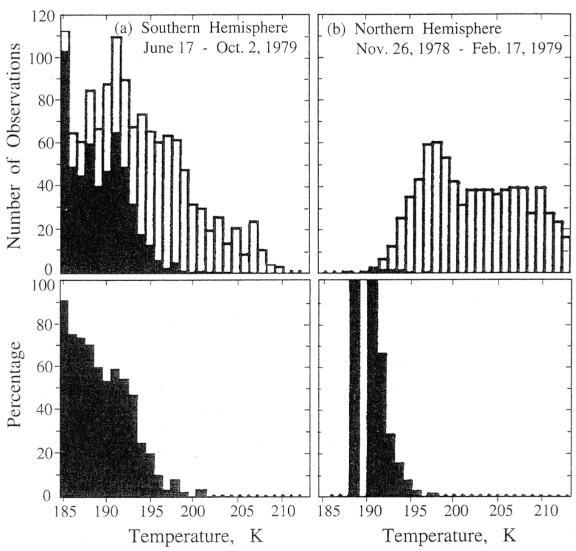
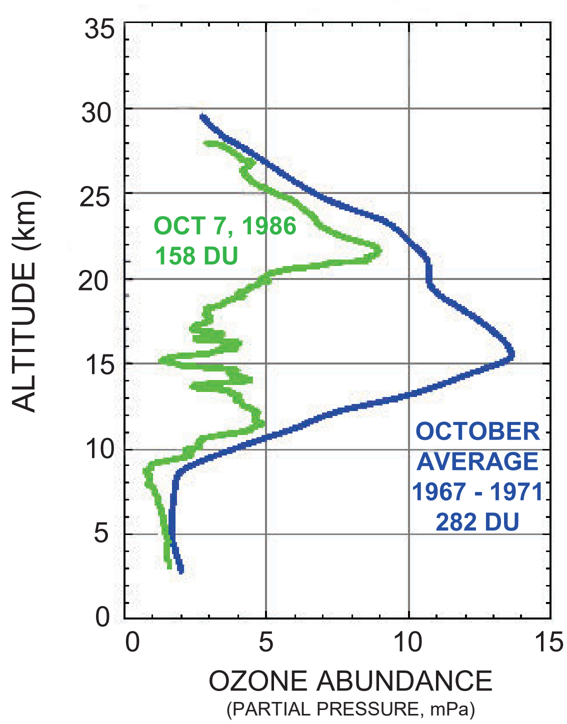


FIGURE 4.20 The top panels show a histogram of the total number of vertical temperature profiles having a given minimum temperature for the Antarctic and Arctic winters. The darkened bars represent observations of PSCs. The lower panel shows the frequency of PSC observations as a percentage of the total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

Balloon-borne ozonesondes showed:

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

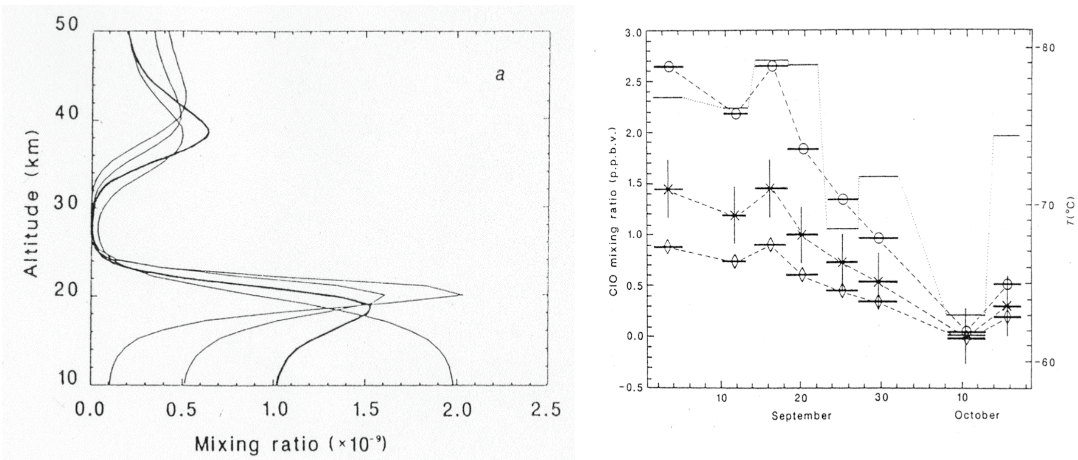


Hofmann et al., *Nature, 326*, 59, 1987.

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

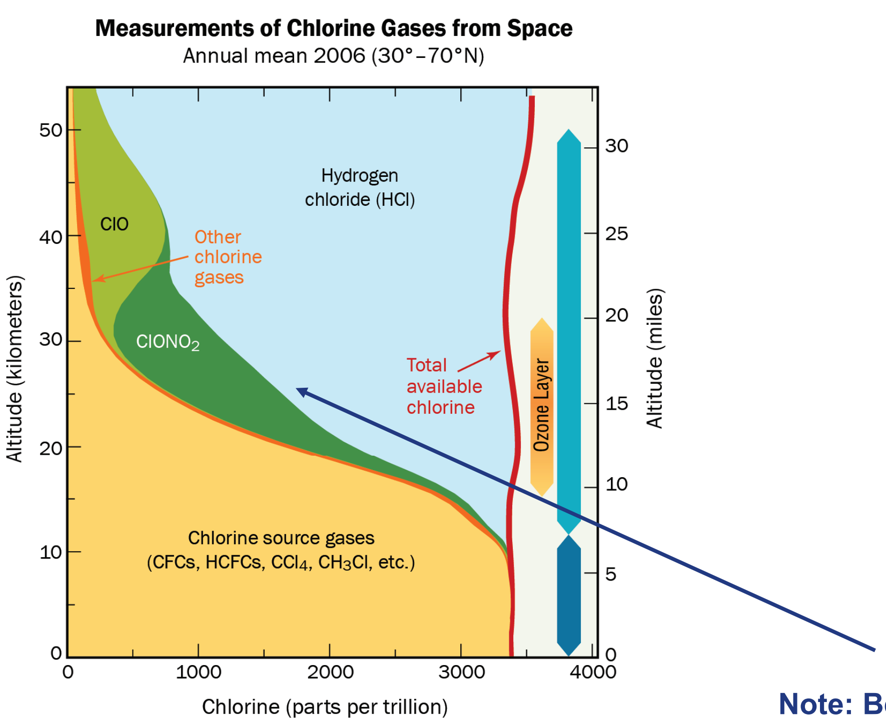


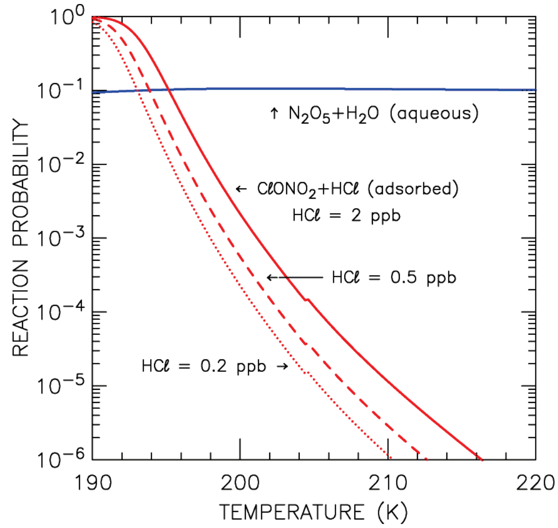
Fig Q8-2, 20 QAs, WMO (2014)

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

Lecture 14, Slide 31

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

Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

a) What type of aerosol particles are present in the mid-latitude stratosphere (i.e., what is the chemical composition of these aerosols?)

b) What heterogeneous chemical reaction occurs on the aerosol particles present in the mid-latitude stratosphere and how is the abundance of ClO affected by this reaction?

c) What type of particles are present in the polar stratosphere during winter (i.e., what are these particles called and what is the chemical composition of a "common type" of these particles?)

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 deplete ozone) and that, while reactive, do not not cause harm to the ozone layer during the darkness 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? Hint: we're looking for a monoxide

f) Why does the ozone hole occur only over Antarctica?

Polar Ozone Loss

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

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

$ClNO_3 + H_2O \rightarrow HOCl + HNO_3$

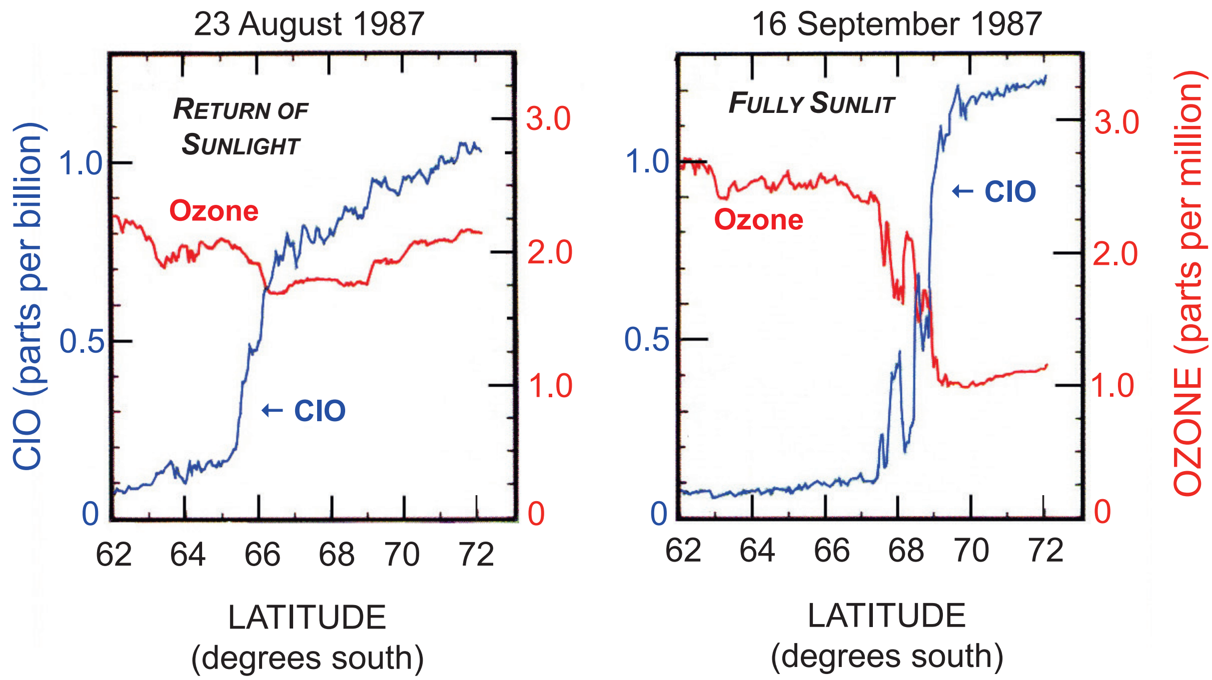
Cl_2 + SUNLIGHT + $O_3 \rightarrow ClO$

$HOCl$ + SUNLIGHT + $O_3 \rightarrow ClO$

HNO_3 SEDIMENTS (PSCs fall due to gravity)

- Elevated **ClO** + <u>Sunlight</u> 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):

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

Cycle (1b):

$ClO + ClO + M \rightarrow ClOOCl + M$
$ClOOCl + heat \rightarrow ClO + ClO$
Net: $M + heat \rightarrow M$

Cycle (2a):

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

Cycle (2b):

$BrO + ClO \rightarrow ClOO + Br$
$Br + O_3 \rightarrow BrO + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
$ClOO + heat \rightarrow Cl + O_2$
Net: $O_3 + O_3 \rightarrow 3\ O_2$

Cycle (2c):

$BrO + ClO \rightarrow OClO + Br$
$OClO + h\nu \rightarrow O + ClO$
$Br + O_3 \rightarrow BrO + O_2$
Net: $O_3 \rightarrow O + O_2$

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

Lecture 11, Slide 21

30.5 kcal/mole   2 × 24.3 kcal/mole

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

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

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

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

In equilibrium:

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

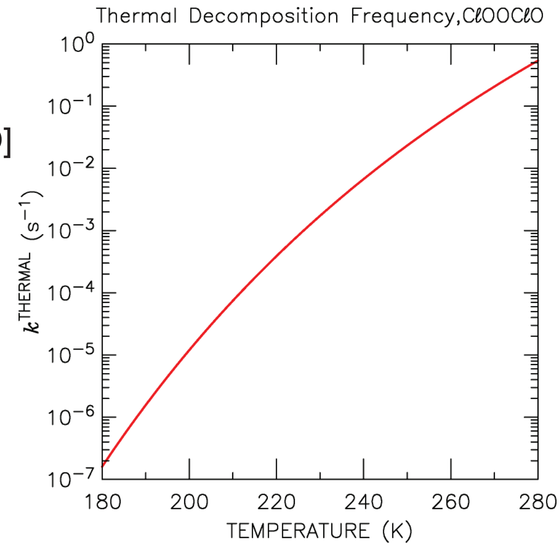
where $k^{\mathrm{THERMAL}} = k^{\mathrm{FORMATION}} \times K^{\mathrm{EQ}}$

