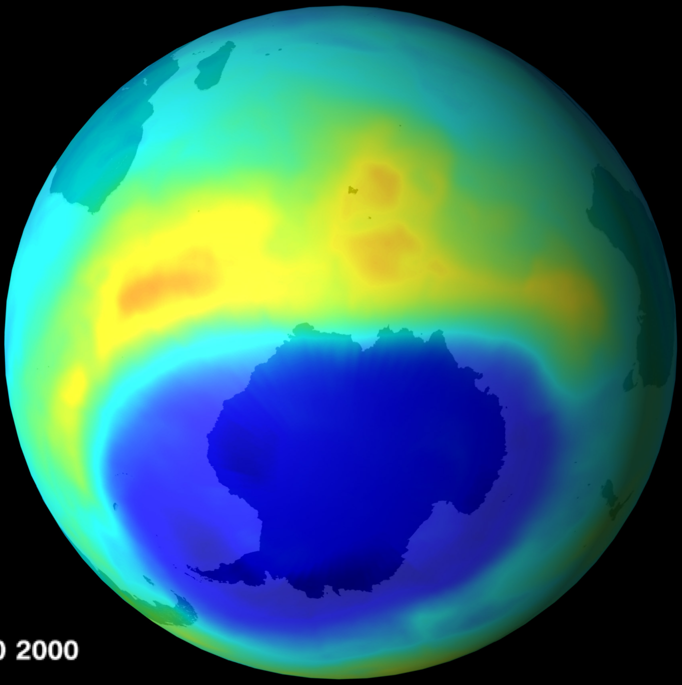
Understanding the Evolution of the Ozone Hole From Depletion to Healing

Susan Solomon   Martin Professor of Environmental Studies, MIT, Cambridge, MA

1. Past: Brief review of the discovery and explanation of the Antarctic ozone hole
2. Present: Mounting evidence that the ozone hole is beginning to heal



Paleo-ozone in the 1970s: Gas phase chemistry

Stratospheric sink for chlorofluoromethanes : chlorine atomc-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$O + ClO \rightarrow Cl + O_2$$

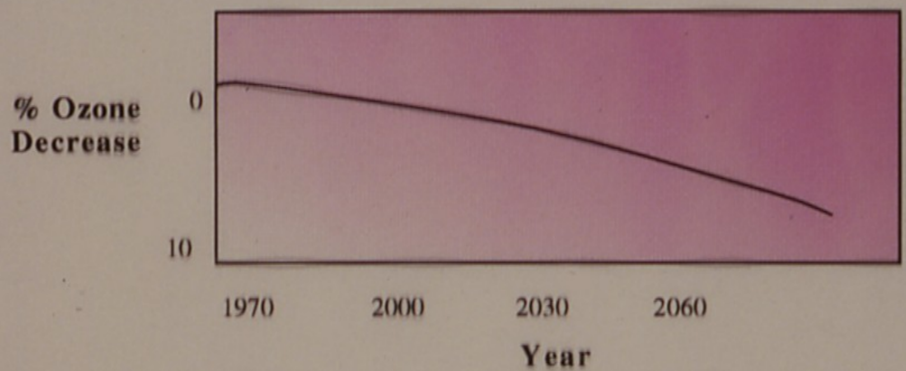
$$\text{Net: } O + O_3 \rightarrow 2O_2$$

(Also: Stolarski and Cicerone)

Reactions among gas molecules only.

The Science: Round 0 and Round 1:

1975-1985. Expected that CFCs and Halons might deplete the ozone layer. Predicted 5-10% in 100 years.

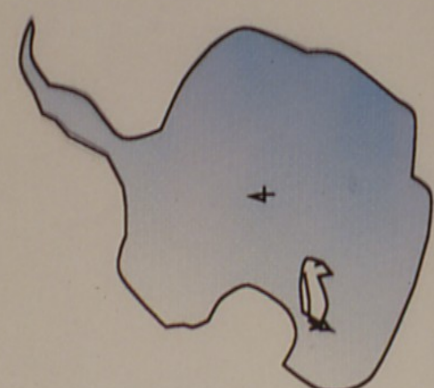


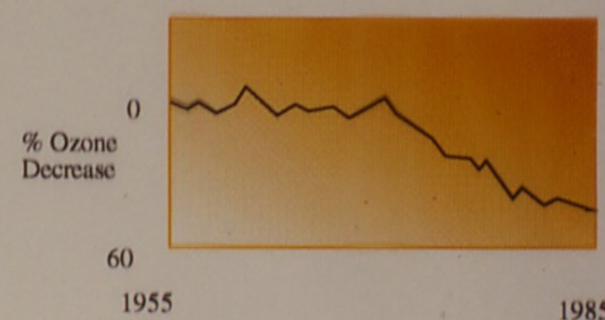
Once used in:

Spray cans
Insulating foams
Refrigeration
AC
Solvents
And more…..

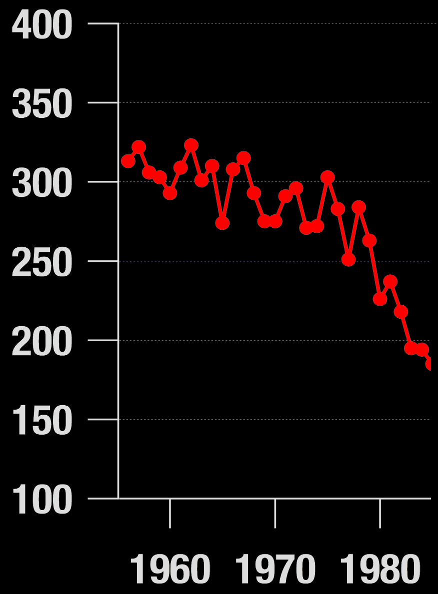
1985. But suddenly everything changed.............

Not 5-10% in a century. 50% now. And in the world's most unlikely place.



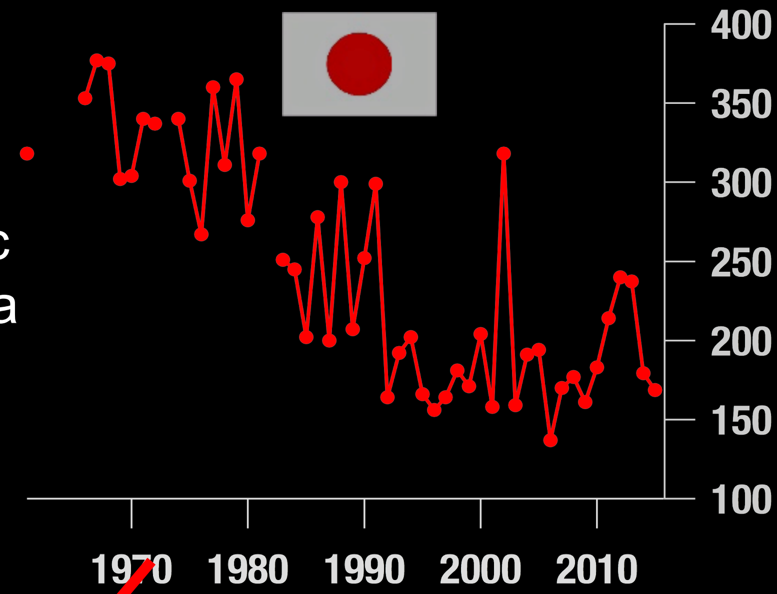


An ozone surprise!!



Oct avg

The Antarctic ozone hole: a challenge to science. Why?

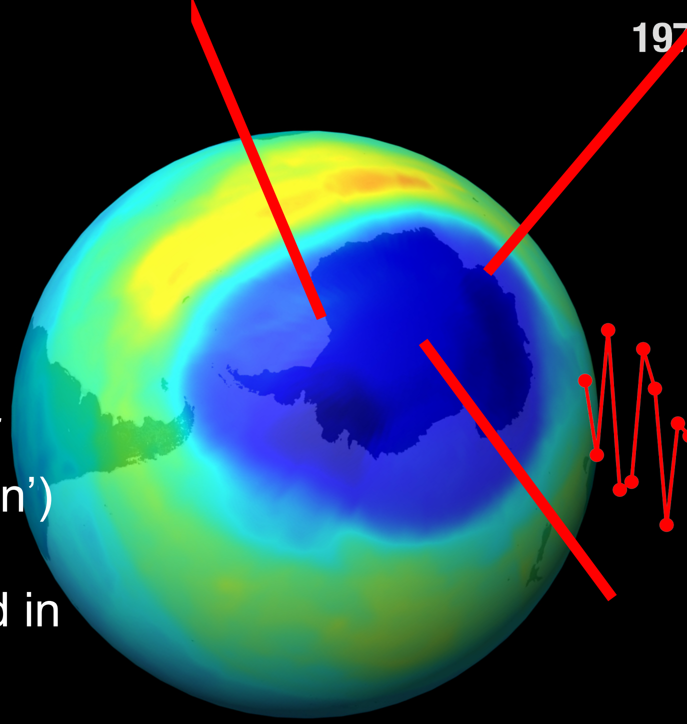


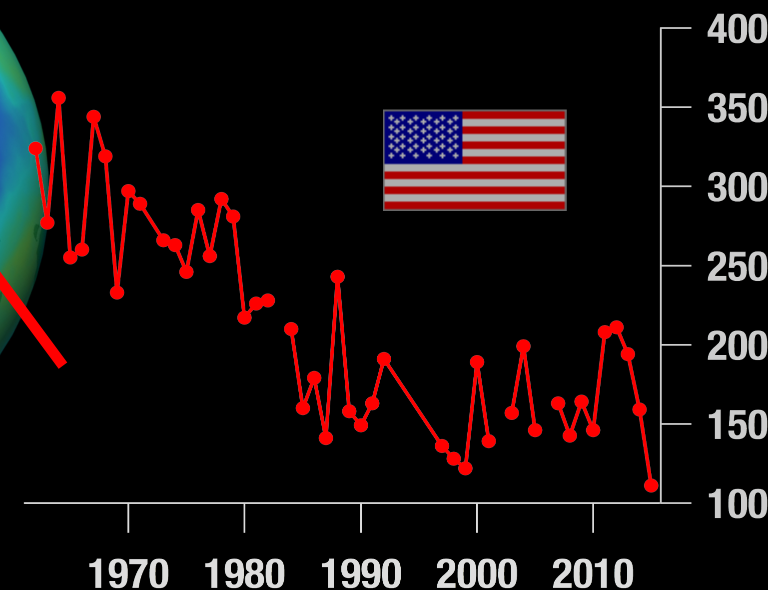
Three stages of ozone 'recovery' (WMO/UNEP):

1) Rate of decline slows down

2) Ozone is flat instead of worsening (in 'remission')

3) Ozone increases -- and in a manner that can be attributed to halogen decreases ('healing')





A letter from the British Antarctic Survey

Mr Harry Bloxom,
Ozone Sonde Mission Manager,
NASA Wallops Flight Center,
Wallops Island,
Virginia,
USA 23337

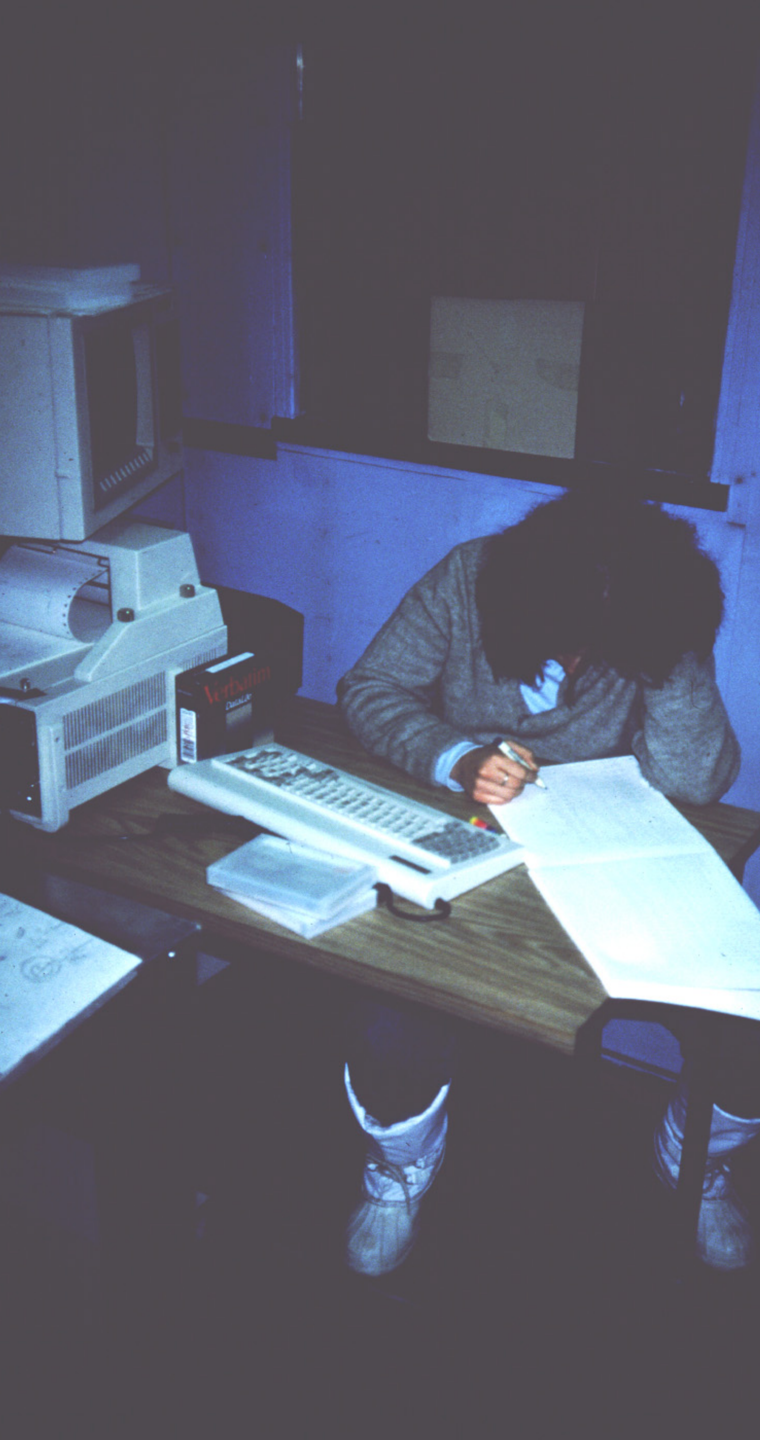
1983 October 10

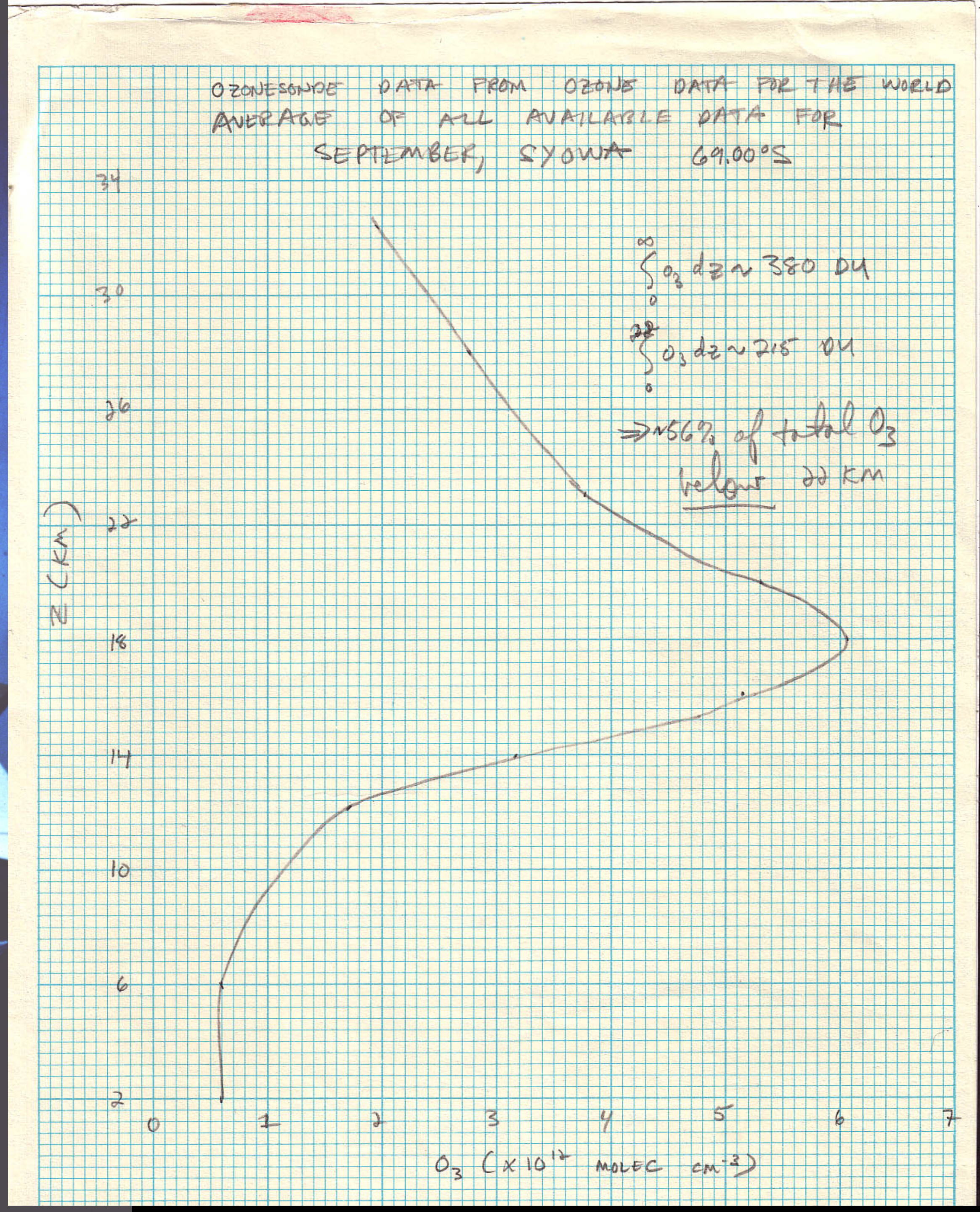
Dear Mr. Bloxom,

Our base at Halley Bay, Antarctica is currently reporting rather low values of ozone. Values are around 200 dobson units, which is considerably lower than our 1957 - 72 average. We would be interested to know if this is confirmed by satellite data. If so, is it possibly connected with the El Chichon erruption - there is some evidence that an increased aerosol load has been detected by turbidity measurements with an angstrom pyrheliometer.