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

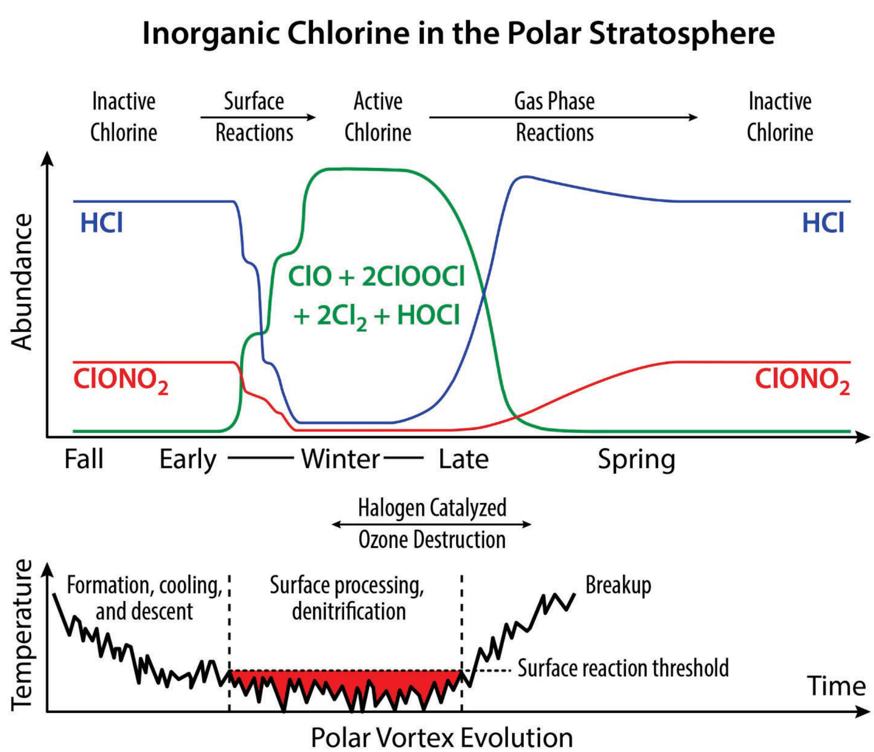
at low T, ClOOCl stable: energy wins !

at high T, ClOOCl unstable: entropy rules !

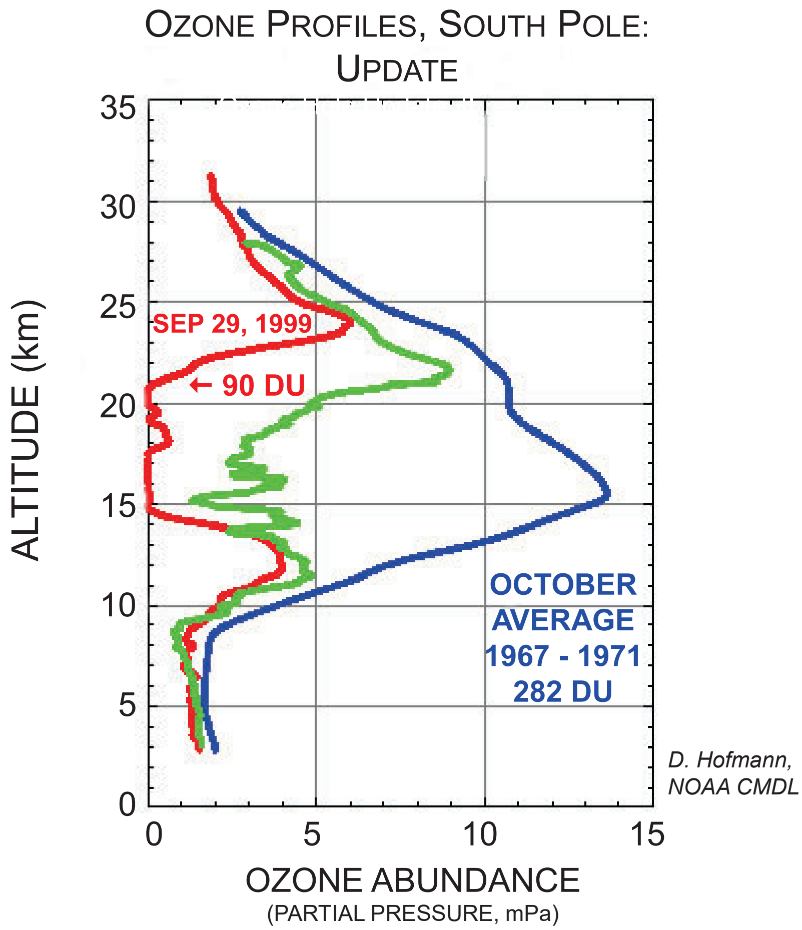
Equilibrium constants given in **Section 3** of the JPL Data Evaluation.



Polar Halogens, Seasonal Evolution

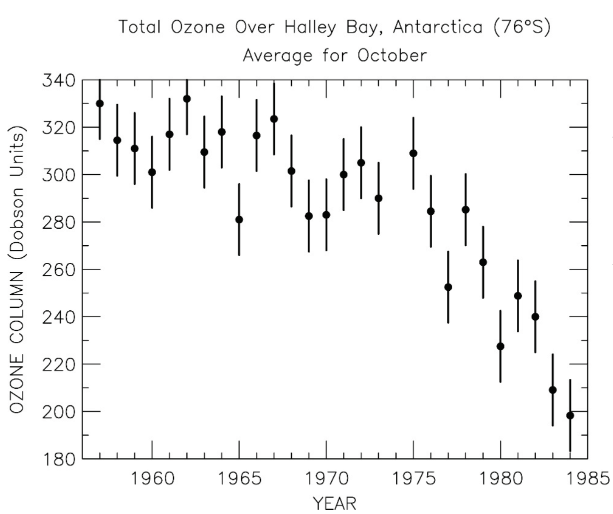


From Wilmouth, Salawitch & Canty, Stratospheric Ozone Depletion and Recovery, 2017



Earth's Atmosphere – Effect of Humans

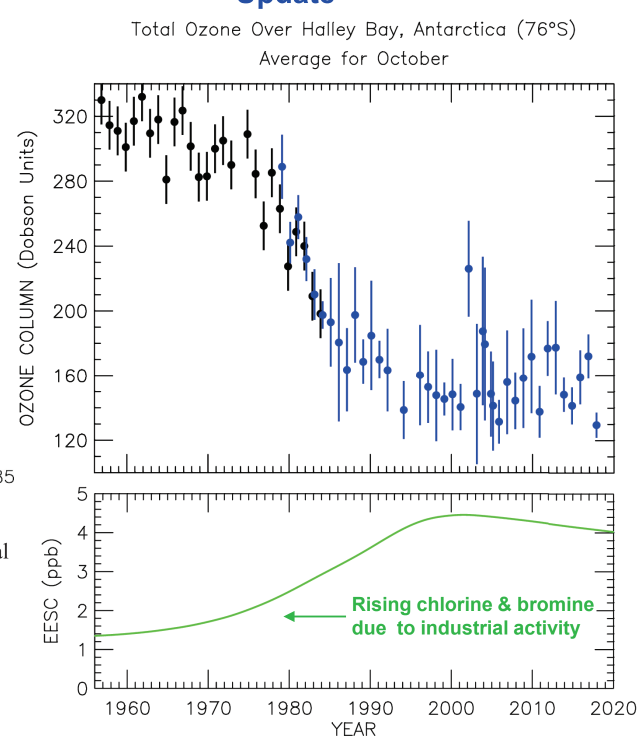
Stratospheric Ozone – shields surface from solar UV radiation



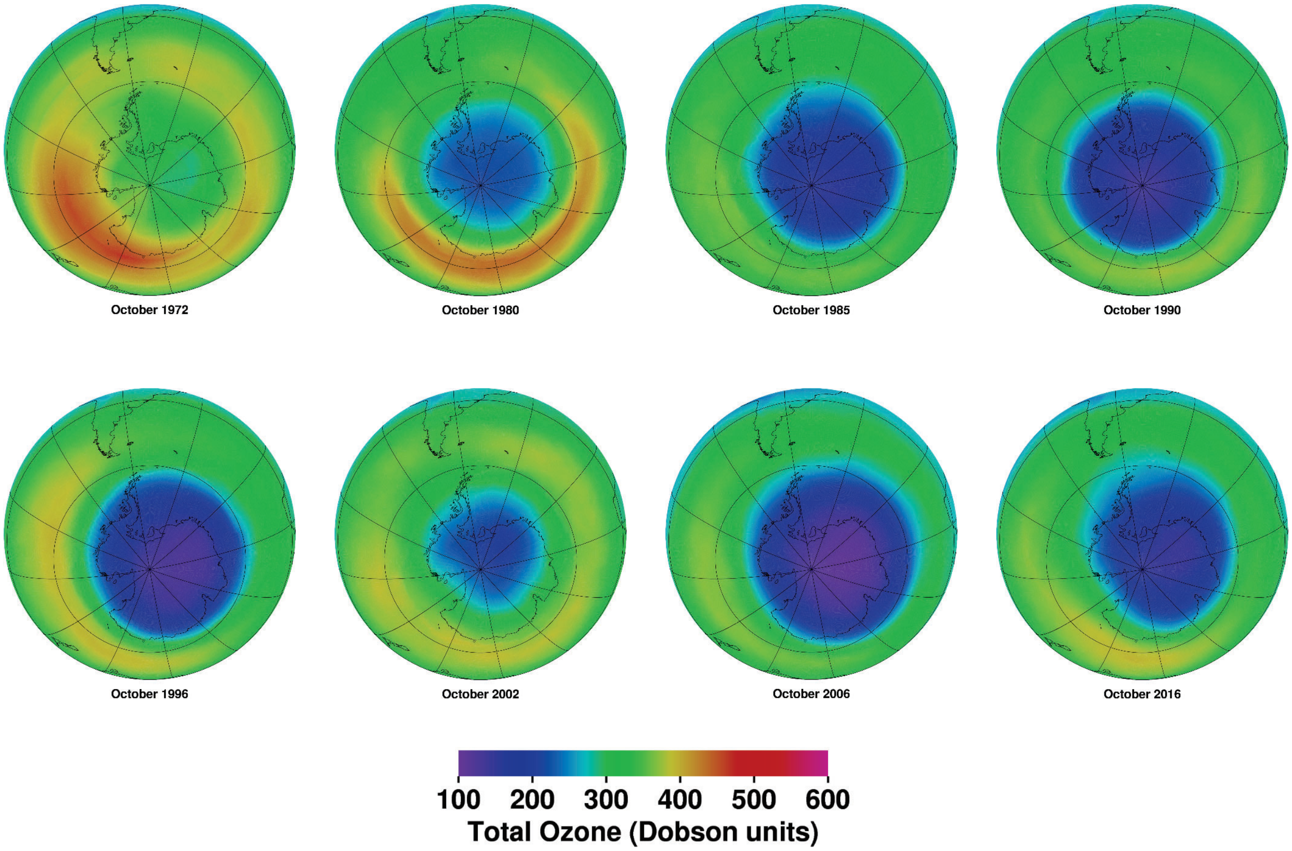
After Farman *et al*., Large losses of total ozone in Antarctica reveal Seasonal ClOx/NOx interaction, Nature, 315, 207, 1985.

EESC = Total Chlorine + 60 × Total Bromine
(actually, scientists use multipliers of 65 for polar regions and 60 for extra-polar regions … don't ask)

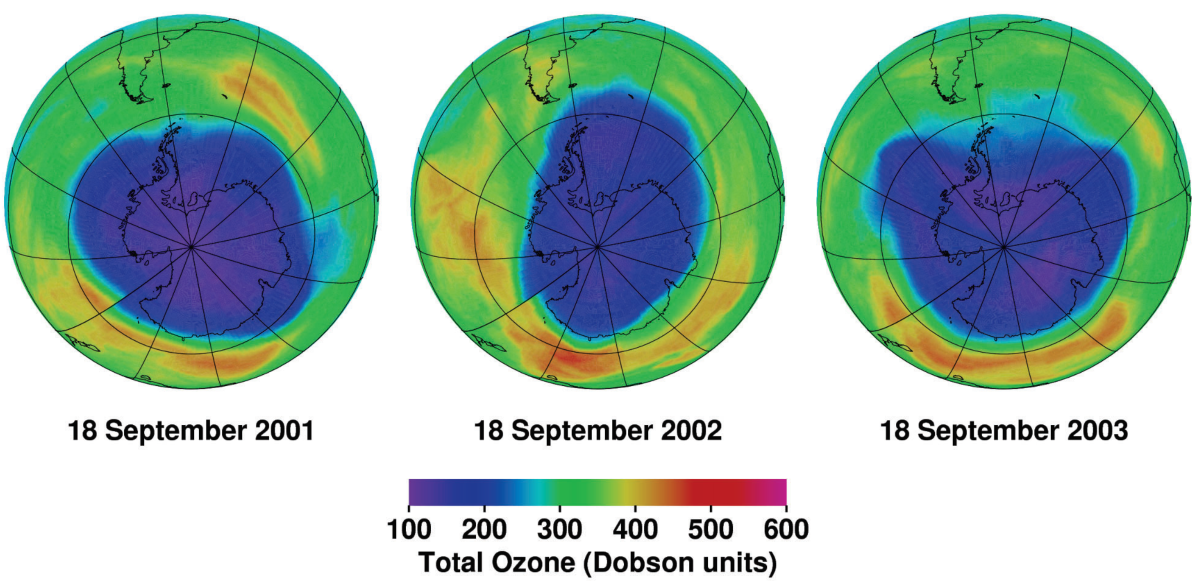
Update



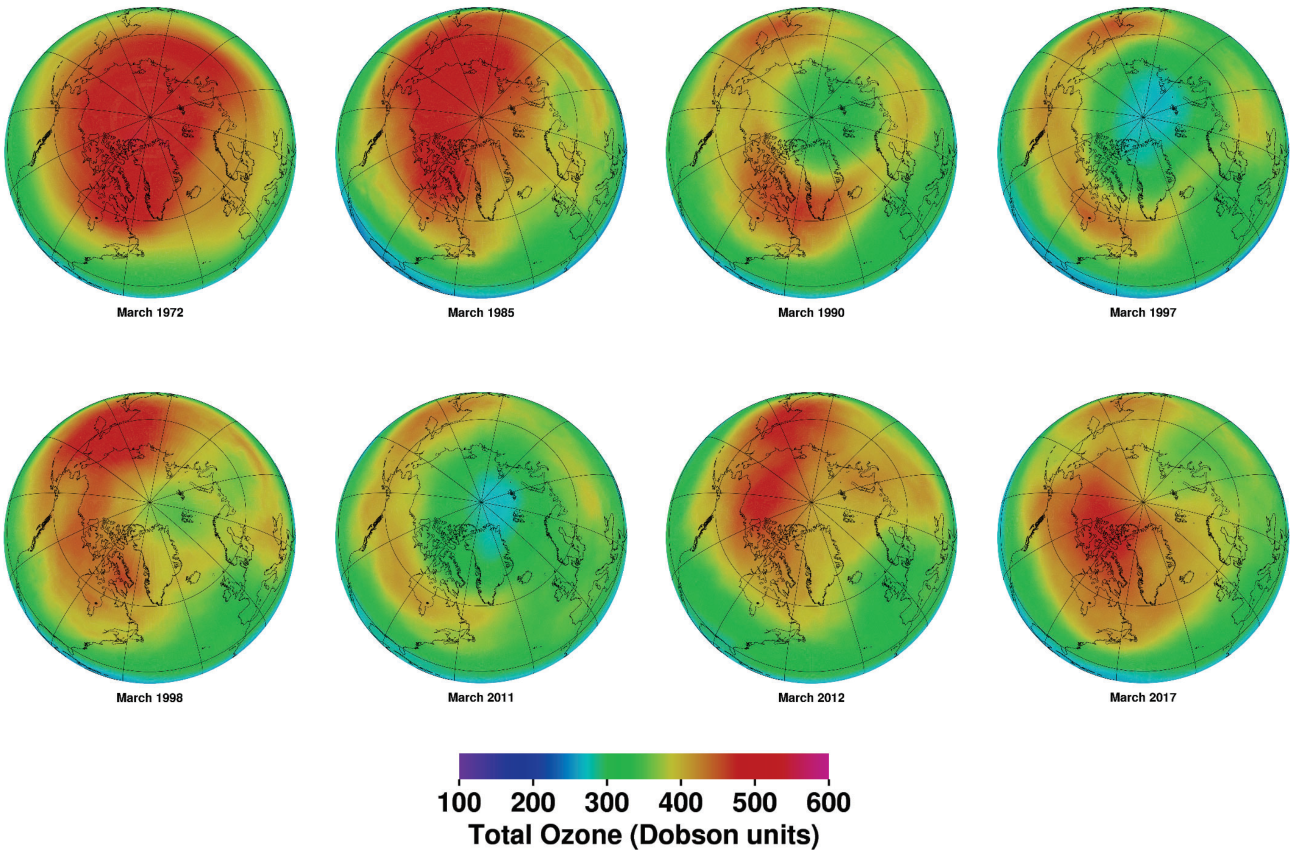
Antarctic Ozone versus Time



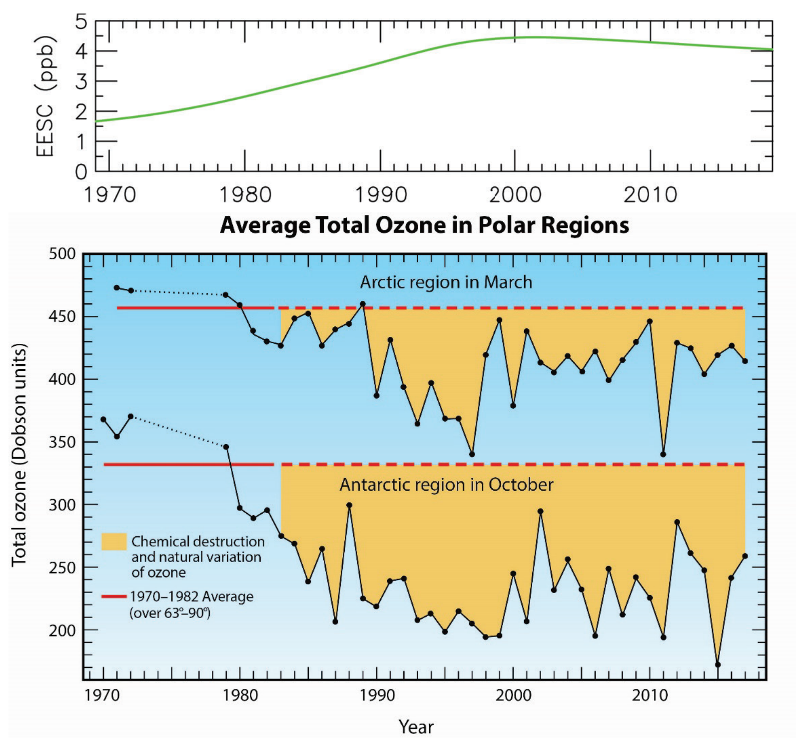
Southern Hemisphere Sudden Warming, 2002



Arctic Ozone versus Time

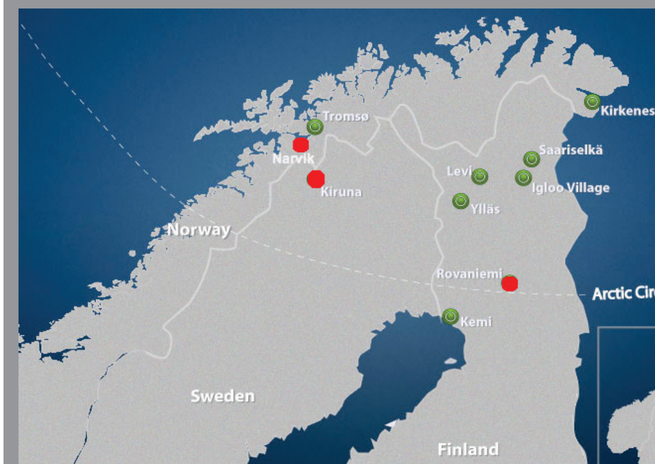


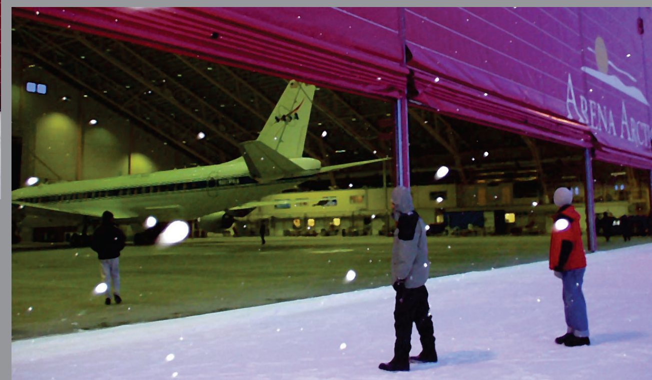
Polar Ozone Depletion: NH and SH



2019 update to Fig Q12-1, 20 QAs

Arena Arctica, Kiruna, Sweden





https://thiswendycity.wordpress.com/magic-laplands/

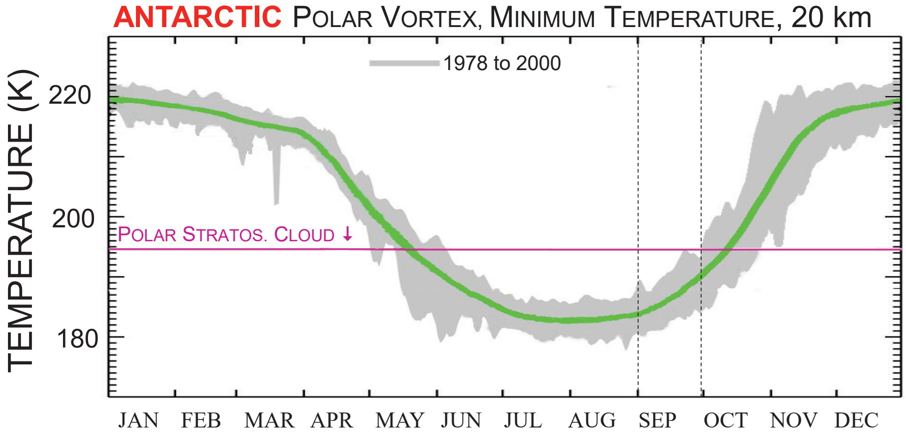
Arctic Overview

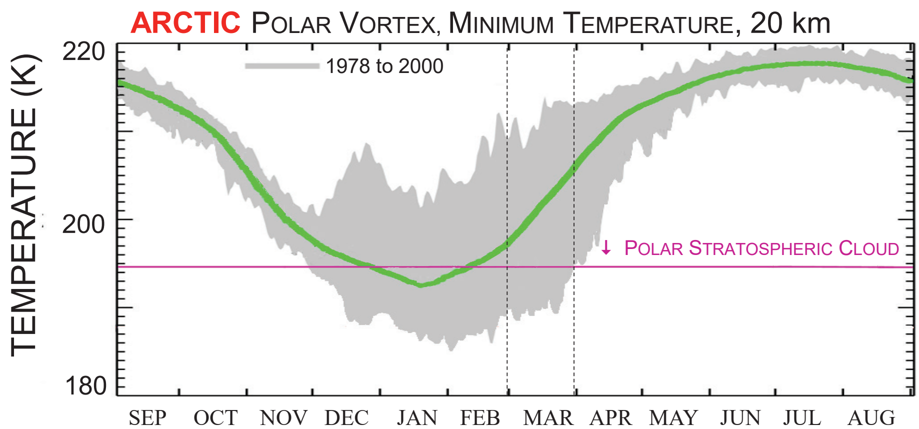
Arctic vortex (polar stratosphere):