Yours sincerely,

Jonathan D. Shanklin




OZONESONDE DATA FROM OZONE DATA FOR THE WORLD
AVERAGE OF ALL AVAILABLE DATA FOR
SEPTEMBER, SYOWA 69.00°S
$\int_0^\infty O_3 \, dz \sim 380$ DU
$\int_0^{22} O_3 \, dz \sim 215$ DU
$\Rightarrow \sim 56\%$ of total O_3
below 22 KM
Z (KM)
34
30
26
22
18
14
10
6
2
0 1 2 3 4 5 6 7
O_3 ($\times 10^{12}$ MOLEC cm^{-3})

1985: A Mystery, With A Few Important Clues

The Halley data:

Missing total ozone, but from WHERE in altitude?

The Syowa data demonstrated WHERE the depletion was happening:

NATURE — NATURE VOL. 321 19 JUNE 1986

On the depletion of Antarctic ozone

Susan Solomon*, Rolando R. Garcia†, F. Sherwood Rowland‡ & Donald J. Wuebbles§

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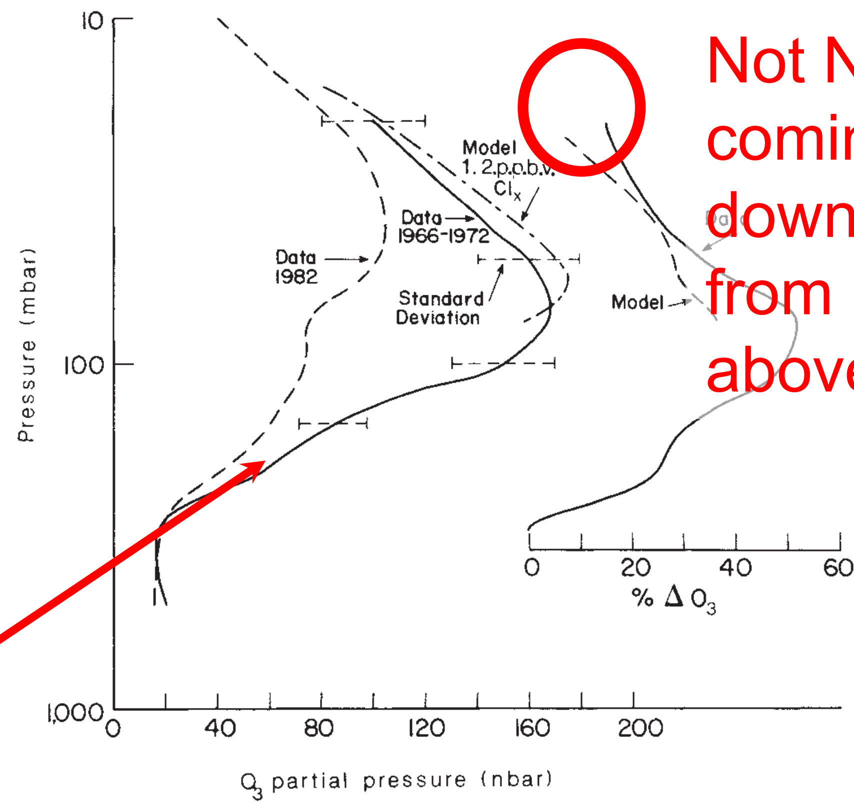
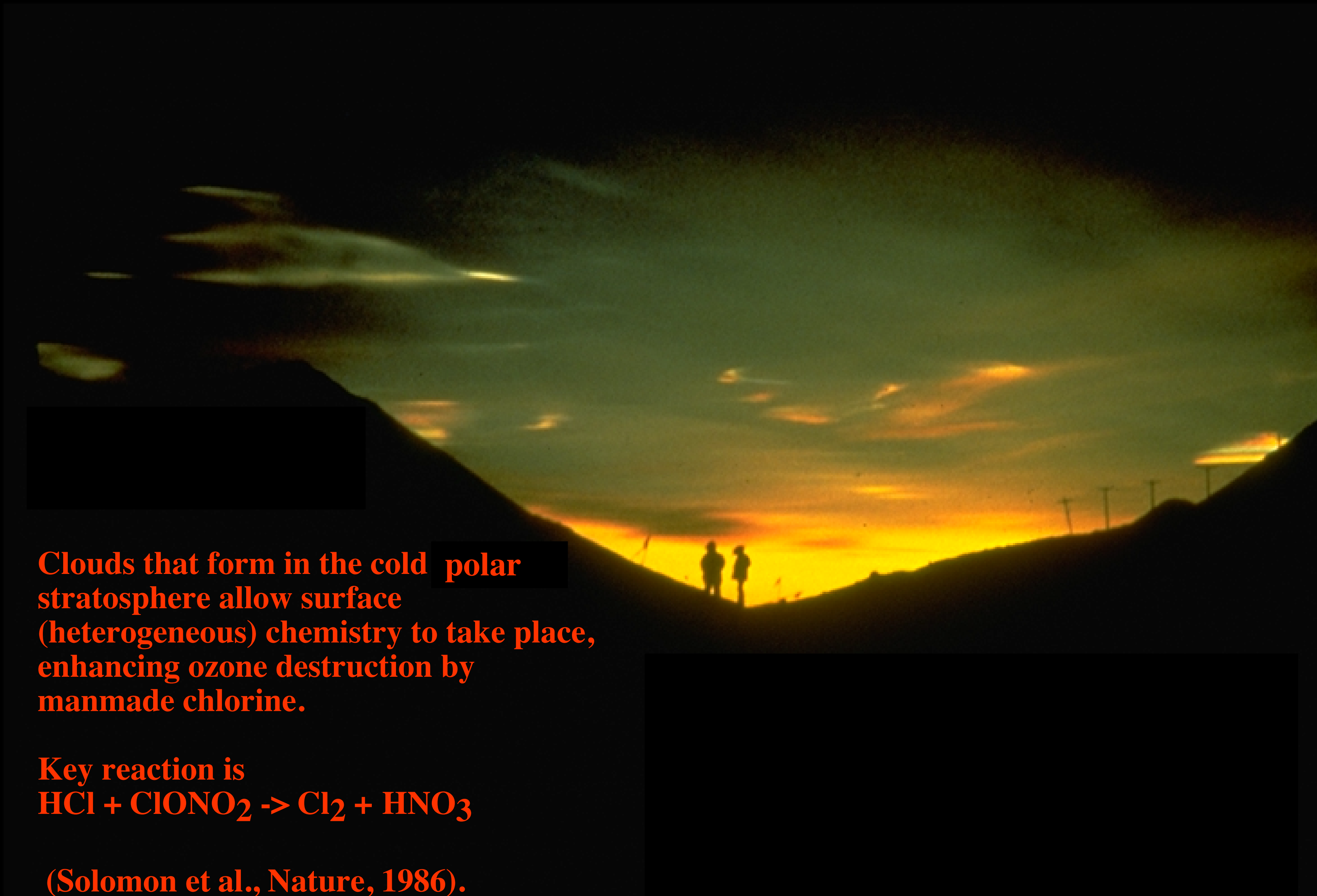
† NCAR, Boulder, Colorado 80307, USA
‡ Department of Chemistry, University of California, Irvine, California 92717, USA
§ Lawrence Livermore Laboratory, Livermore, California 94550, USA



Not NOx coming down from above

Fig. 2 Vertical profile of the ozone partial pressure observed over Syowa in the late 1960s and early 1970s, and the standard deviation, compared with observations in 1982, for the month of October[3,4]. The model vertical profile in the late 1960s is shown for comparison. Percentage changes of the model and the data for the same time period are also indicated.

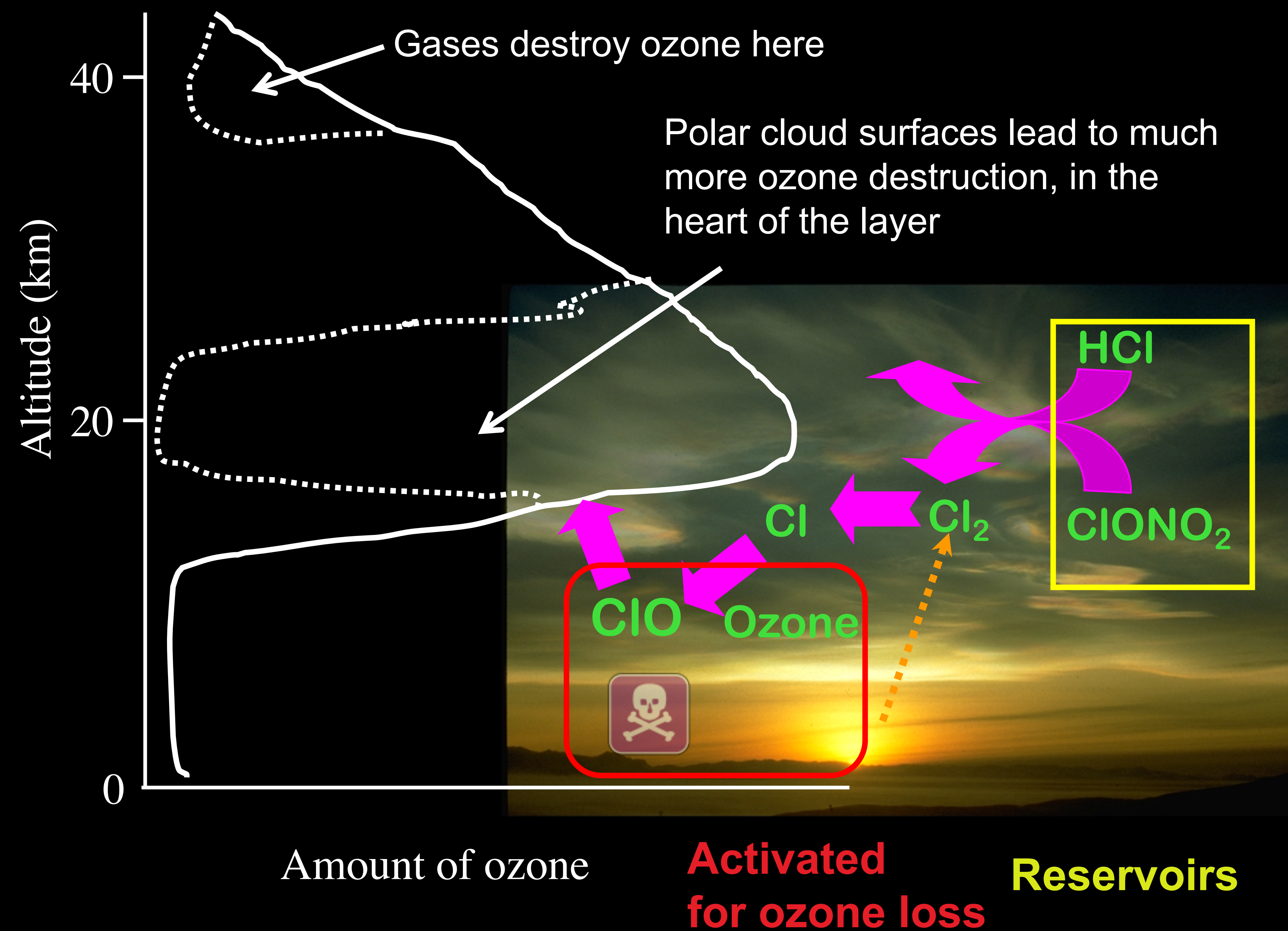
Fingerprint in altitude: The ozone was missing from the heart of the layer, 10-25 km, not 40 km as predicted from gas-phase chemistry



Clouds that form in the cold polar stratosphere allow surface (heterogeneous) chemistry to take place, enhancing ozone destruction by manmade chlorine.

Key reaction is
$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$

(Solomon et al., Nature, 1986).