- 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

Temperature: NH and SH

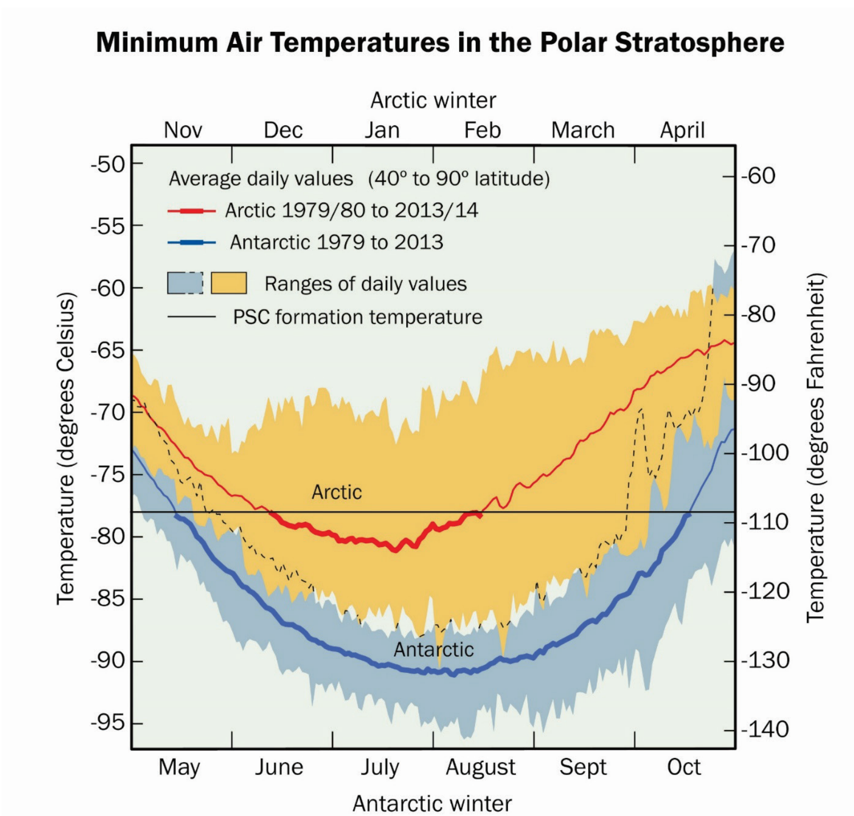
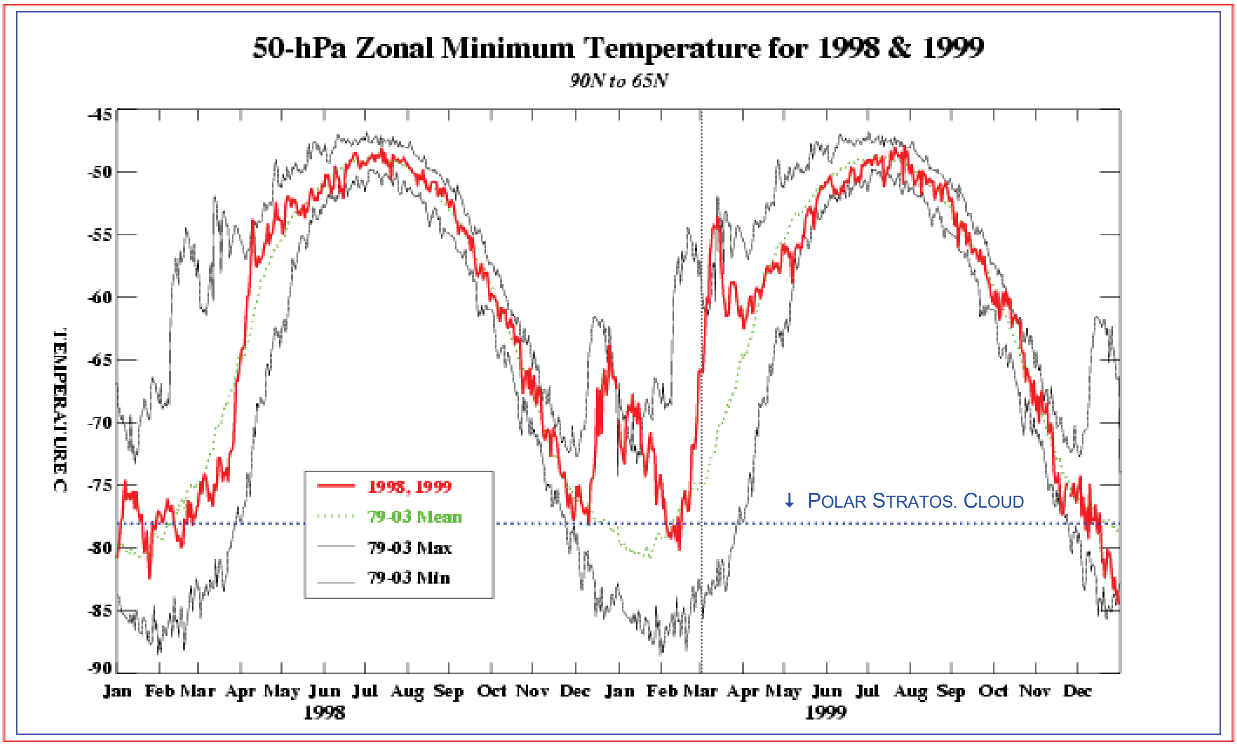


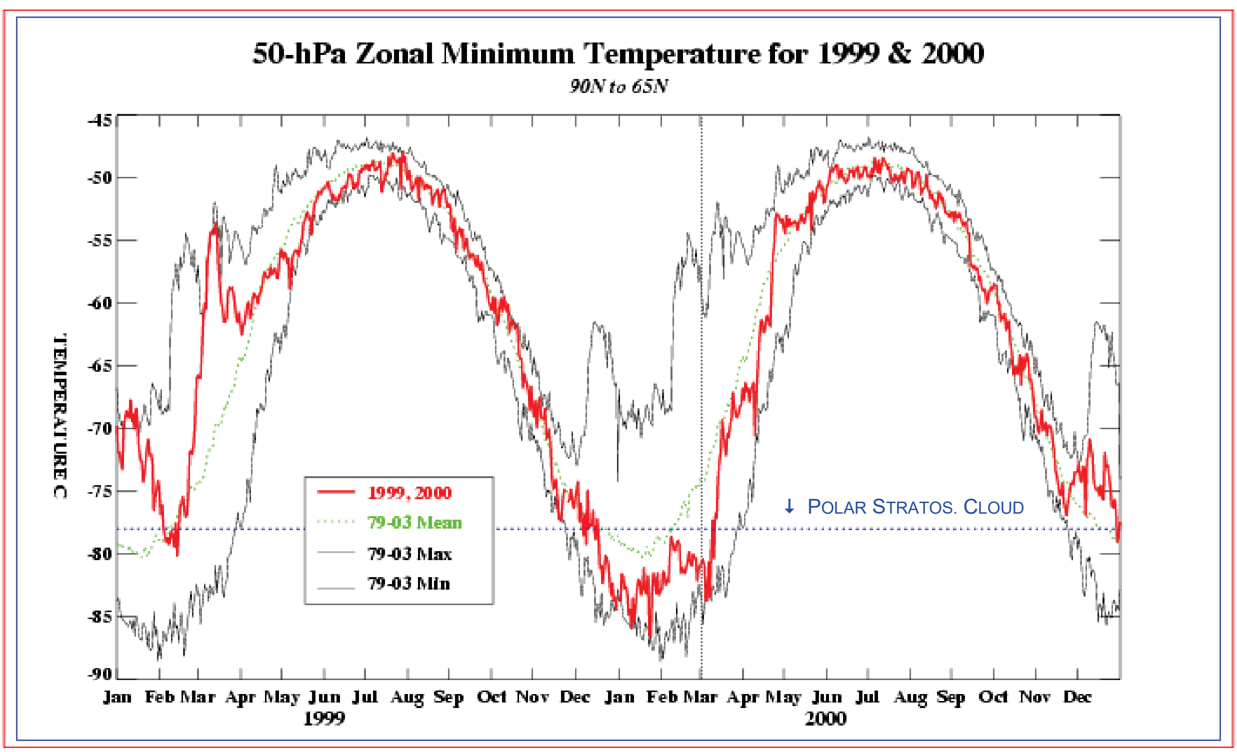
Fig Q10-1, 20 QAs, WMO (2014)