Gases destroy ozone here
Polar cloud surfaces lead to much more ozone destruction, in the heart of the layer
40
20
0
Altitude (km)
Amount of ozone
HCl
$ClONO_2$
Cl_2
Cl
ClO
Ozone
Activated for ozone loss
Reservoirs

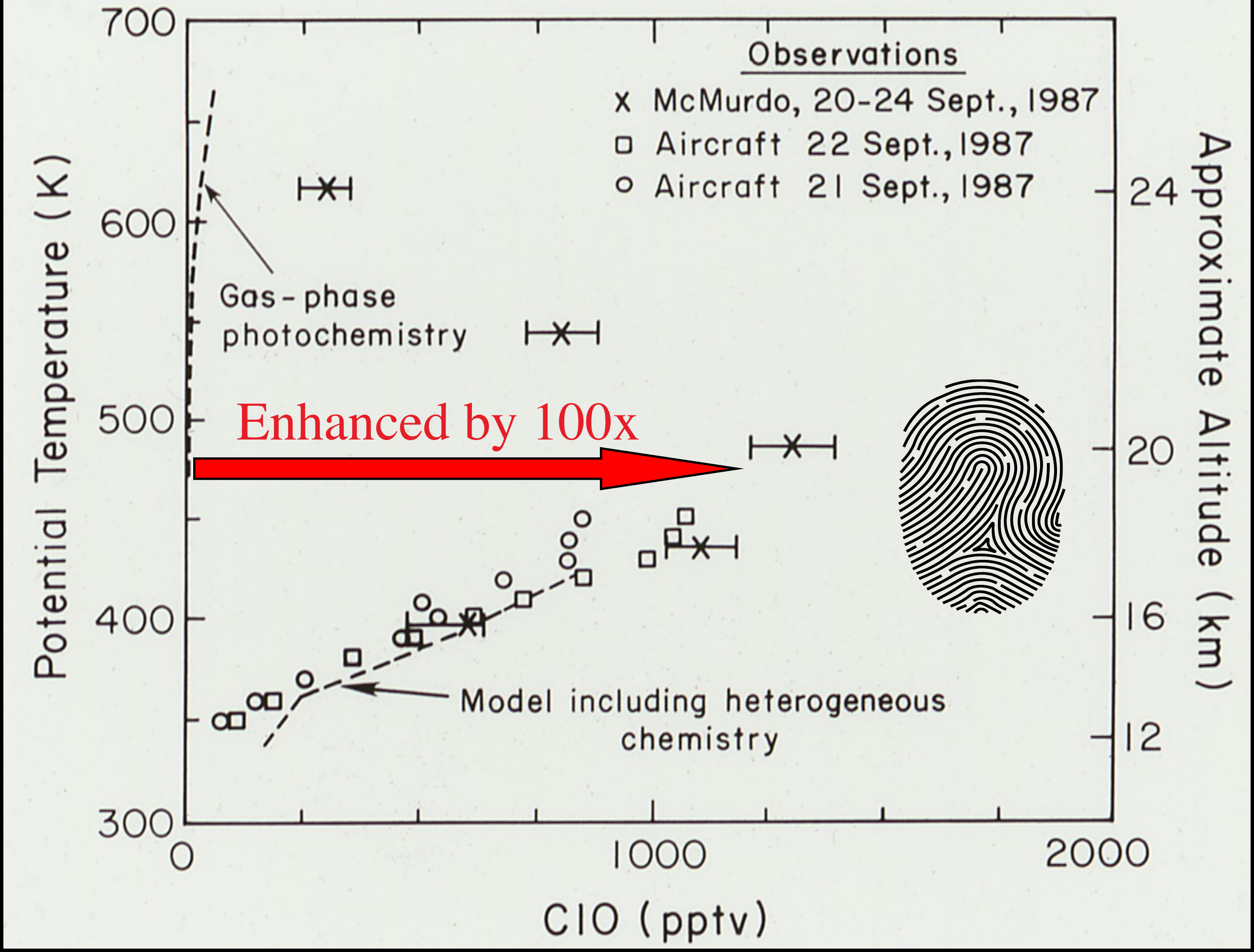
Susan Solomon, August 1986 noon
The opportunity of a scientific lifetime

Measuring ClO in Antarctica:

Ground-based microwave spectroscopy by de Zafra and colleagues, SUNY

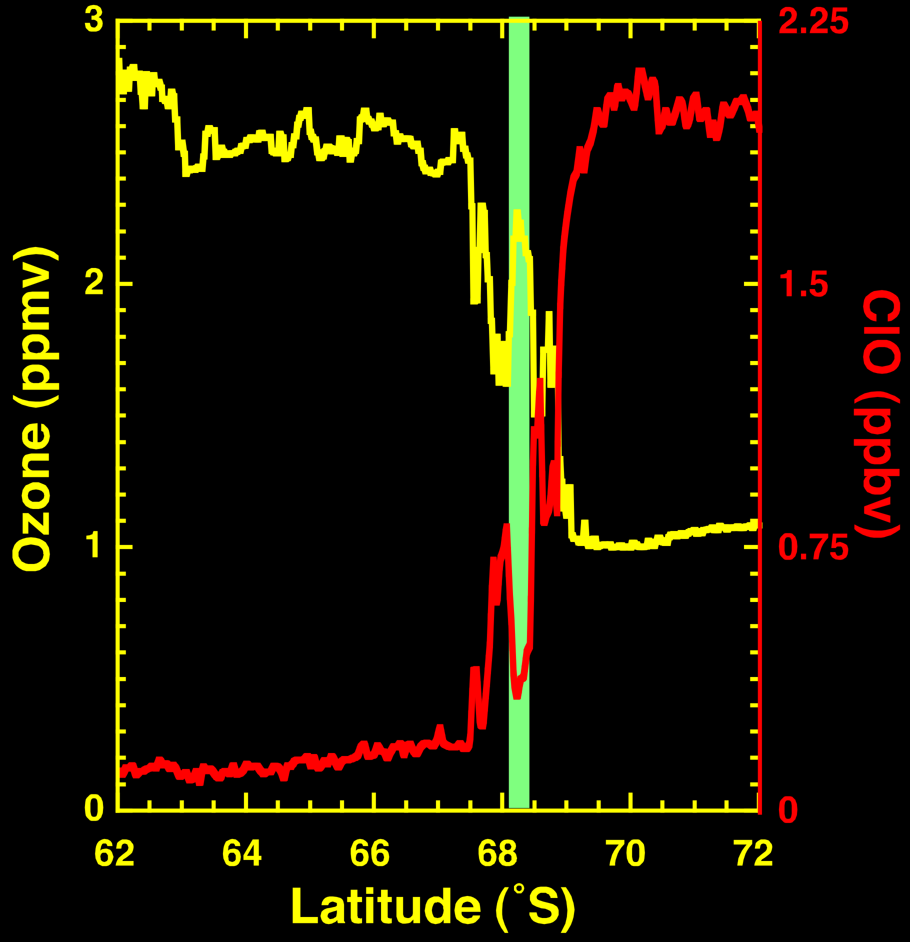
Airborne resonance fluorescence: Anderson and colleagues, Harvard

Matching fingerprint in altitude: Enhanced ClO from 12-24 km, just where the ozone was missing



1000 pptv ClO destroys about 2-3% of the ozone per day based on known chemistry …so ozone all gone in about 5 weeks….

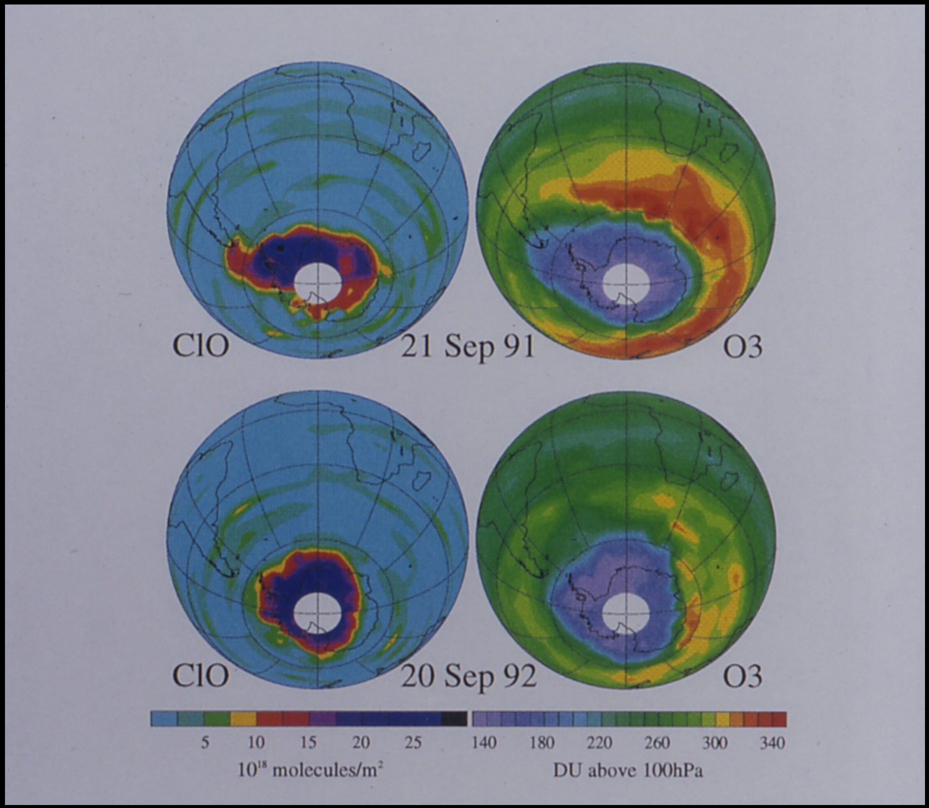
Fingerprint in latitude



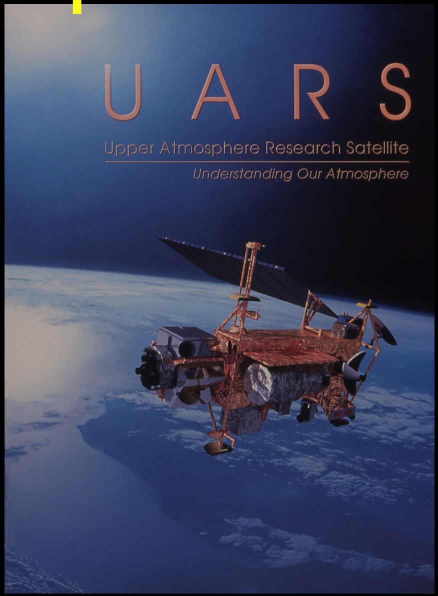
AAOE mission in August-September 1987:

observations inside the polar vortex show high ClO is related to a strong decrease of ozone over the course of the Antarctic spring, as sunlight returns to the polar cap

A Bird's Eye Fingerprint from Space



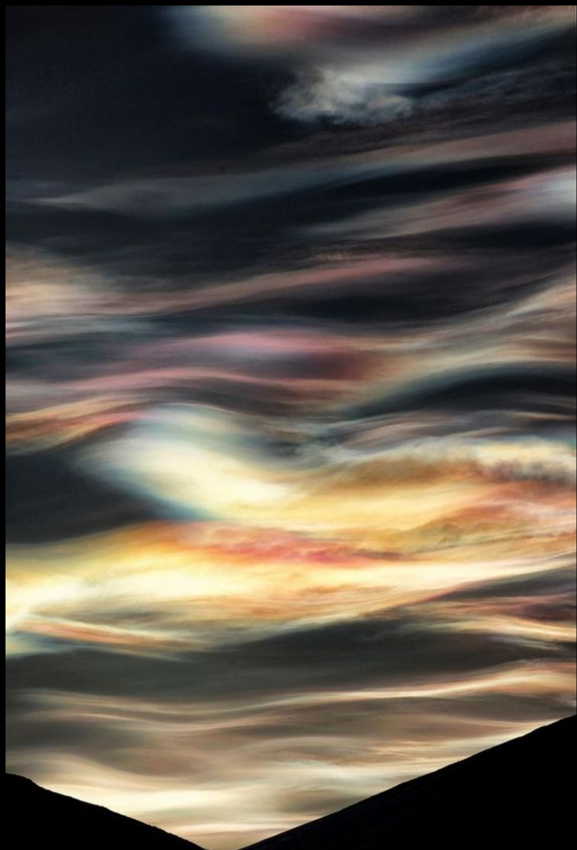
Waters, Santee, and colleagues

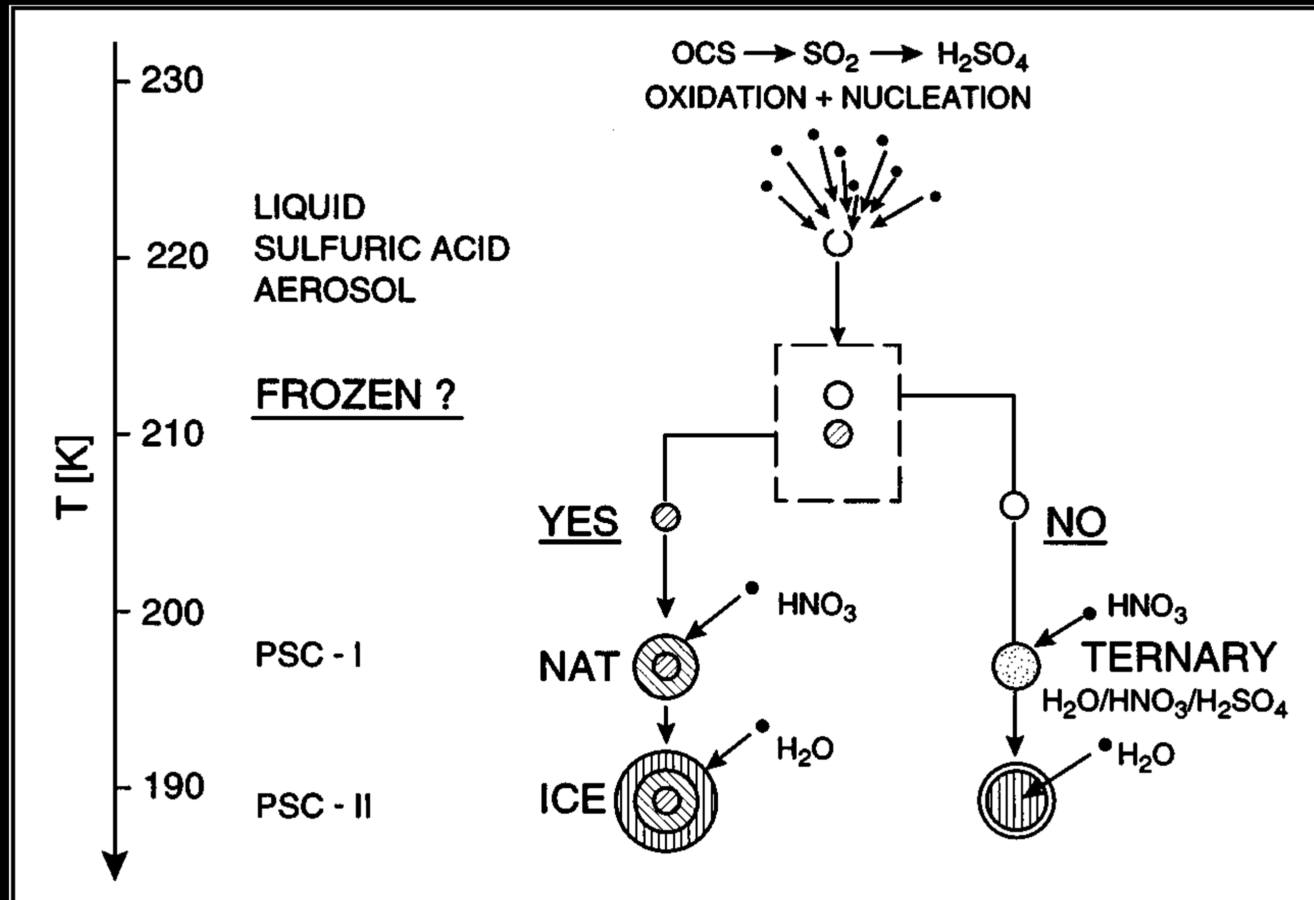


Antarctica: cold nearly every year, with some variability

Arctic: more variable, and pushed by waves, so generally warmer; less ozone depletion

Types of PSC: Frozen and Liquid



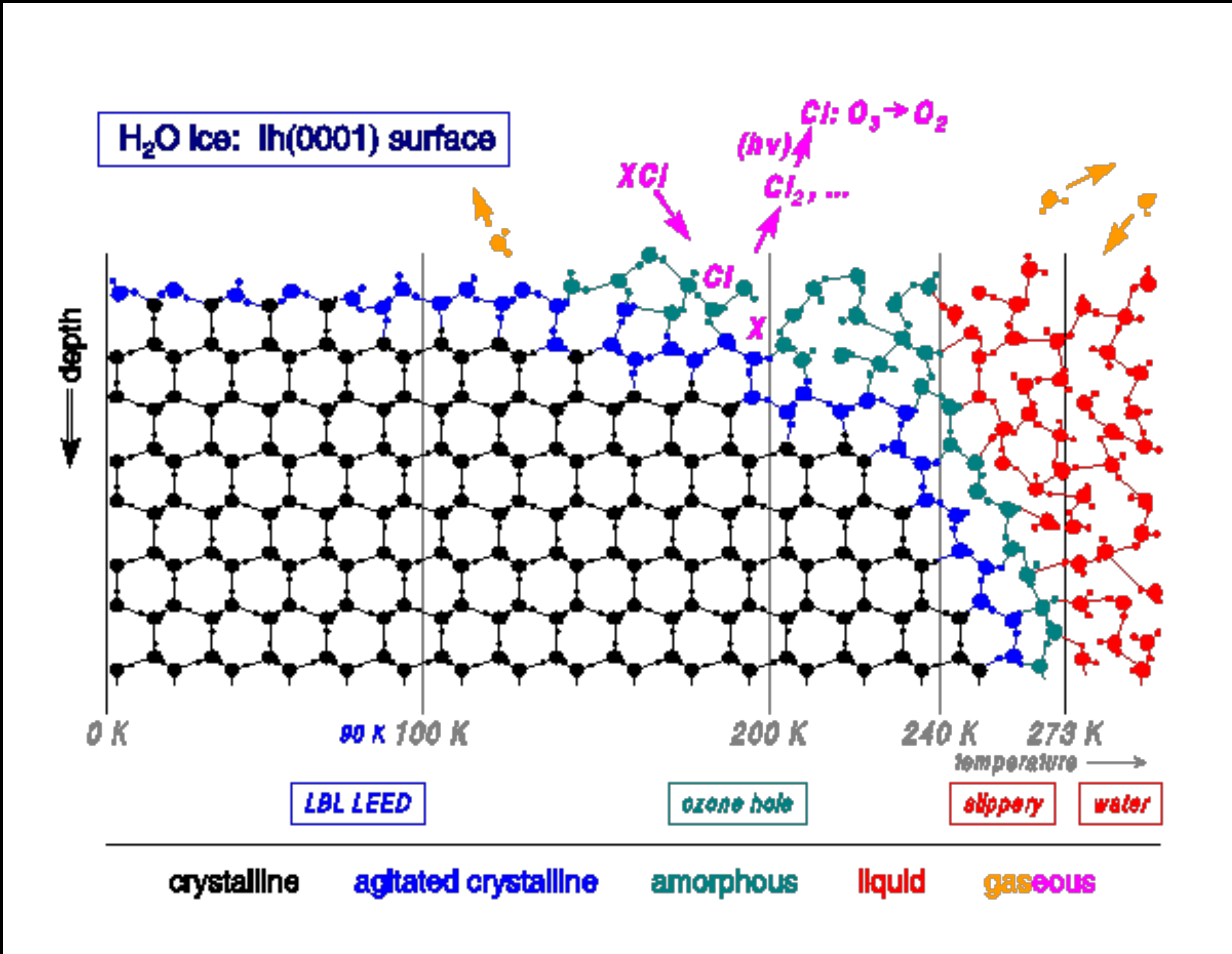


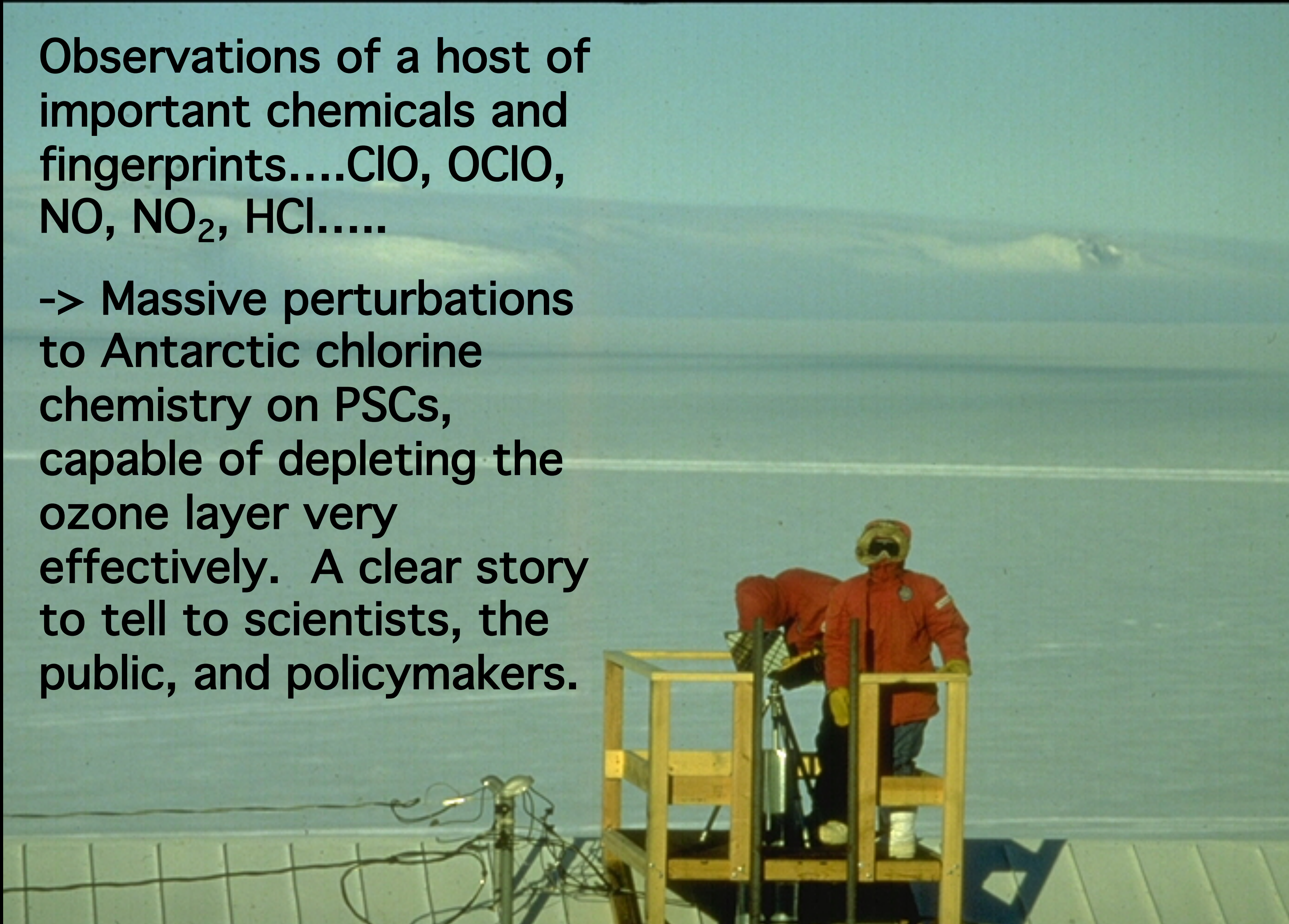
Composition, chemistry, and microphysical PSC processes advanced through the work of many [Tolbert, Molina, Ravi, Toon, Crutzen, Arnold, Carlsaw, Peter, Tabazadeh, Koop, and…..].

A Key Common Feature in Ice and Liquid Particles

Quasi-liquid on solid and liquid PSC, so all take up HCl and become reactive enough to make an ozone hole if temperatures drop below 192K (see Solomon et al., JGR, 2015).

Significant remaining uncertainties in kinetics – but v few kineticists!

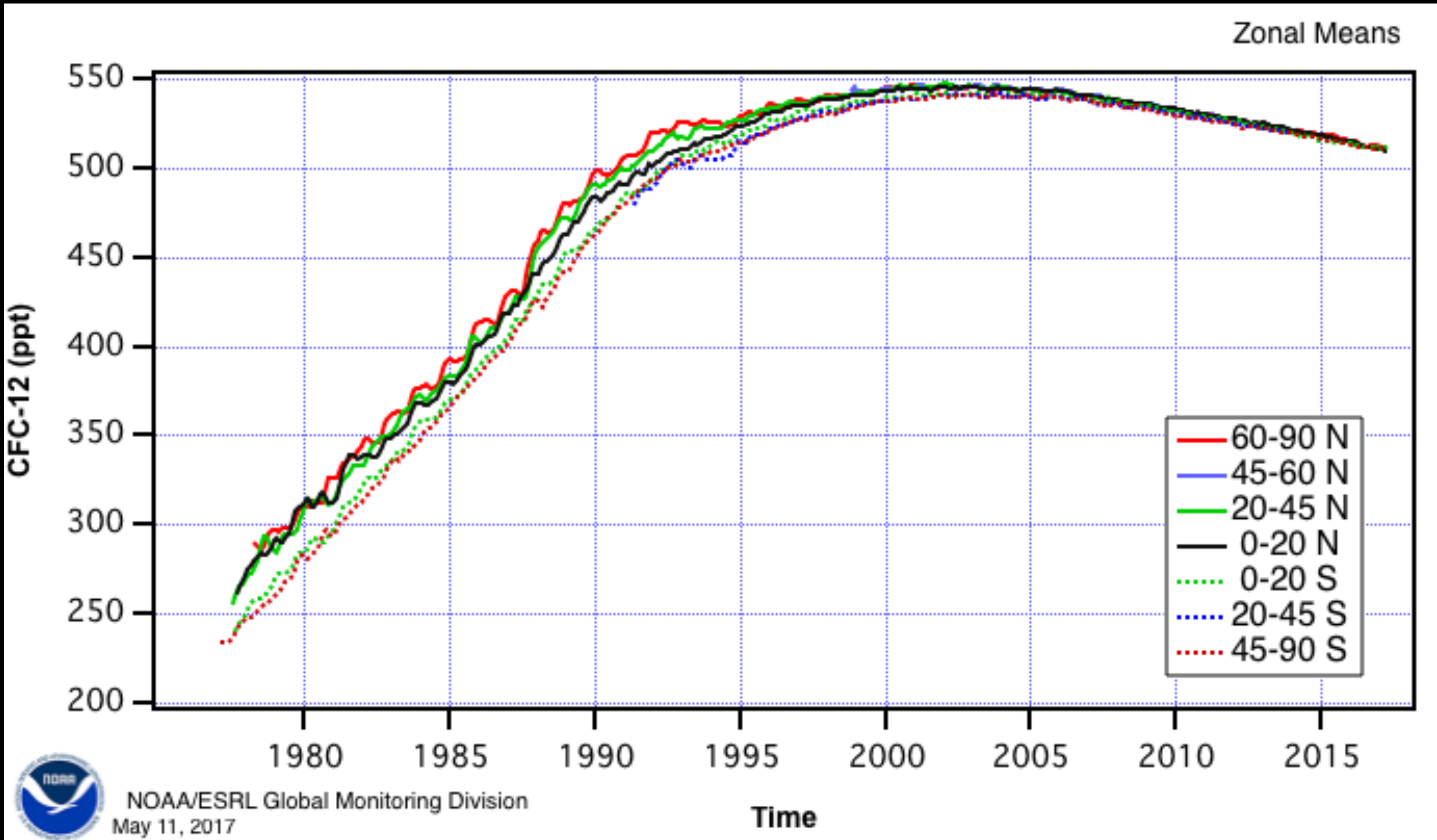




Observations of a host of important chemicals and fingerprints....ClO, OClO, NO, NO_2, HCl.....

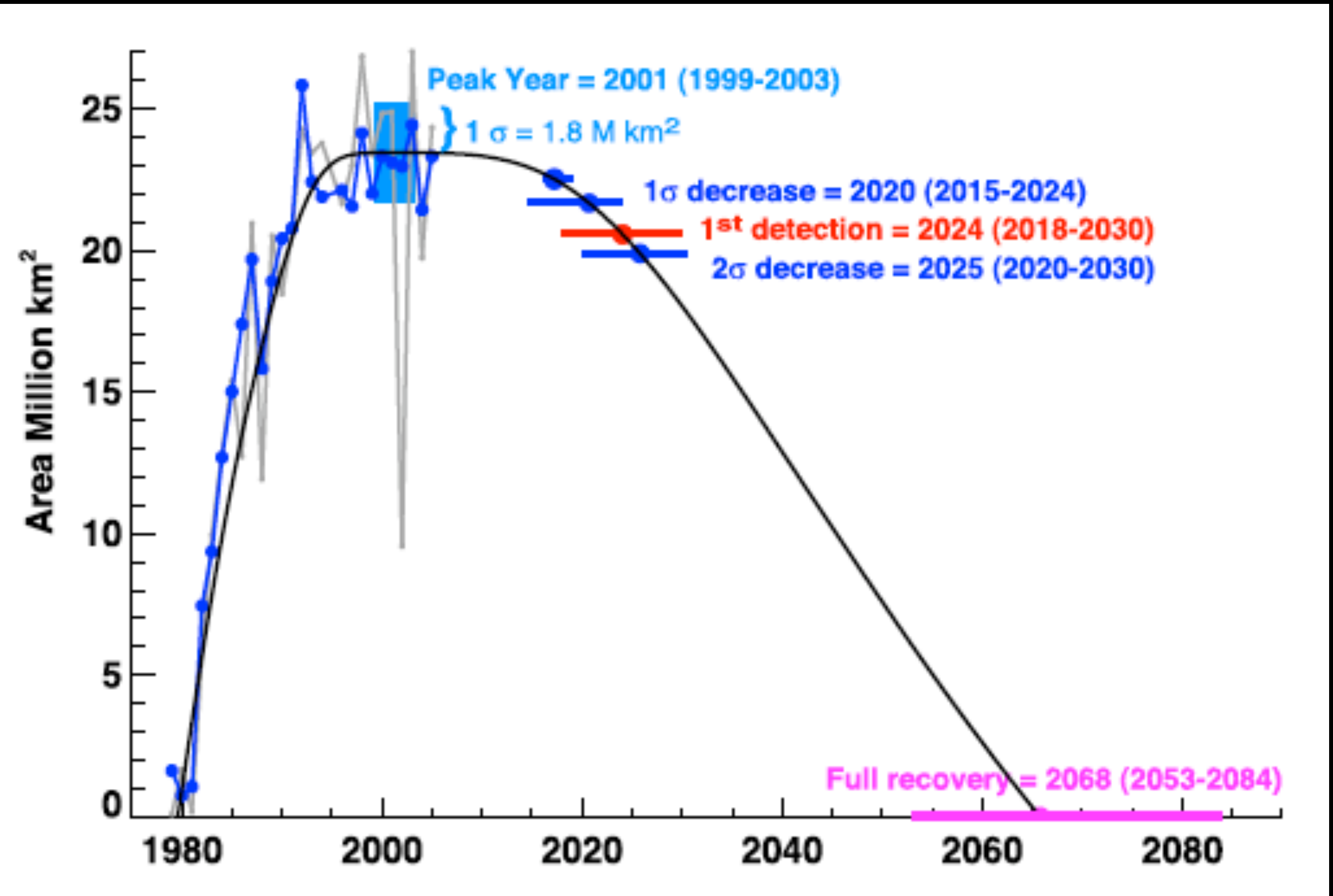
-> Massive perturbations to Antarctic chlorine chemistry on PSCs, capable of depleting the ozone layer very effectively. A clear story to tell to scientists, the public, and policymakers.

Is the Montreal Protocol Working?   Definitely.