Arctic Temperature, 1998 &1999



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

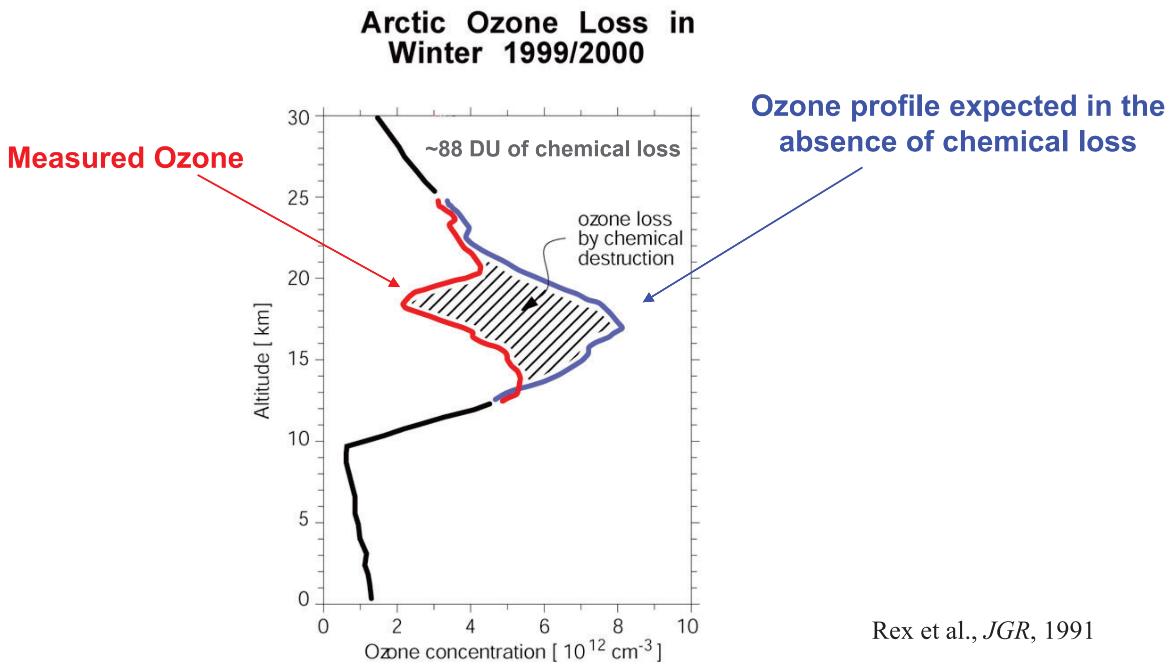
Arctic Temperature, 1999 & 2000



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

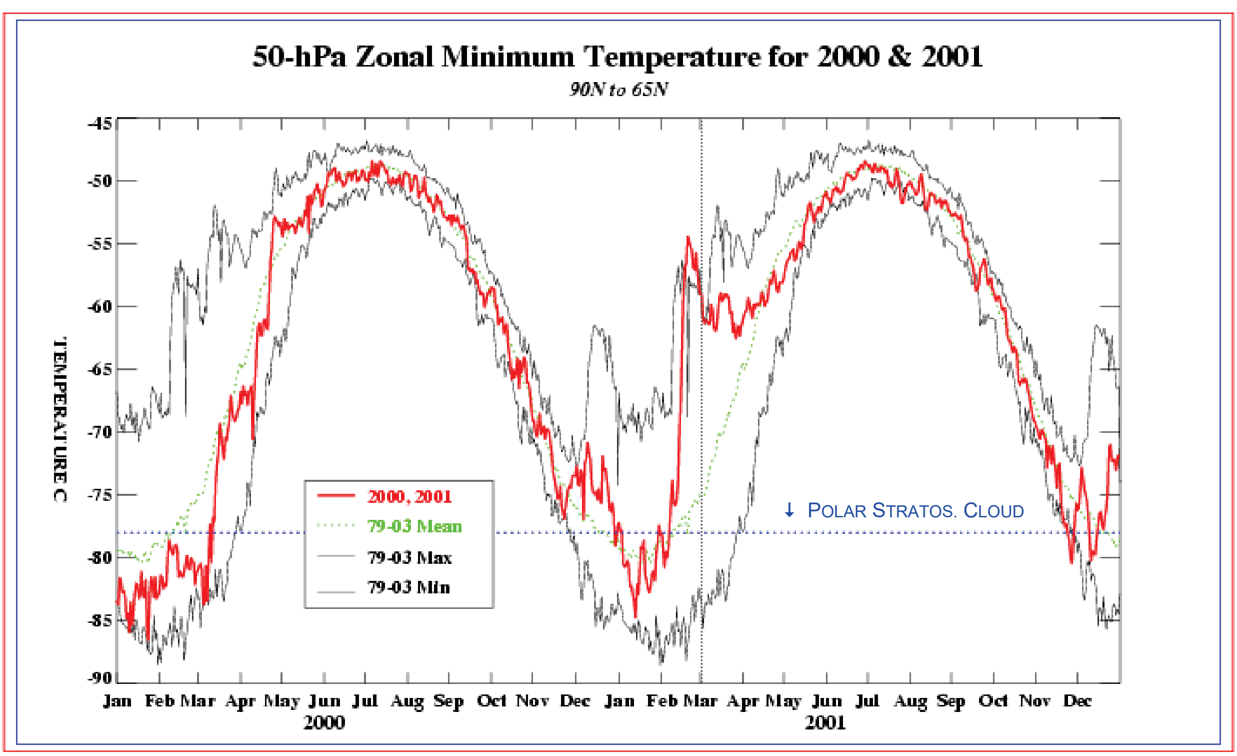
Arctic Winter of 1999/2000

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



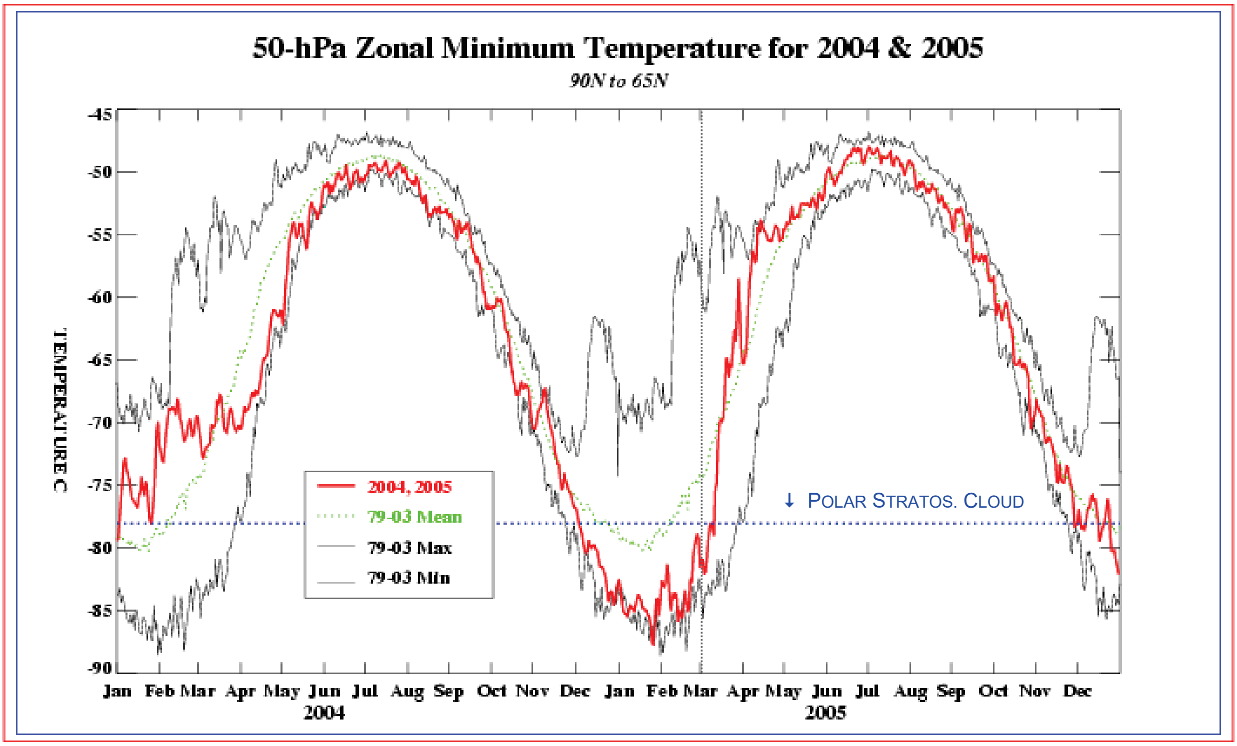
Rex et al., *JGR*, 1991

Arctic Temperature, 2000 & 2001



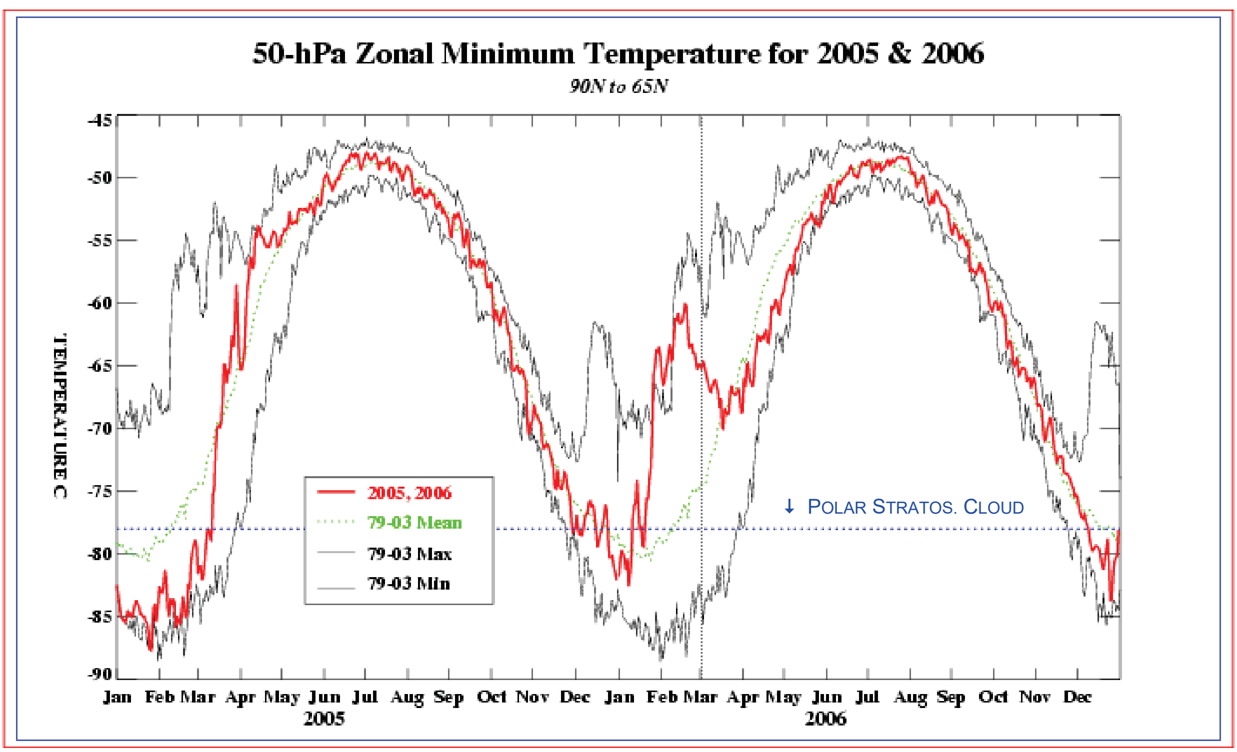
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2001.gif

Arctic Temperature, 2004 & 2005



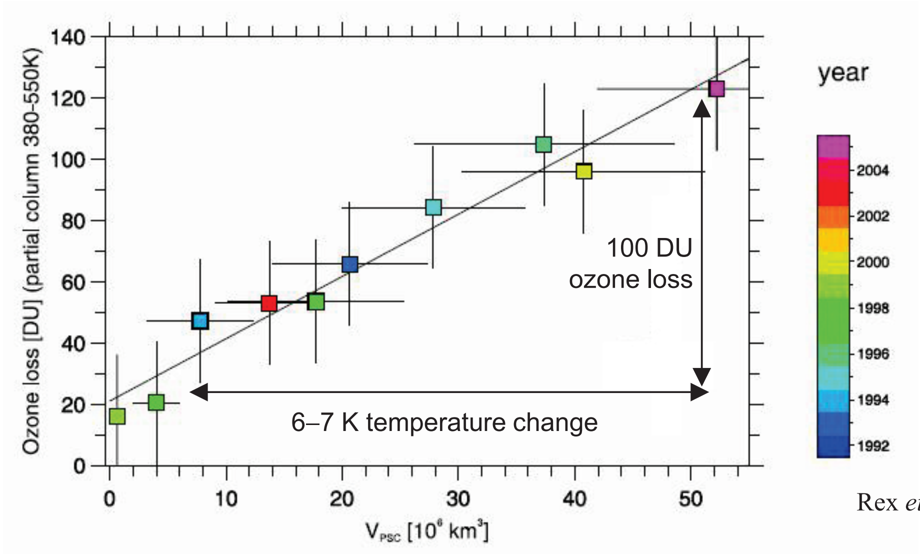
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2005.gif

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 !

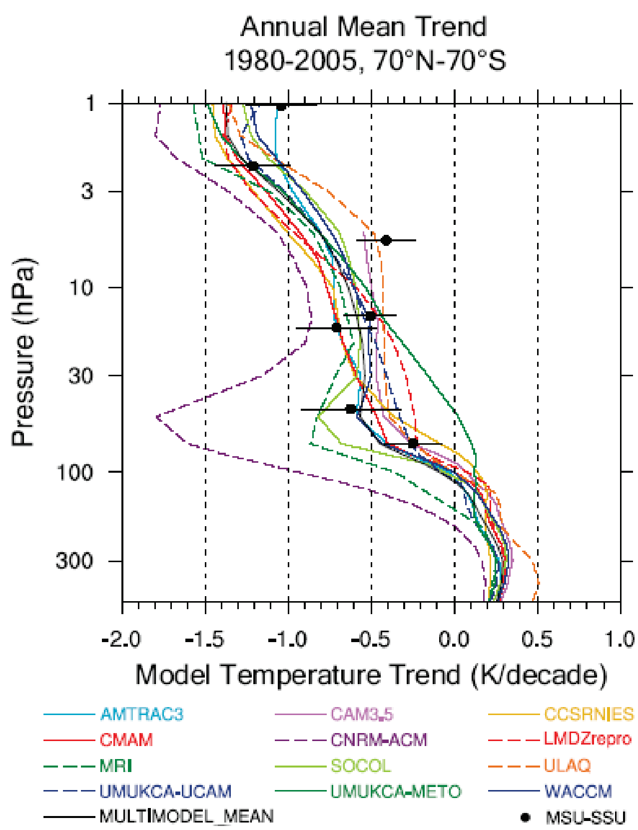


Figure 4−11, WMO/UNEP (2011)

The Stratosphere Cools as the Surface Warms !

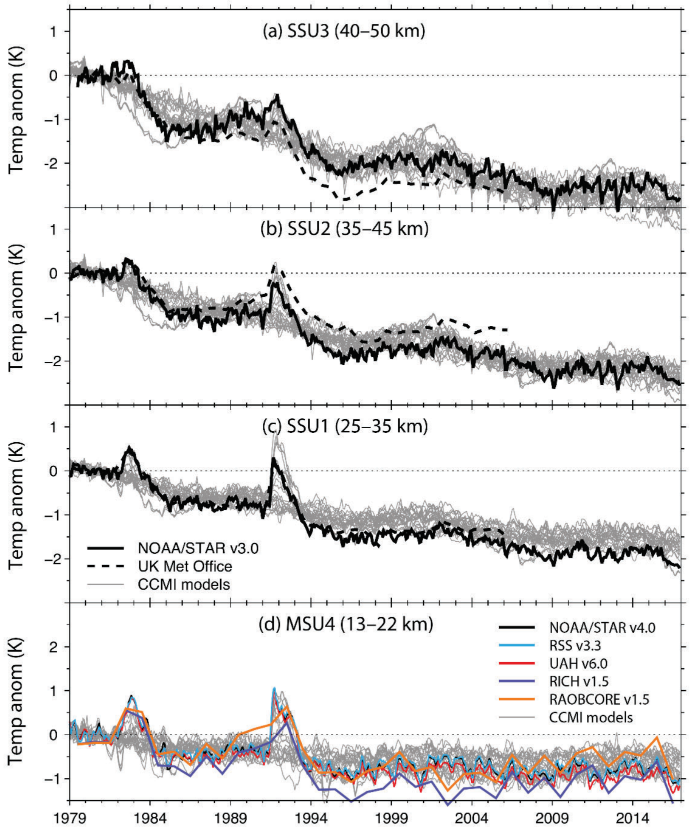


Figure 5-4. Time series of global mean stratospheric temperature anomalies from 1979 to 2016. Panels show SSU Channels 3, 2, 1 (SSU3, SSU2, SSU1; a, b, c) and MSU channel 4 (MSU4; d) for the altitude ranges, datasets, and model outputs indicated in the legends. Gray lines indicate results from a total of 23 ensemble members across 14 Chemistry-Climate Model Initiative (CCMI) models for the REF-C2 experiment, weighted by the appropriate satellite weighting function for comparison with observations. All data in panel d are shown as monthly averages except the UK Met Office dataset, which uses 6-month averages, and the two radiosonde datasets, which are annual means. The radiosonde data are as in Figure 2.8 of Blunden and Arndt (2017). Anomalies are shown relative to 1979–1981. Adapted from Maycock et al. (2018).