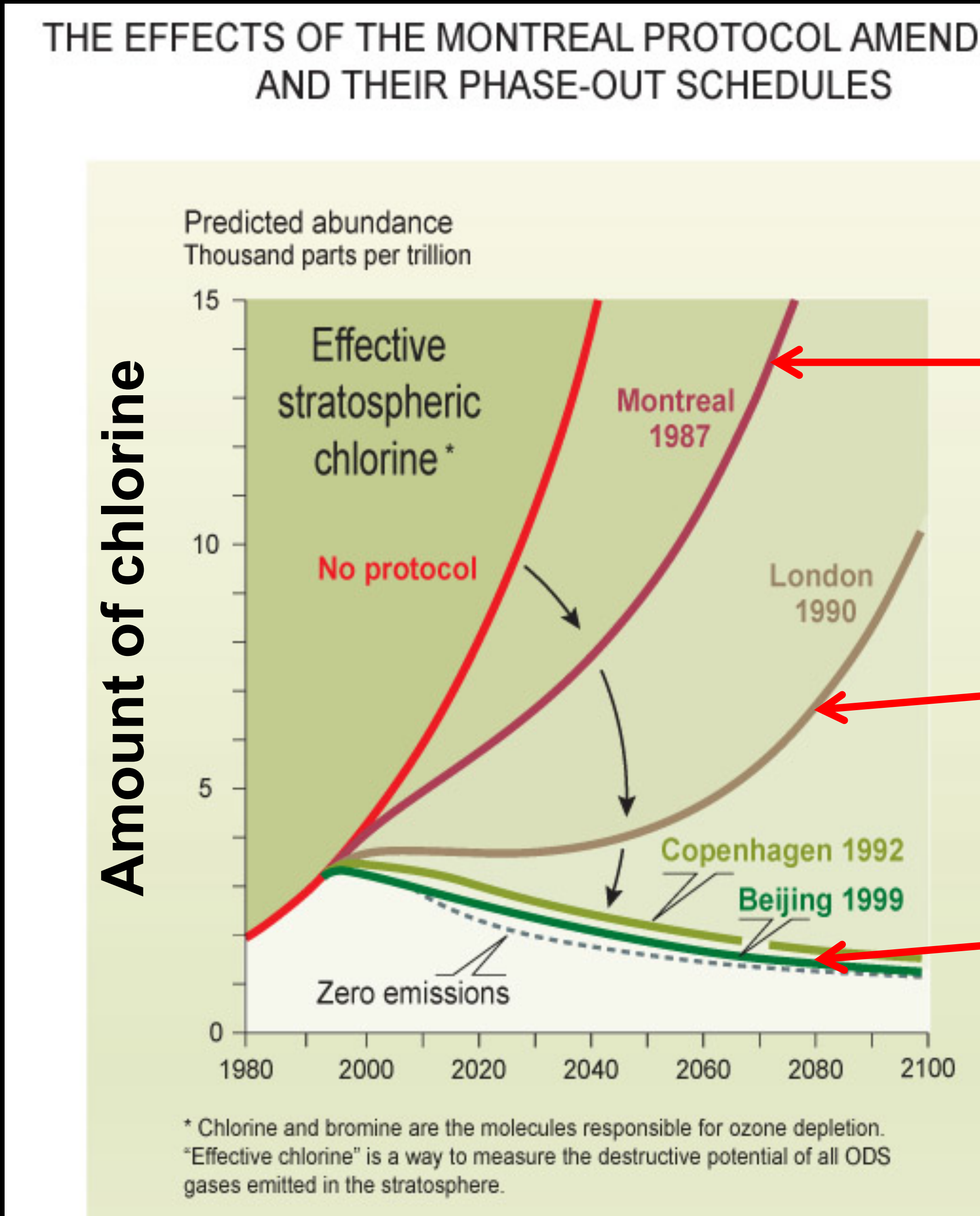
http://www.esrl.noaa.gov/gmd/hats/

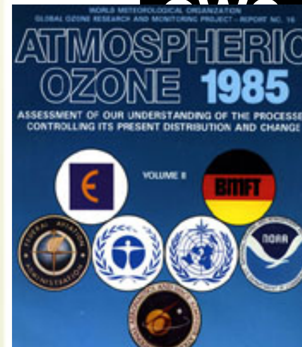
- NH, SH differences
- Lifetimes of gases, global trends
- Many decades to really 'recover'



The full recovery of the Ozone Hole: late compared to other latitudes because Antarctic air is both cold and 'old'

Newman et al., GRL, 2005





Changes in targets over time ... much to ... ntific ... ssments.

Ozone hole discovered

... tton's ... ht on three ... ases in ... ence-policy ... eractions on ... vironmental ... ues:

Ozone hole explained; also depletion in mid-lats

Also depletion in summer mid-lats

Credibility

Manageability

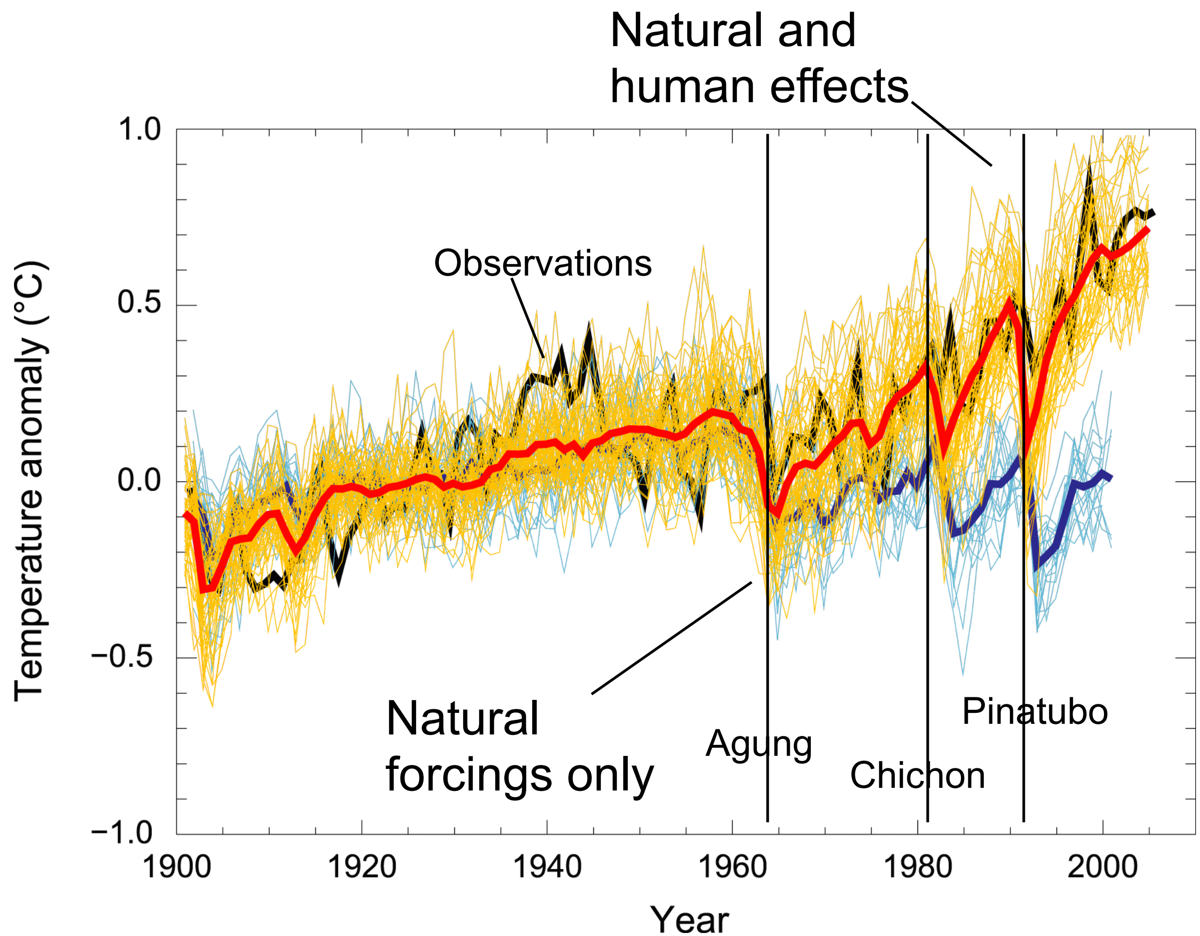
Accountability

Attribution of Global Climate Change

IPCC (1995):
"Balance of evidence suggests discernible human influence"

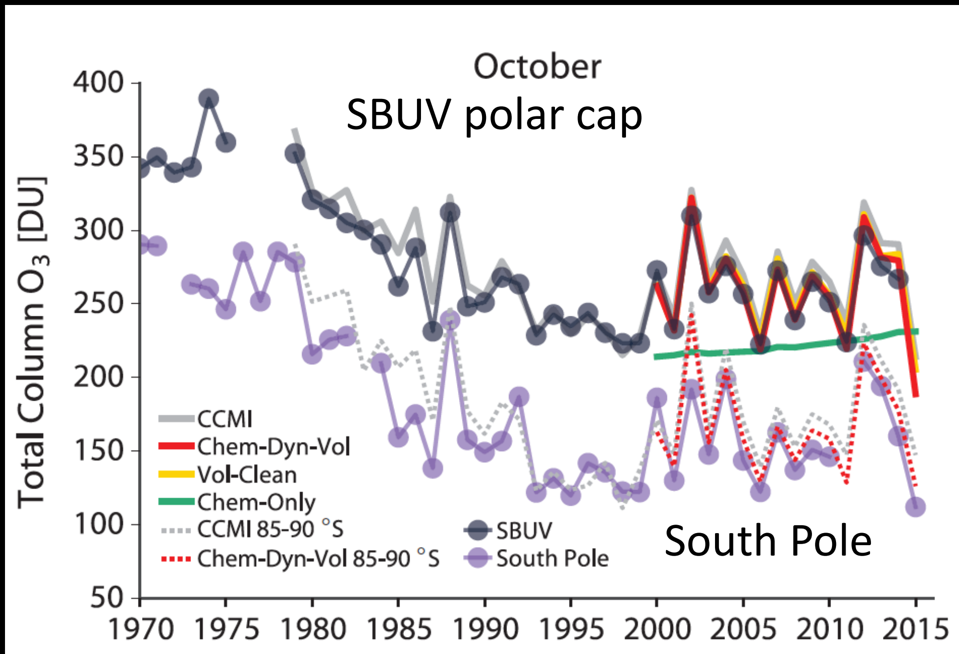
IPCC (2001):
"Most of global warming of past 50 years *likely* (odds 2 out of 3) due to human activities"

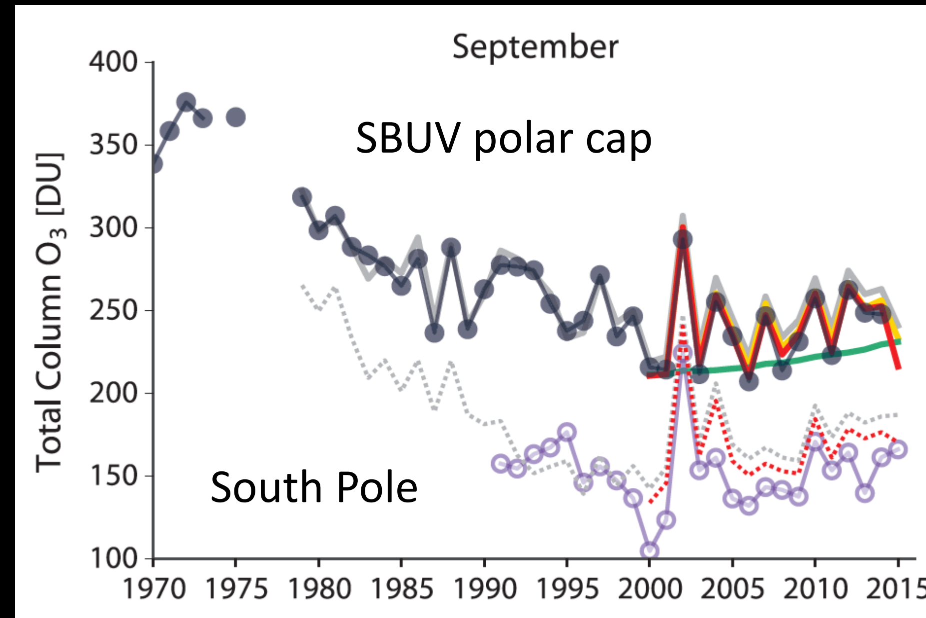
IPCC (2007):
"Most of global warming of past 50 years *very likely* (odds 9 out of 10) due to greenhouse gases"



Quantitative attribution: not just simple trend statistics, account for confounding factors.
Next part of the talk: data, models with/without volcanoes, dynamics/temperature from data and 'free-running' (WACCM)

Depth of the Antarctic Total Ozone Loss





October avg – highly variable. Well simulated by model. No statistically significant healing trend (90% confidence).

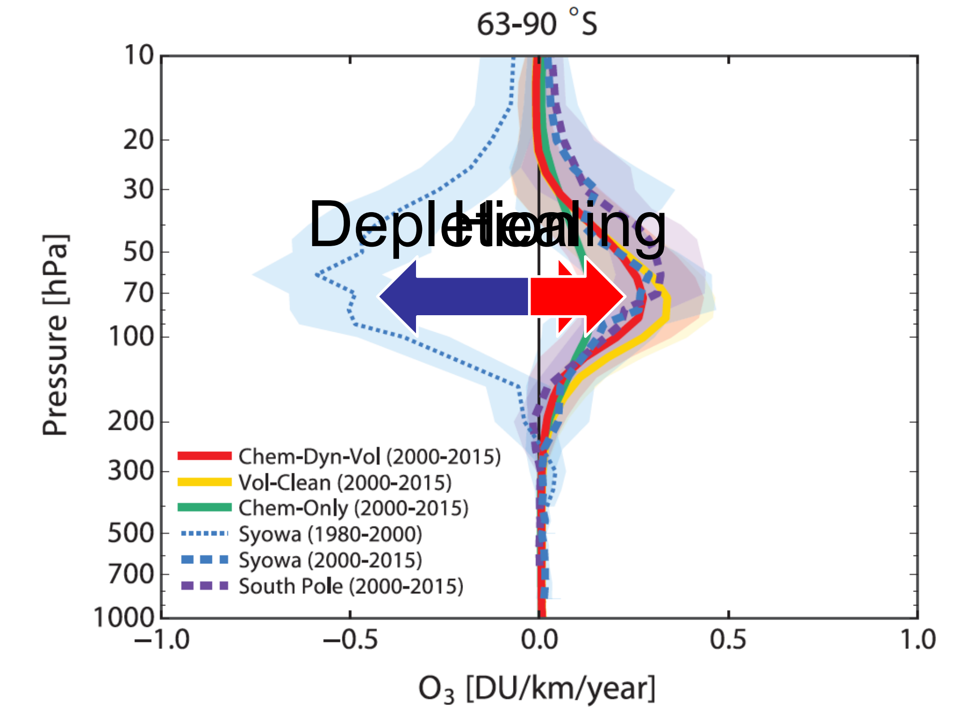
September avg – healing suggested ✔

[Note: 2002 not included in Antarctic trend analyses]

Remarkable model/data agreement. Large interannual dynamical/temperature variation, but it is no mystery! We can model it well with current reanalyses, and this has to be included in evaluating uncertainty.

From Solomon et al., Science, 2016

Profile of the Antarctic Ozone Loss



What is the role of ozone/temperature feedback?

More ozone → warmer → less depletion

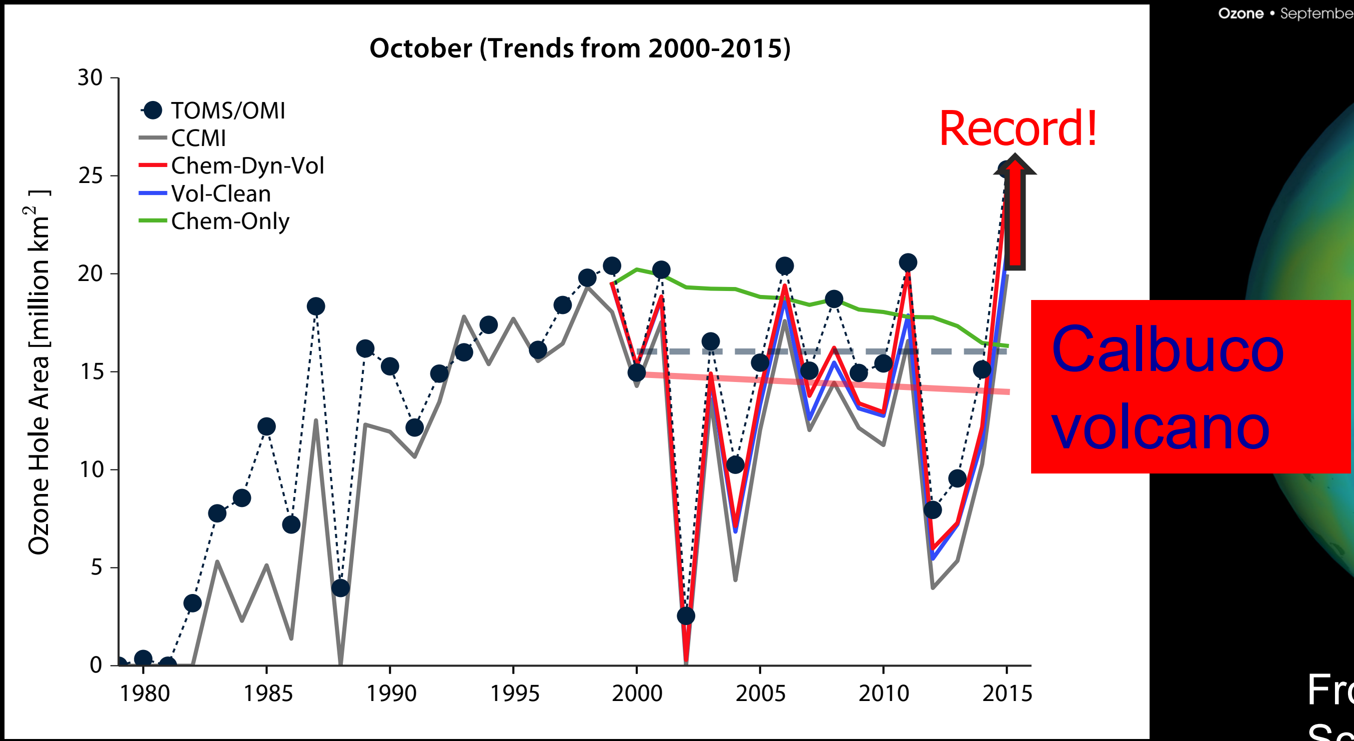
SD-WACCM uses observed temperatures, so any such contributions are credited to chem/dyn/vol here, even those that are chemically driven.

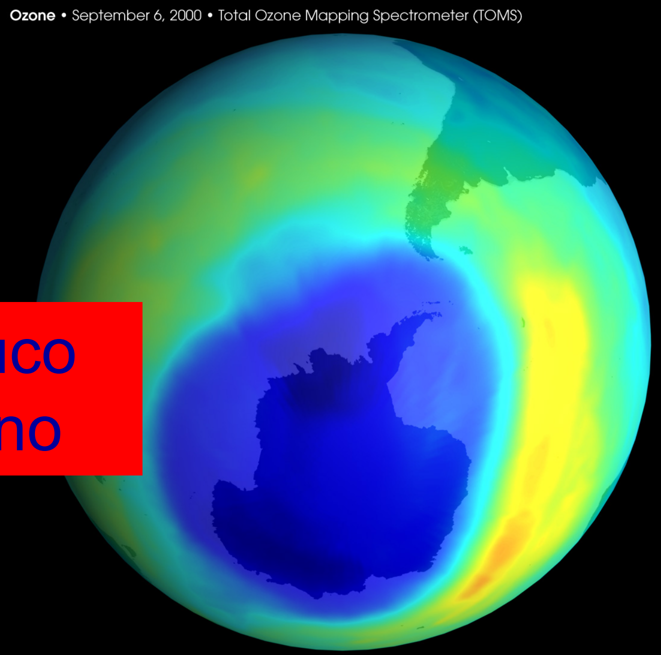
Shape of the trend in the September profile of increased concentrations since 2000, at two different stations. ✔✔✔

Model suggests as a best estimate that about half of the September recovery near 15 km is chemical (while half is dynamics/temperature). But within uncertainties ≈100% may be chemical.

Solomon et al., Science, 2016.

What About the Size of the Hole?



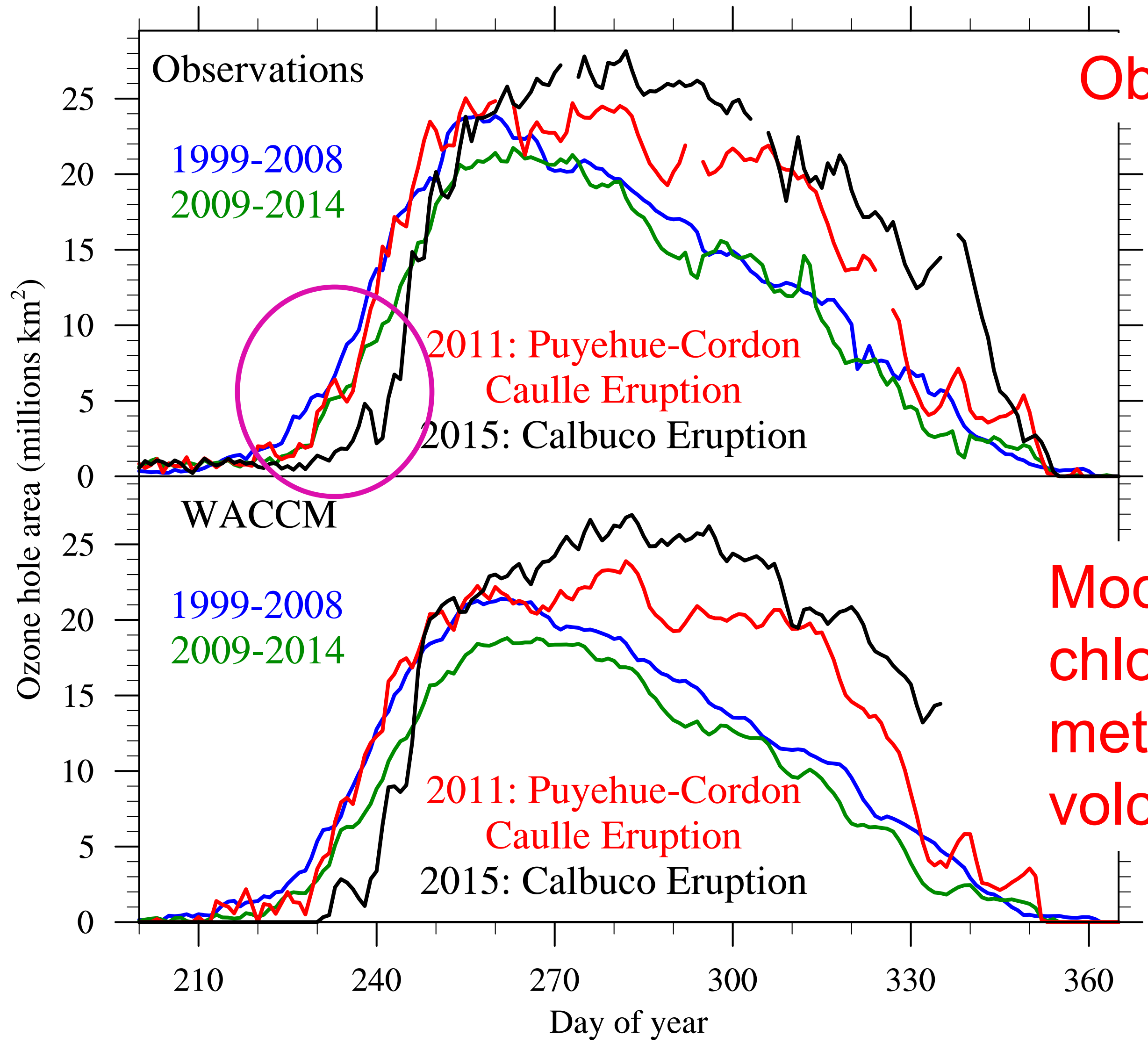


From Solomon et al., Science, 2016.

Hole is area where total ozone is < 220 DU; observed variations are well simulated in this chemistry model using observed temperatures and winds with calculated PSC and volcanic aerosols.

Record large size in October 2015 well reproduced in the model when Calbuco volcano enhancements to PSCs are included. And there are significant volcanic effects in other years too.

What about the seasonal evolution?



Observations

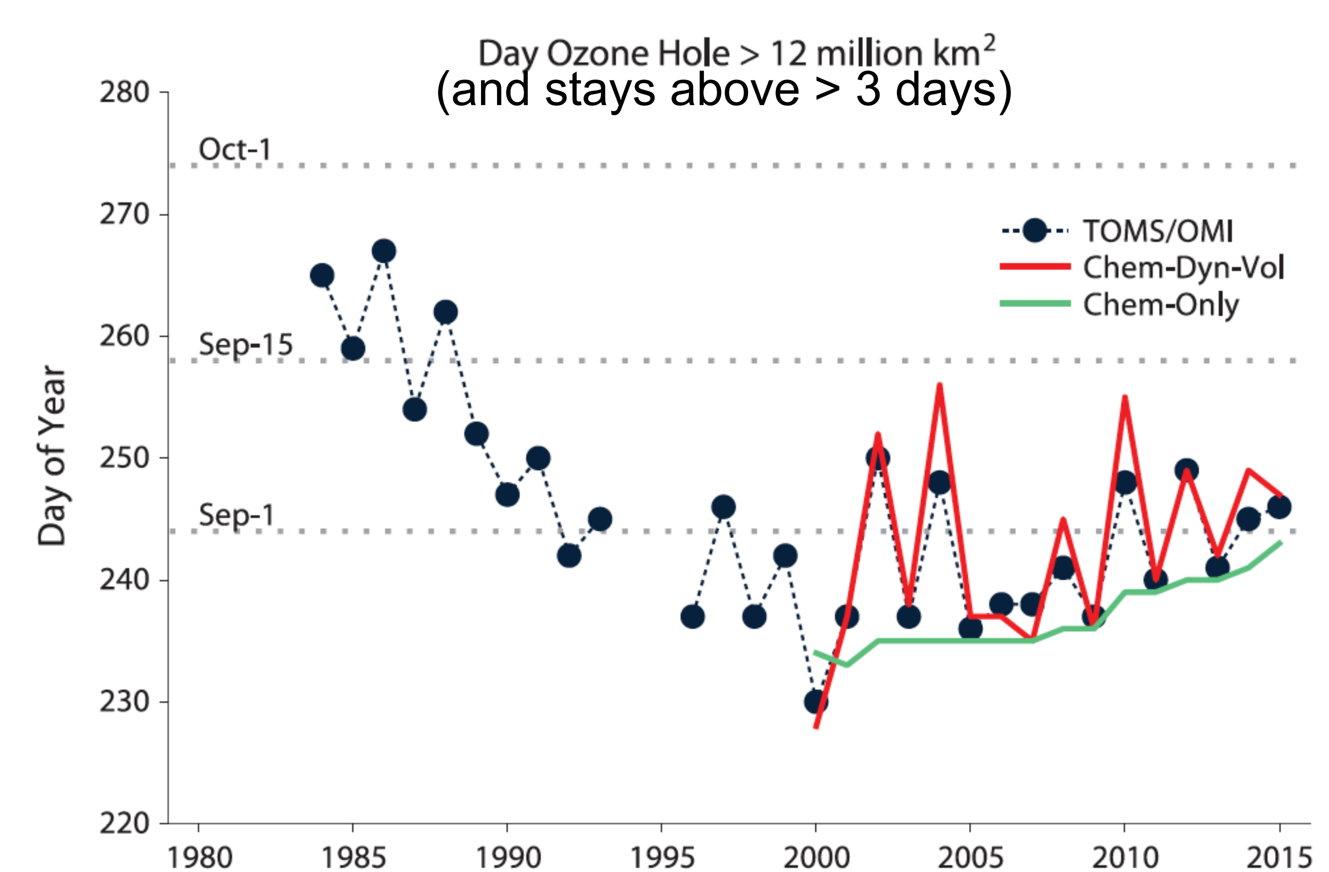
Late Aug-Early Sep is key to healing.

Volcanoes enhance *October* holes in cold years.

Model including chlorine, meteorology, and volcanoes

From Solomon et al., Science, 2016; see also Ivy et al, GRL, 2016 for similar free-running WACCM ensemble simulation findings.

The Early Season: Slower Opening of the Hole



From Solomon et al., Science, 2016.

Ups and downs are well reproduced by the model → no mystery. Clear that the ozone hole is opening more slowly on average, even in cold and/or volcanically-perturbed years.

Affects the *monthly average for September* -- but by October the hole has had enough time to be fully formed, and is more sensitive to other factors besides Cly.

Why is less chlorine key in the early season (but not so much later)? Simple kinetics…

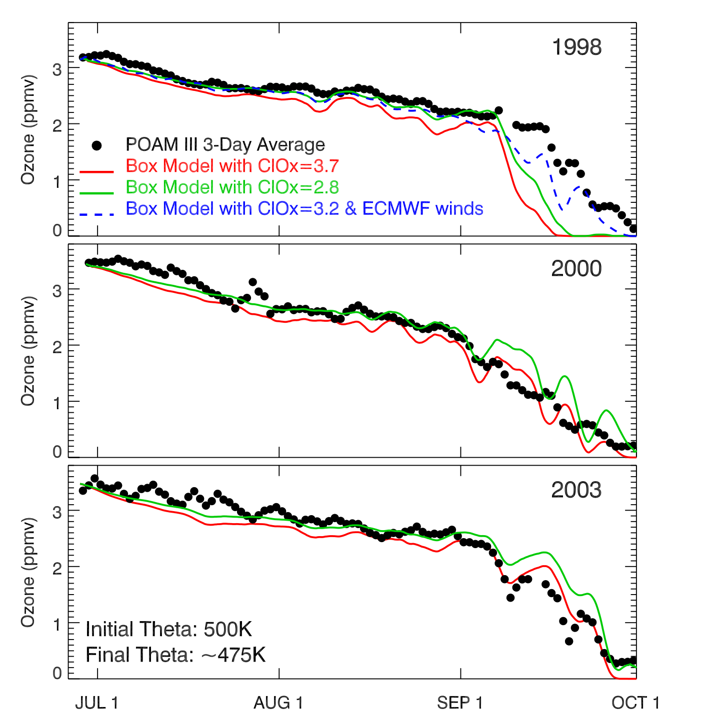
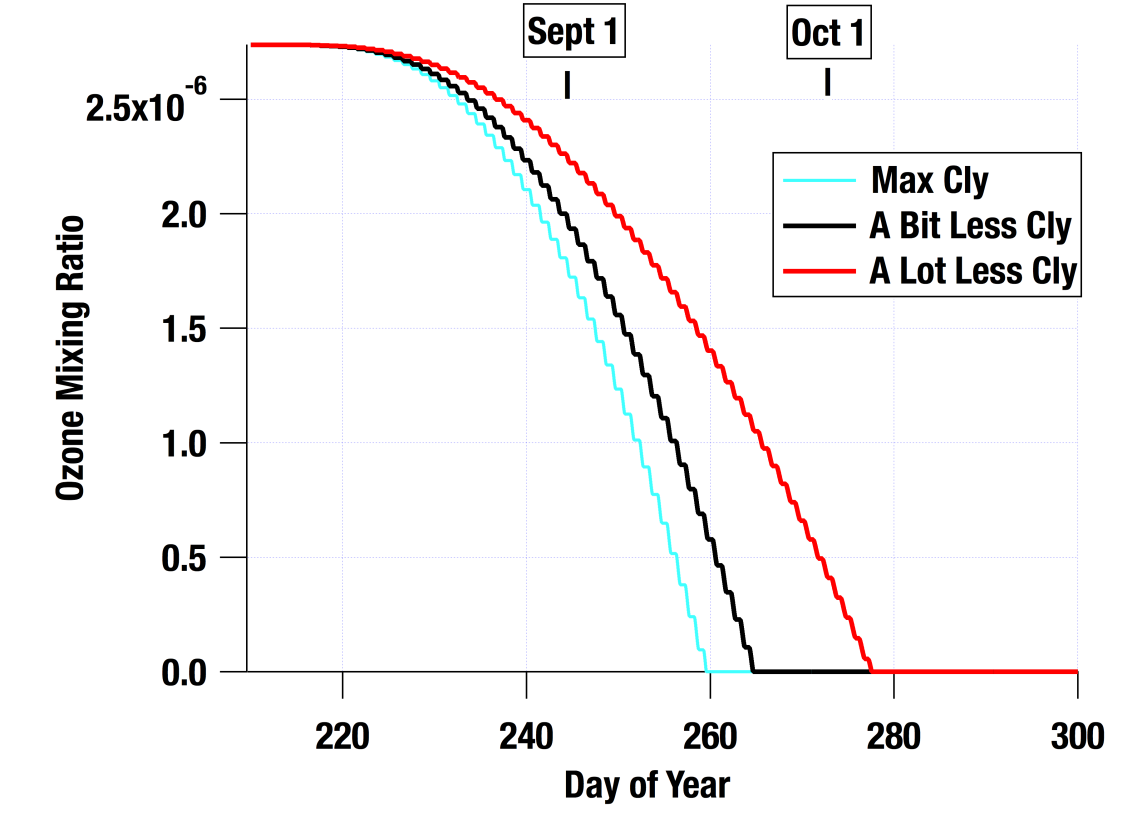