Figure 5-4, WMO/UNEP (2018)

Arctic Ozone Loss and Climate Change

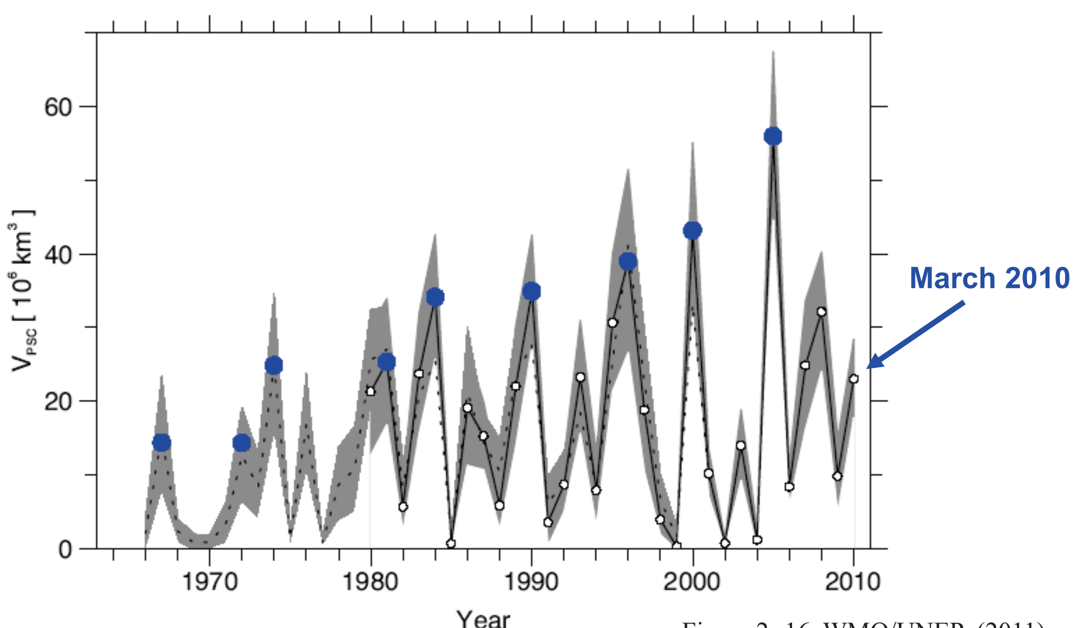
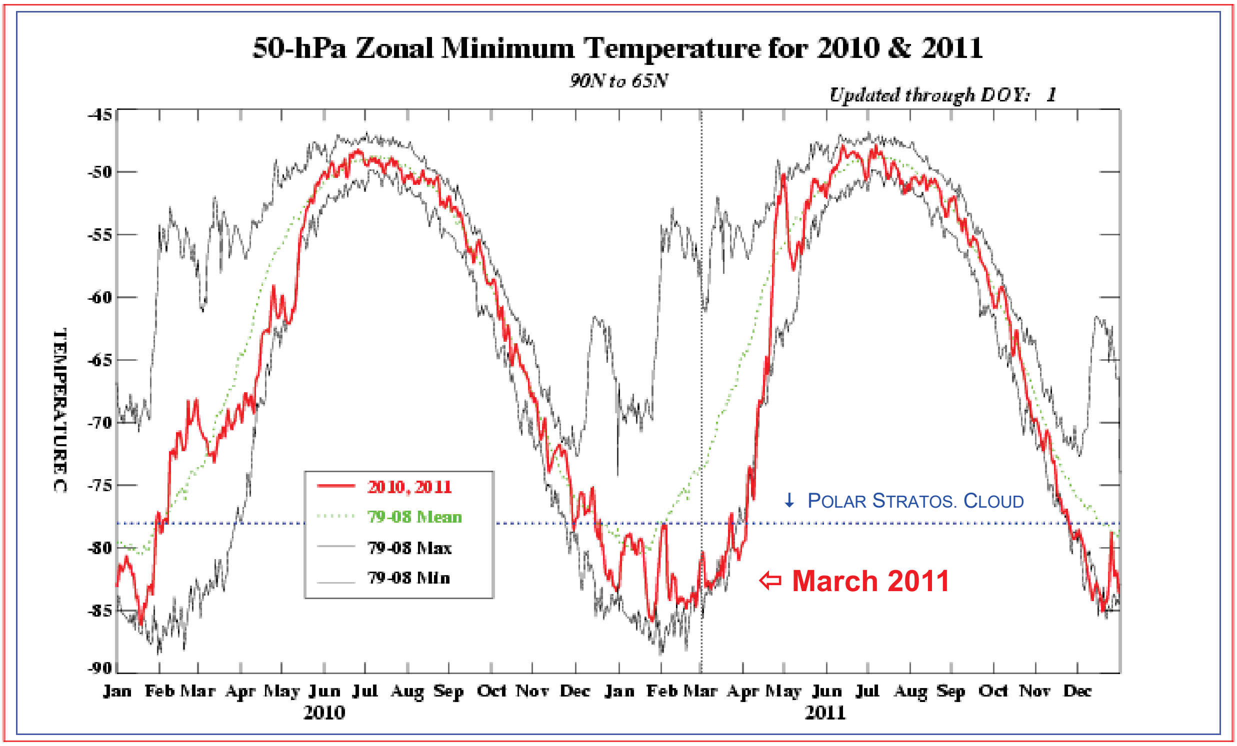


Figure 2−16, WMO/UNEP (2011)
Updated from Rex et al., GRL, 2006
URL in Supplemental Reading

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

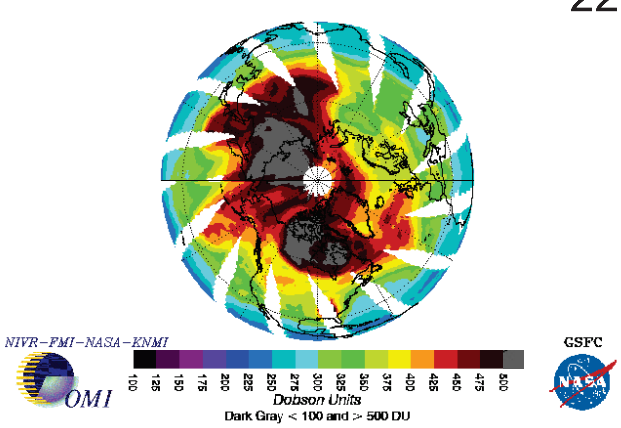
Arctic Temperature: Mar 2011



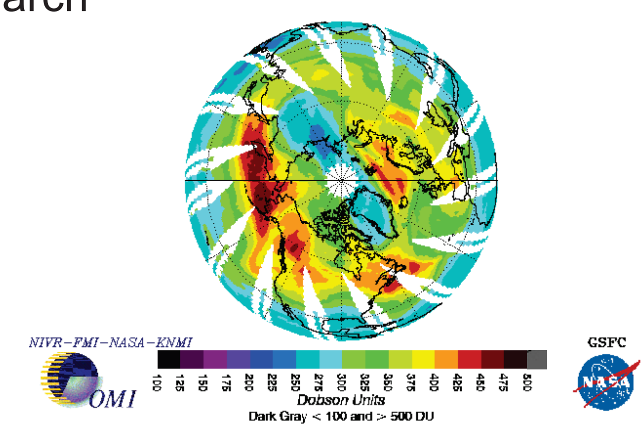
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2011.gif

22 March

OMI Total Ozone for Mar 22, 2010

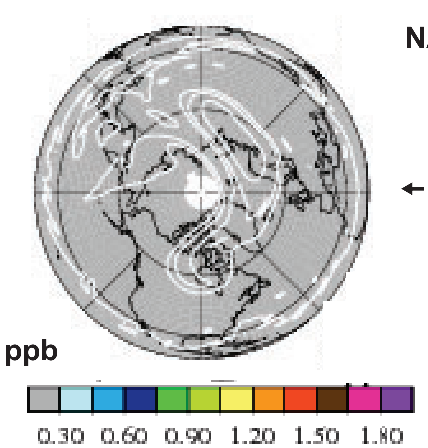


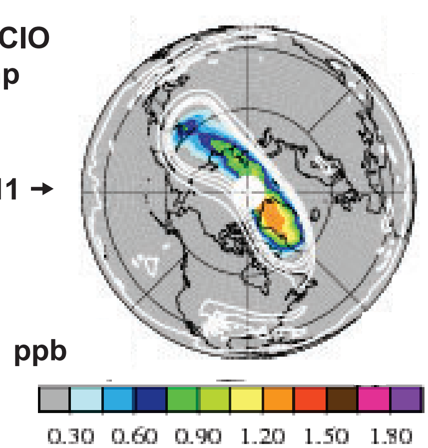
OMI Total Ozone for Mar 22, 2011



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

22 March
← 2010 2011 →





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:

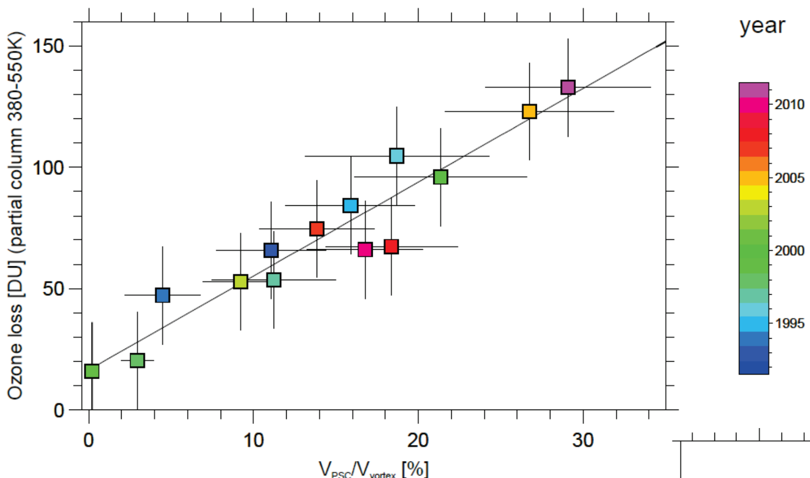
a) Was 2011 really an "Arctic Ozone hole"?

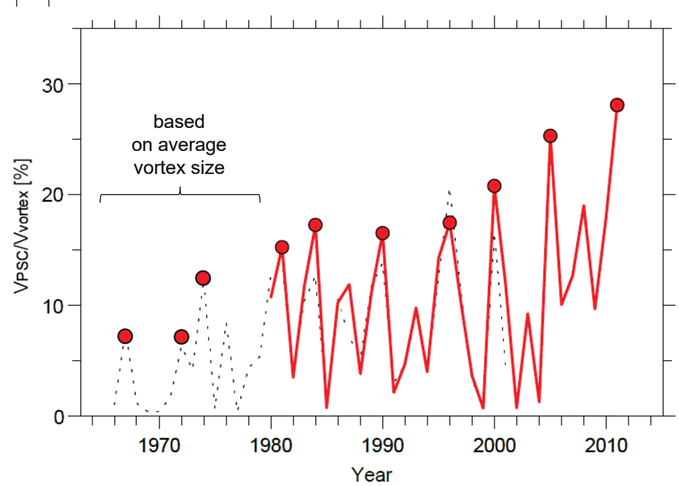
⇒ many in the community strongly resist use of these words to describe Arctic Ozone 2011, despite what is written in Manney et al.