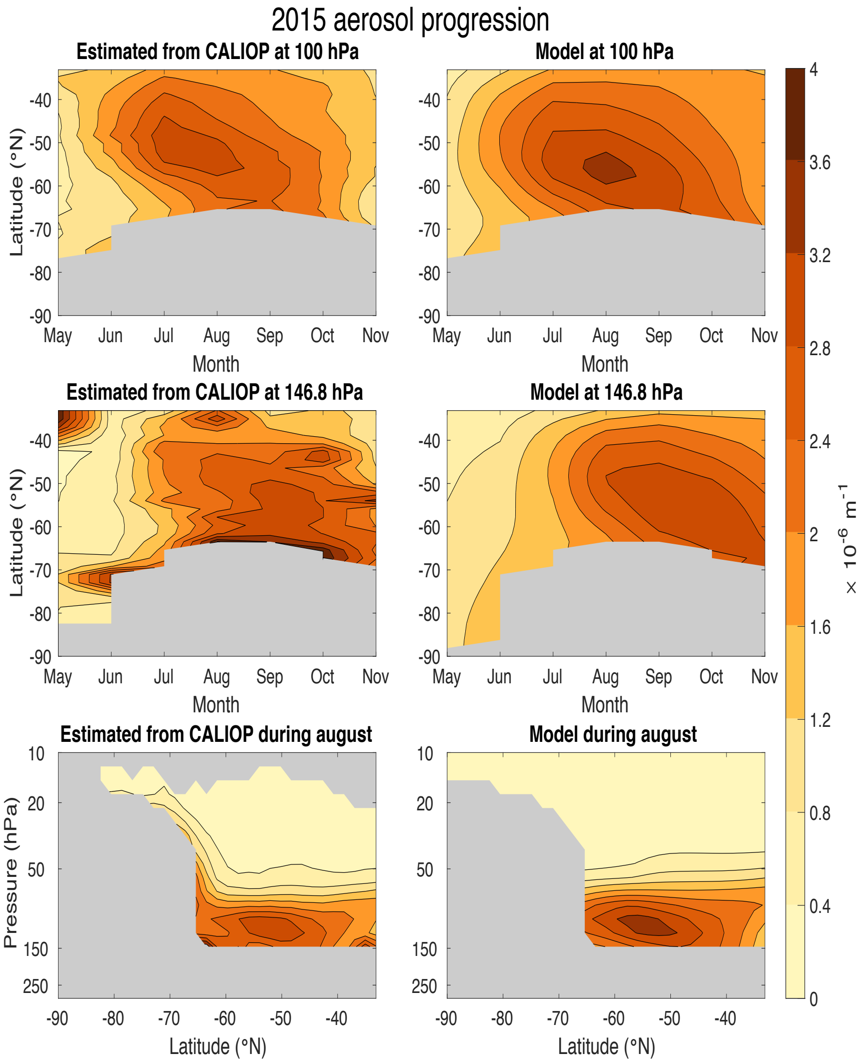
Figure 5. Comparison of the POAM and model ozone time series for 3 years. Only the model air parcels within ±2° of the POAM latitude were averaged. The POAM measurements for each day were sampled at the average potential temperature of the model trajectories, which were initialized at 500 K and descended to about 475 K. UKMO winds were used for all model runs except for the single case in 1998 as indicated.



Hoppel et al., JGR, 2005

2015 Calbuco volcanic eruption: Observed and Modeled Aerosols

- The Chilean volcano Calbuco erupted on April 22 2015 at a latitude of 41˚S
- Injected an estimated .4 Tg of sulfur into the stratosphere up to an altitude of 21 km
- Pinatubo injected an estimated 14-23 Tg

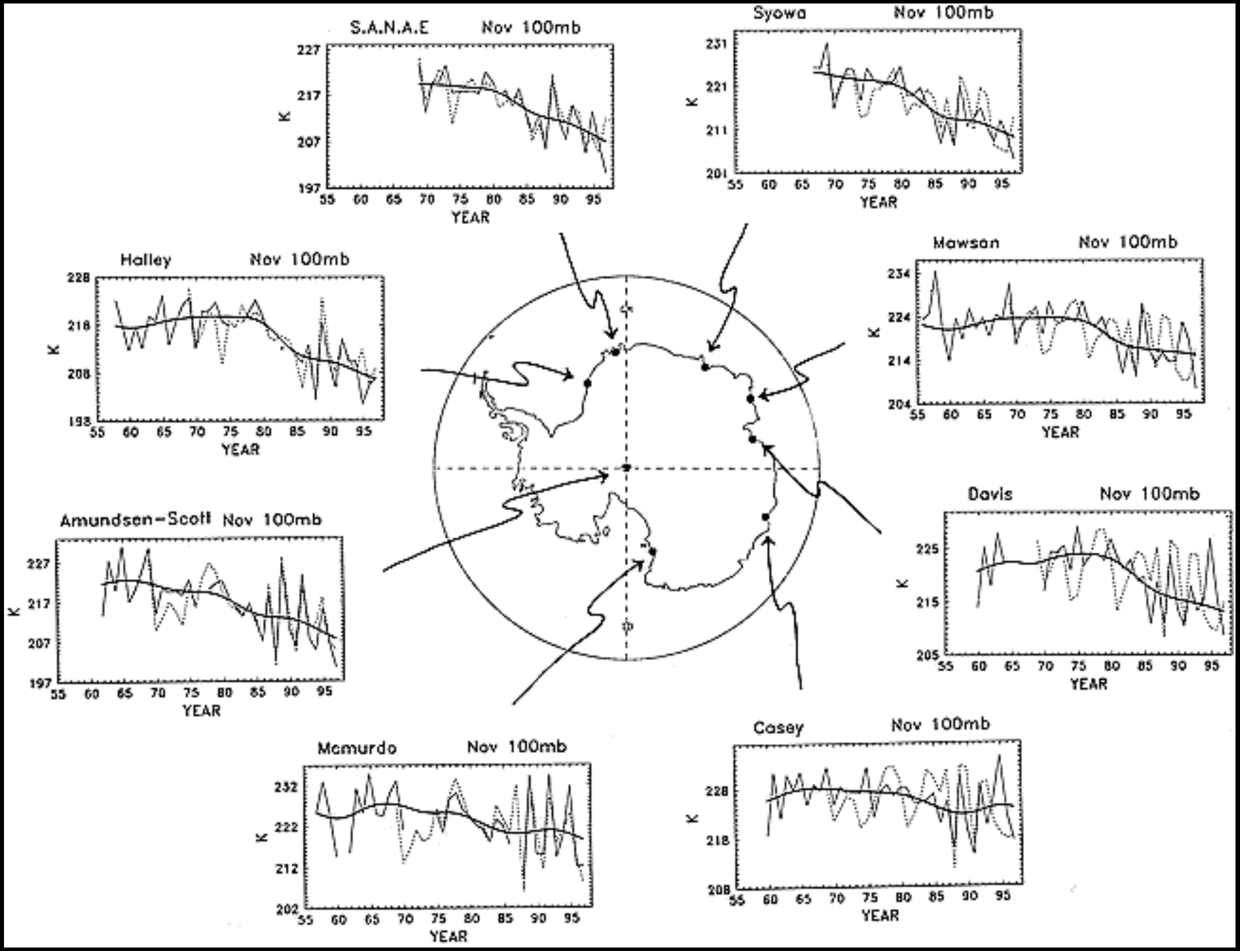


Stone et al., submitted to JGR, 2017

Ozone Hole Cools The Antarctic Stratosphere

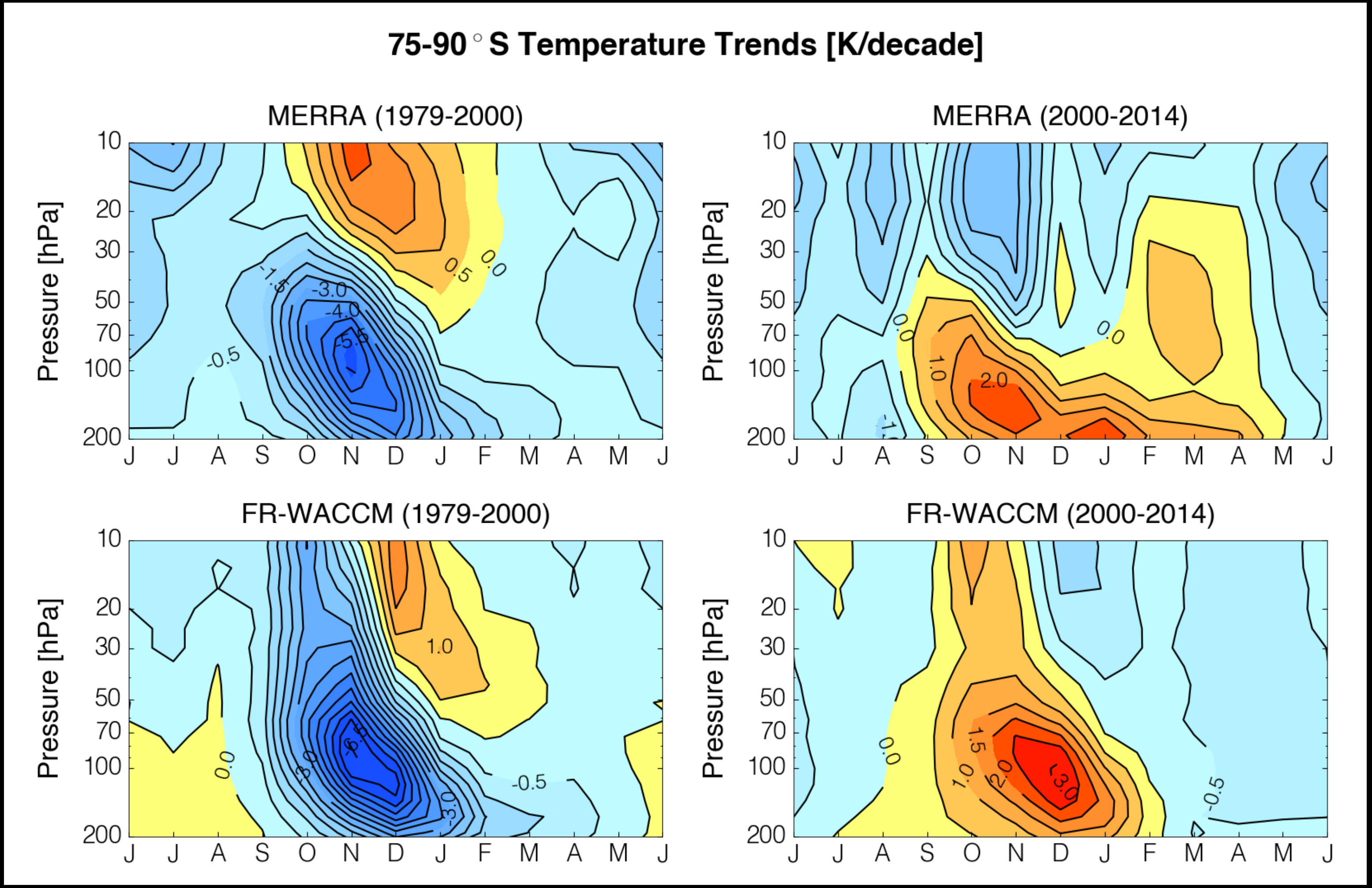
With so much less ozone, the Antarctic spring stratosphere became much colder (5-10° C in November), a remarkable change in stratospheric climate.

→ Ozone-temperature feedback.
→ Do we see a mirror image of warming now?



Randel and Wu, J. Clim, 1999; see Shine, GRL, 1986

Remarkable 'Mirroring' of Temperature Changes in the Depletion and Healing Eras: Observed and Free-Running Model



From reanalysis

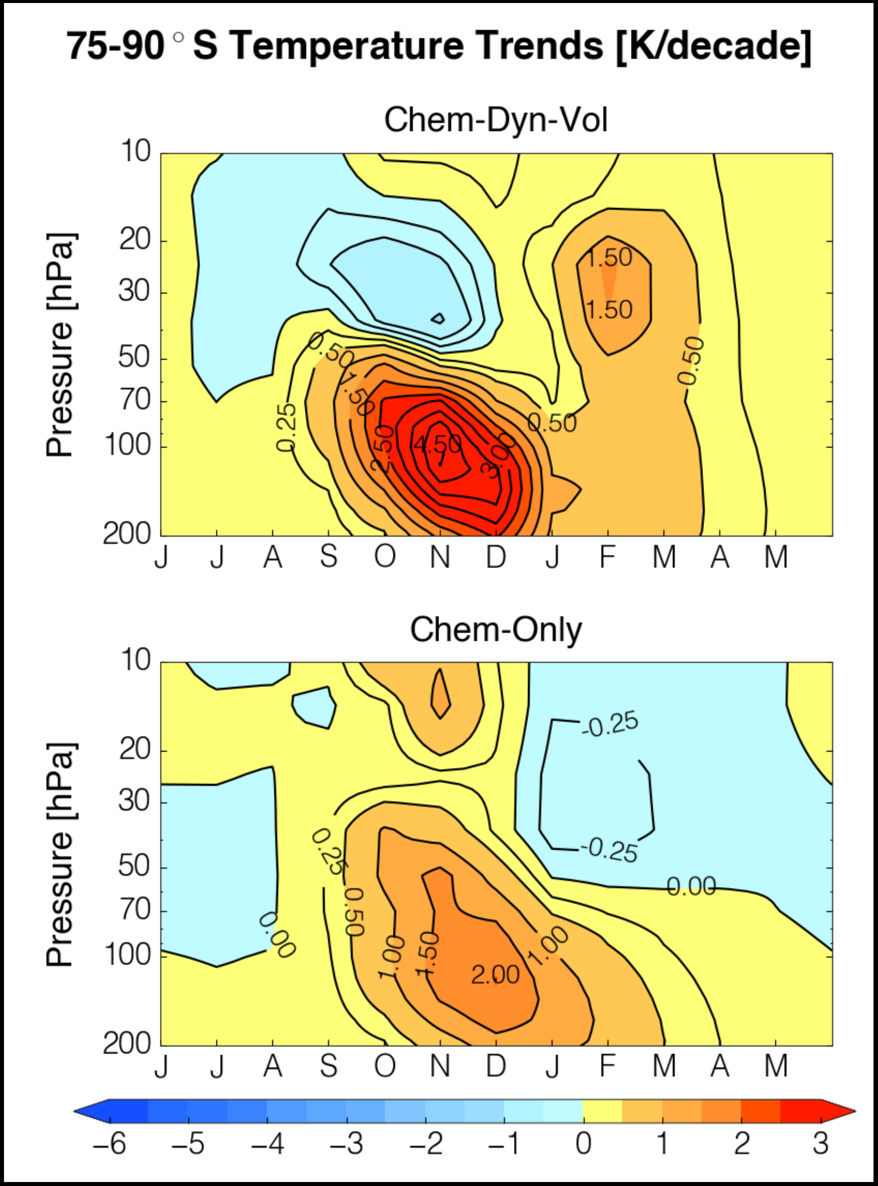
Model

Depletion Era

Healing Era

From Solomon et al., in press, JGR, 2017

How Much Do Purely Radiative Impacts of Ozone Changes in the Healing Era Contribute to the Temperature Trends?



Impose modelled ozone anomalies in radiative code with fixed dynamics.

→ Significant warming due to ozone changes that are purely due to chemistry.

→ Ozone-temperature feedback is an assist to the healing!