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

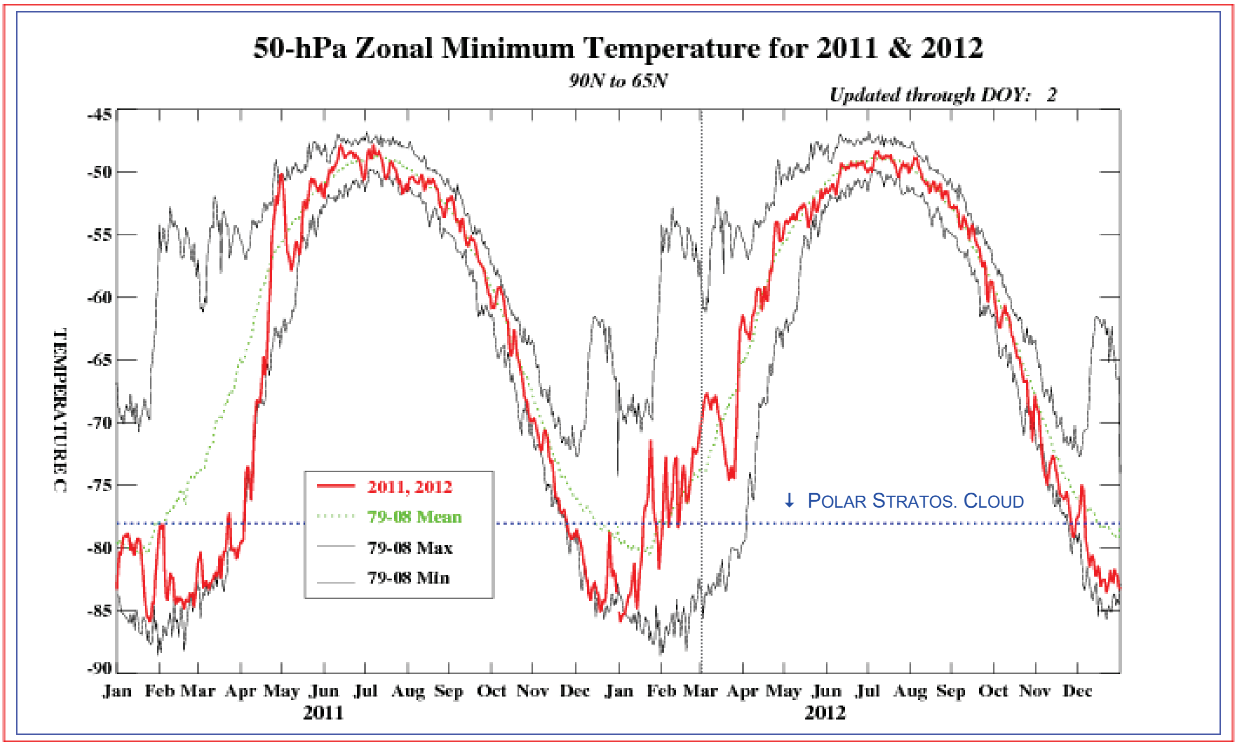
⇒ vitally important active research

Arctic Ozone 2011 in Context of Prior Years



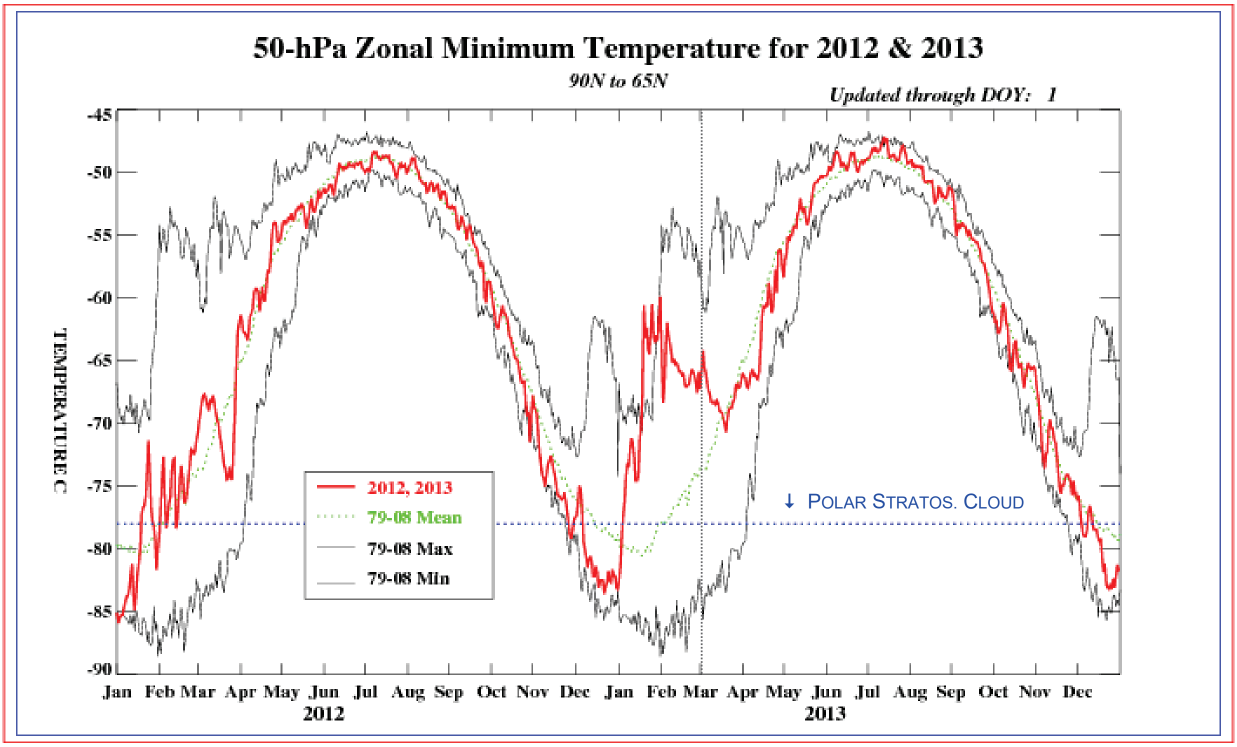


Arctic Temperature: Mar 2012



http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2012.gif

Arctic Temperature: Mar 2013



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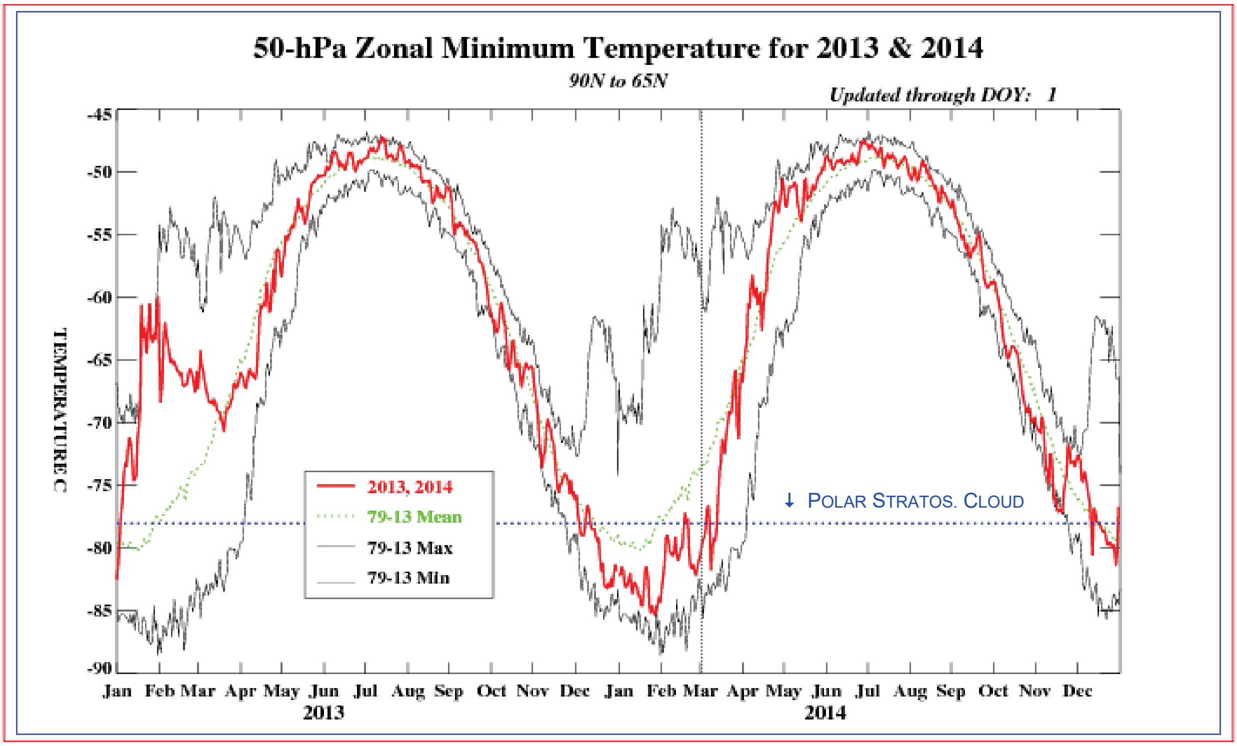
Arctic Temperature: Mar 2014



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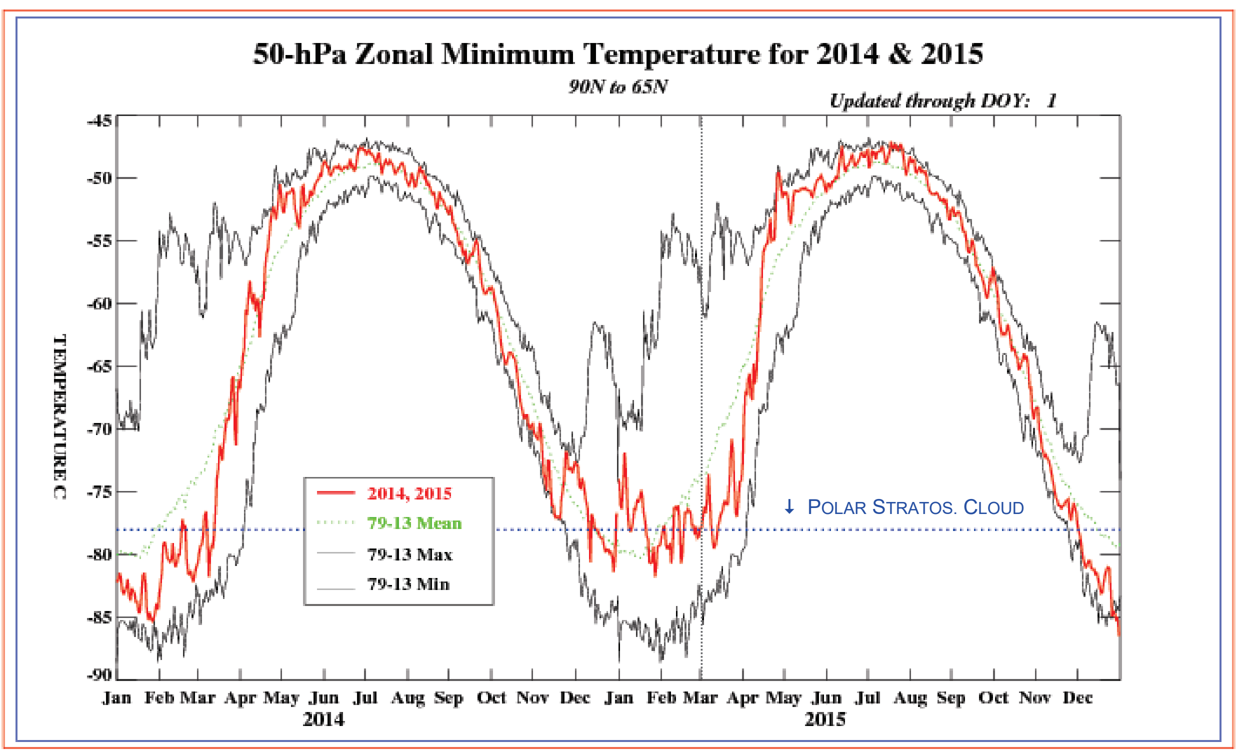
Arctic Temperature: Mar 2015



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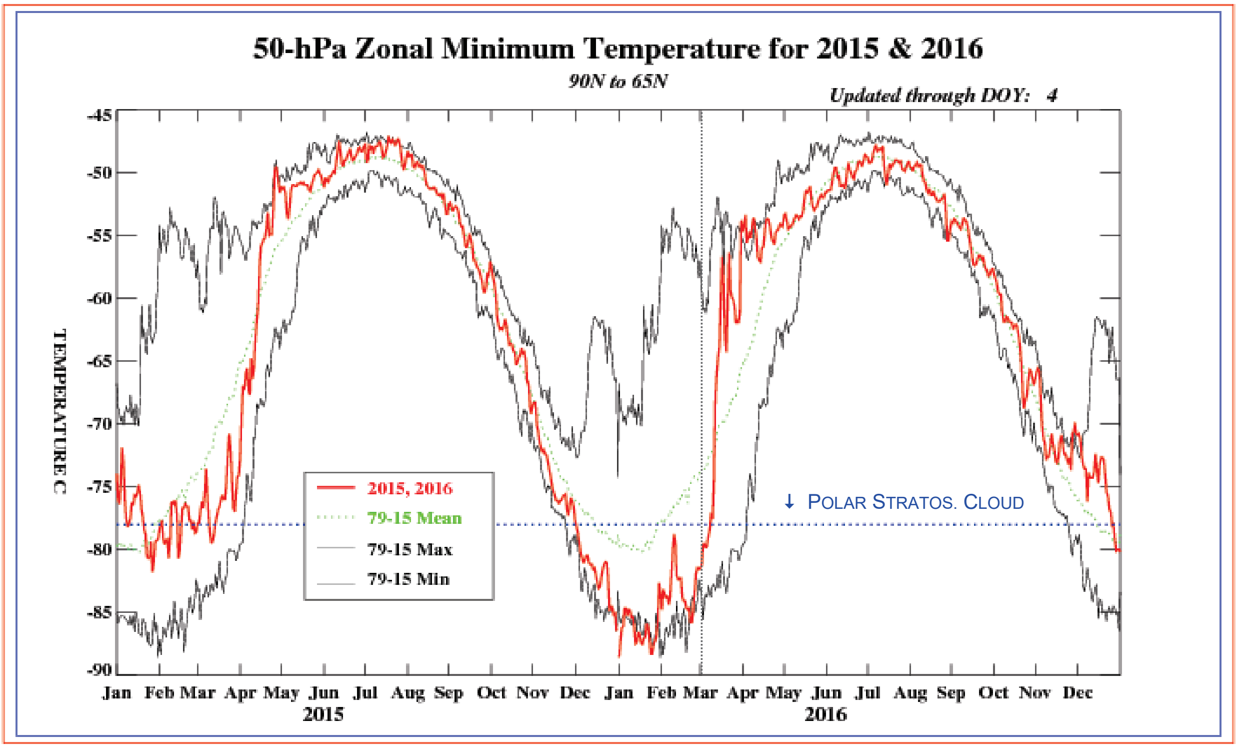
Arctic Temperature: Mar 2016



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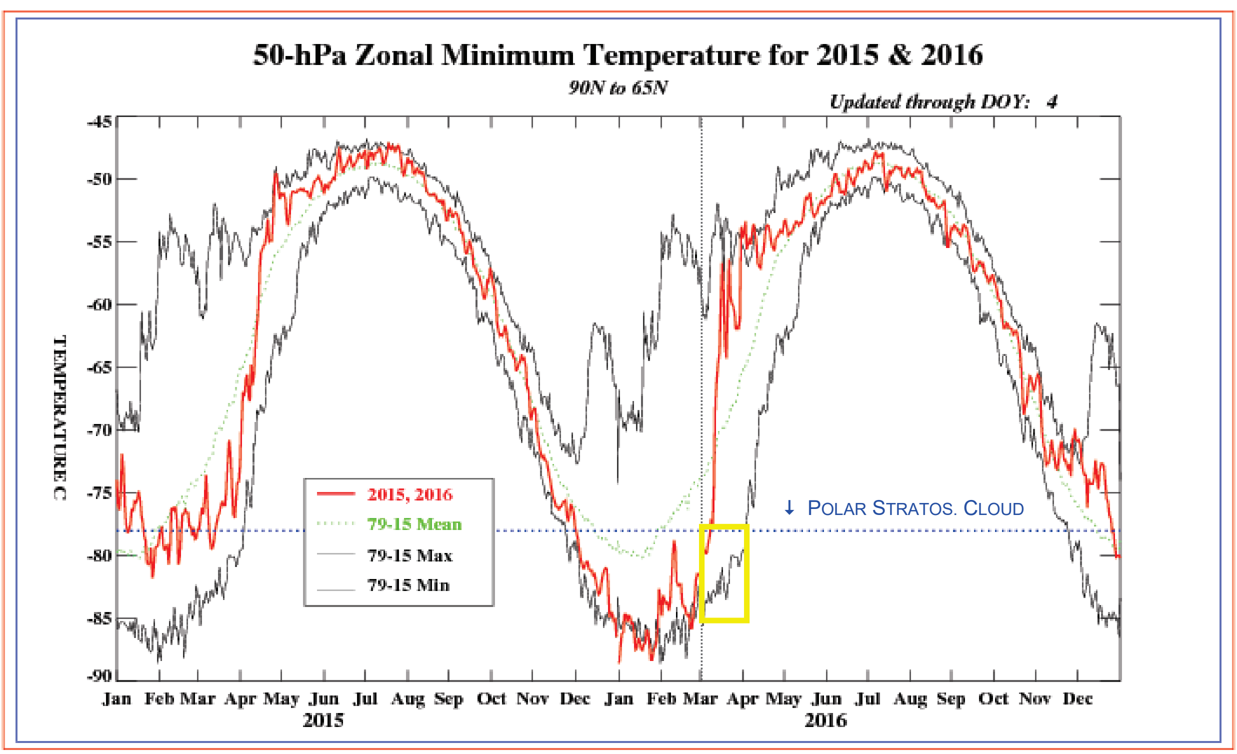
Arctic Temperature: Mar 2016



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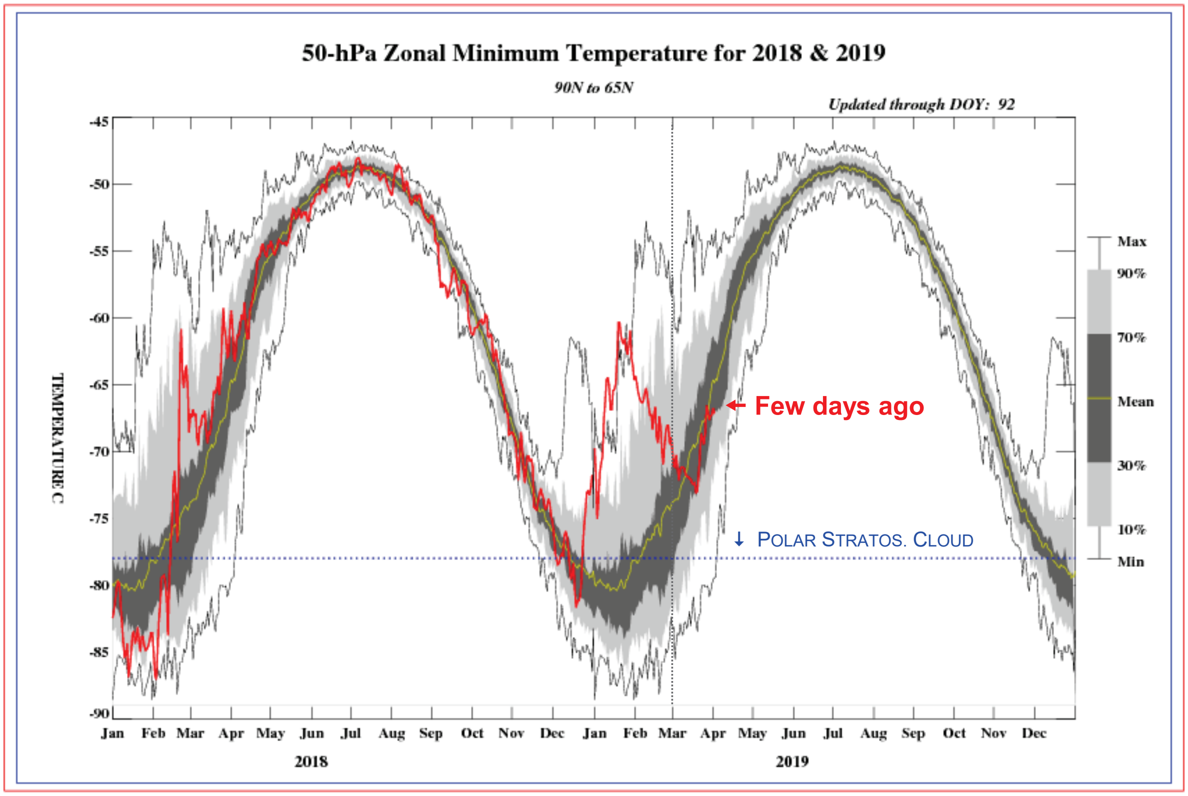
Arctic Temperature: Mar 2019



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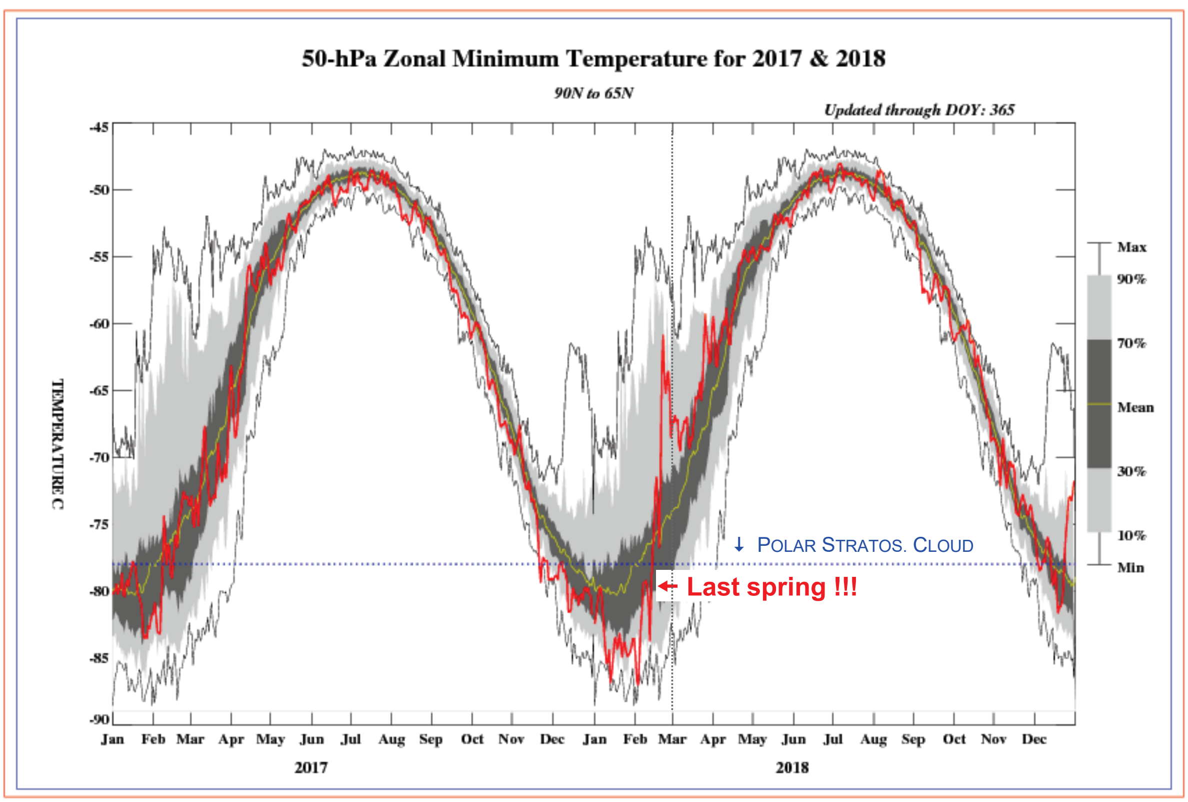
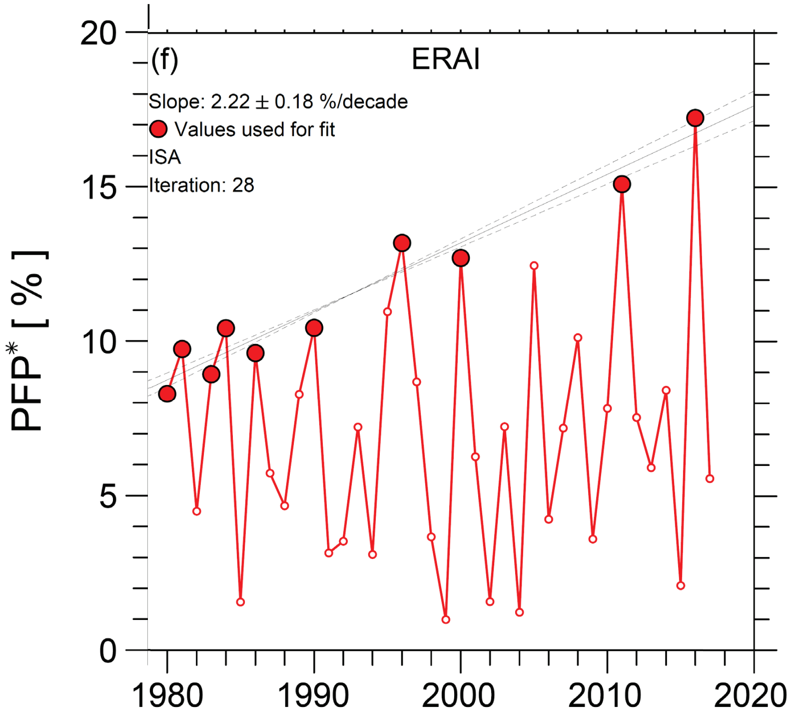
Arctic Temperature: Mar 2018



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

Figure for an upcoming paper



PFP: Potential of vortex cold enough for PSC formation