From Solomon et al., in press, JGR, 2017

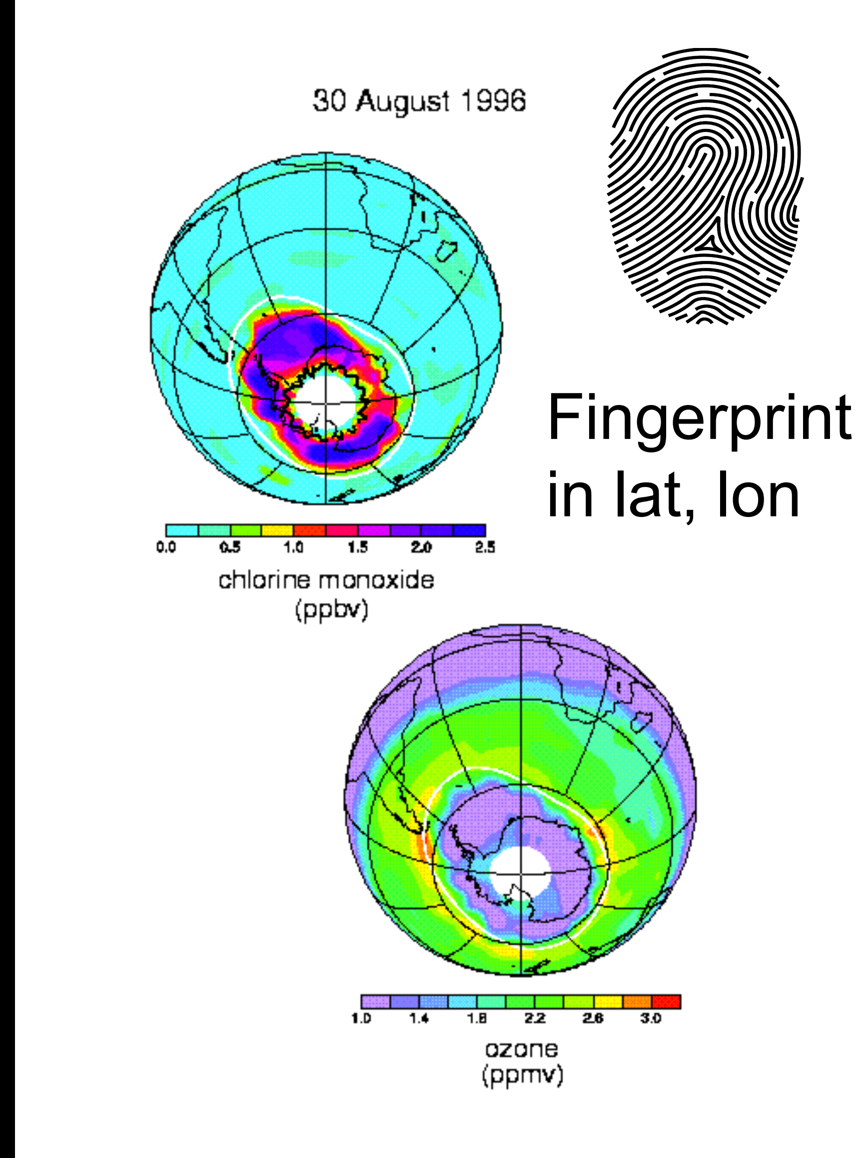

Thanks….for
many things

Cold temperatures lead to polar stratospheric clouds.

These in turn ‘activate’ the chlorine from CFCs to form Cl_2. Formation of the ClO dimer in cold sunlit air then drives depletion (Molina et al, 1987)

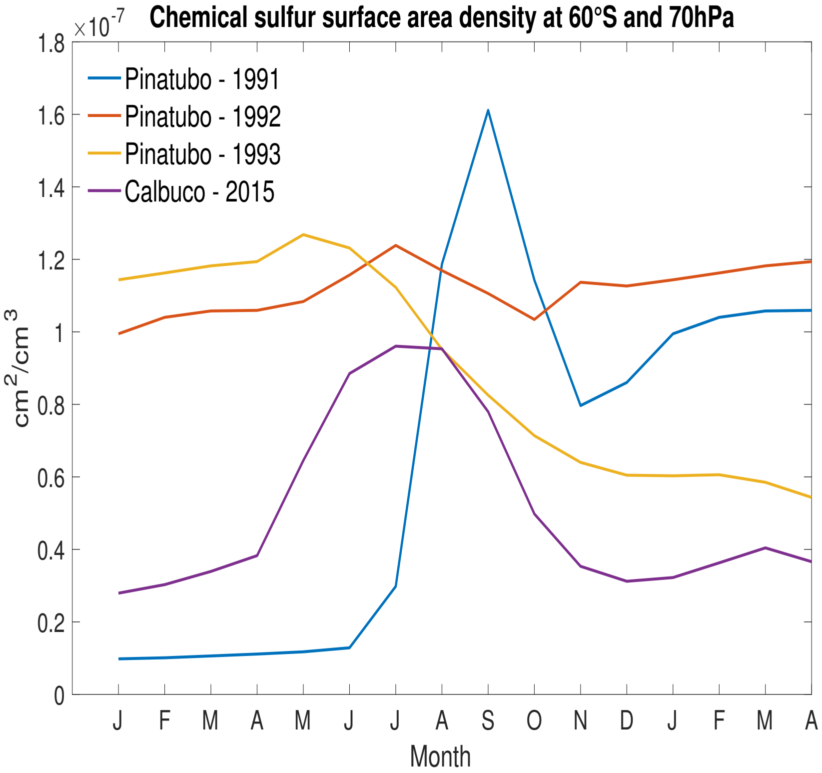
Cl_2 + light $\rightarrow$ 2Cl
$Cl + O_3 \rightarrow ClO + O_2$
$Cl + O_3 \rightarrow ClO + O_2$
$ClO + ClO \rightarrow Cl_2O_2$
Cl_2O_2 + light $\rightarrow$ $Cl + Cl + O_2$

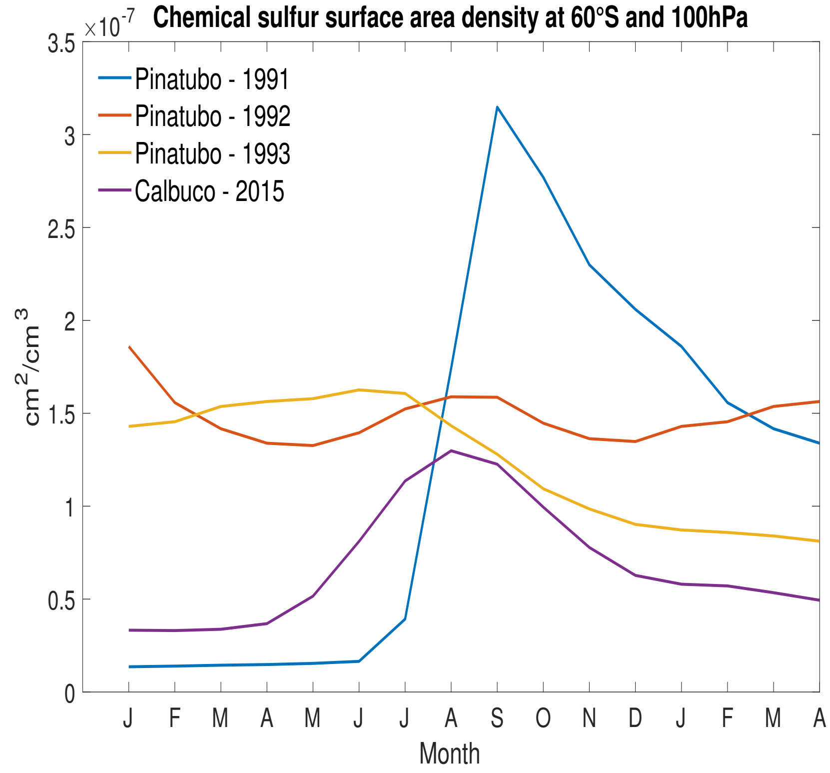
Net: $2O_3$ + light $\rightarrow$ $3\ O_2$



Bird’s eye fingerprint from space by Waters, Santee, and colleagues. NB: Arctic is warmer in spring

Comparison to Pinatubo: Calbuco Packed a Local Wallop



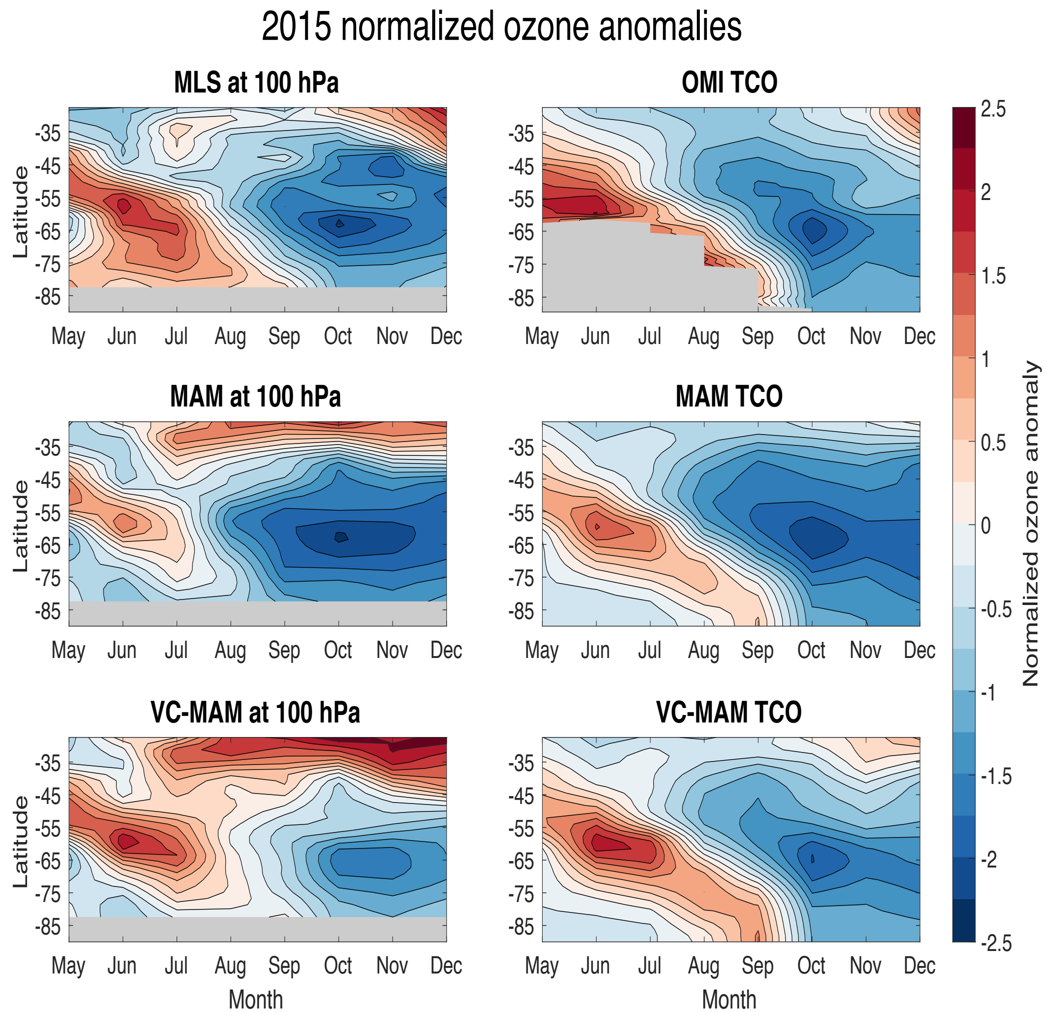


EAPS
Earth, Atmospheric and Planetary Sciences

Stone et al., submitted to JGR, 2017

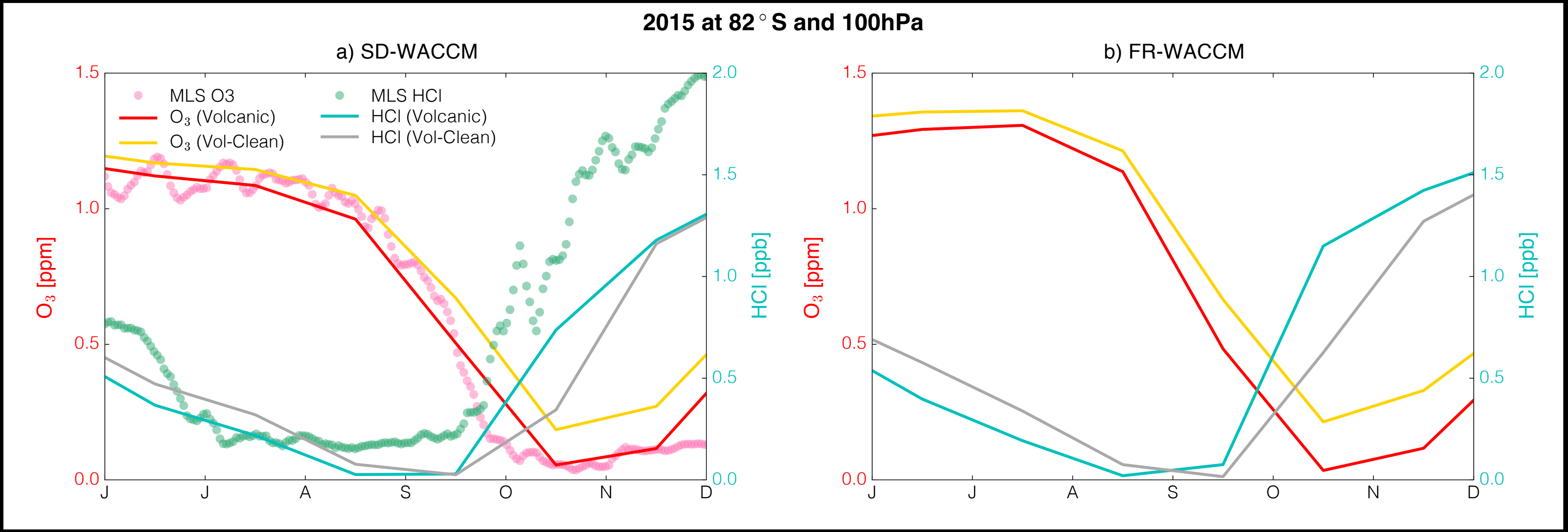
Ozone normalized anomalies: Observed and modelled

- Normalized ozone anomalies gives each dataset a mean of 0 and a standard deviation of 1
- The Calbuco aerosols, under the ideal cold conditions, enhance ozone depletion.   Note: aerosol-temperature-dynamics interactions imply that linear regression cannot be expected to be a good tool.
- The latitude of large anomalies is in the same location as elevated aerosols → subpolar max



Stone et al., submitted to JGR, 2017

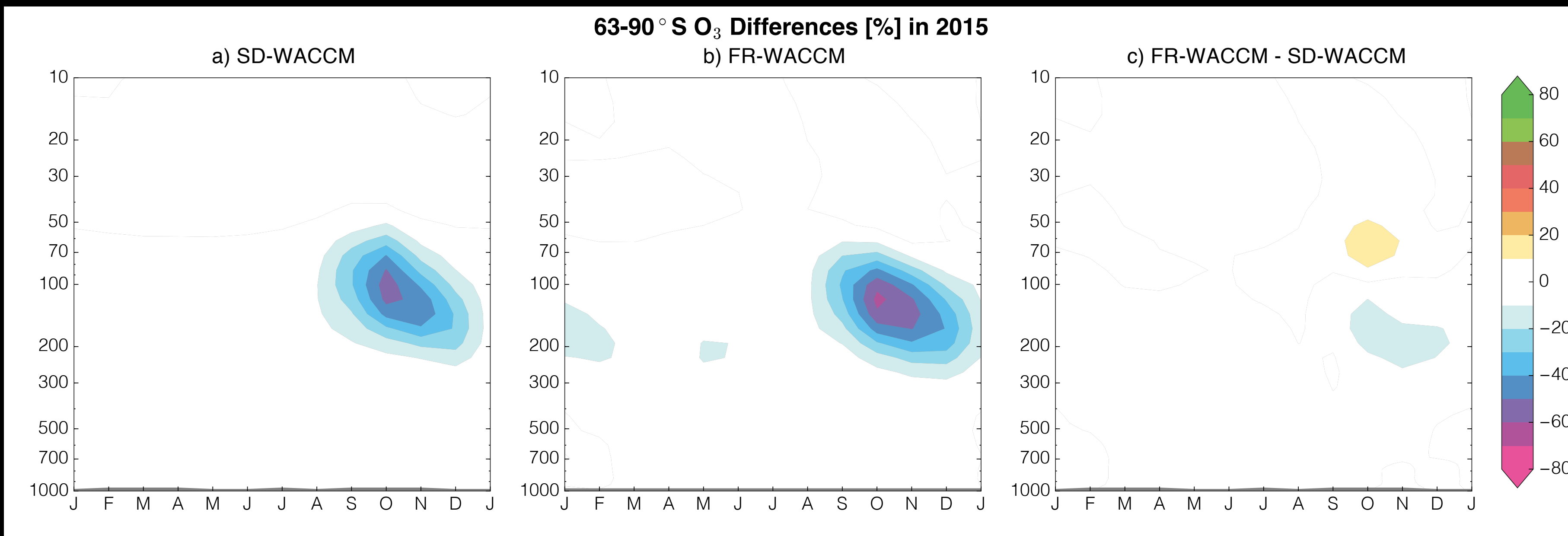
Calbuco Simulations with Free-Running Model



Cold conditions set the stage, but the record large hole required Calbuco

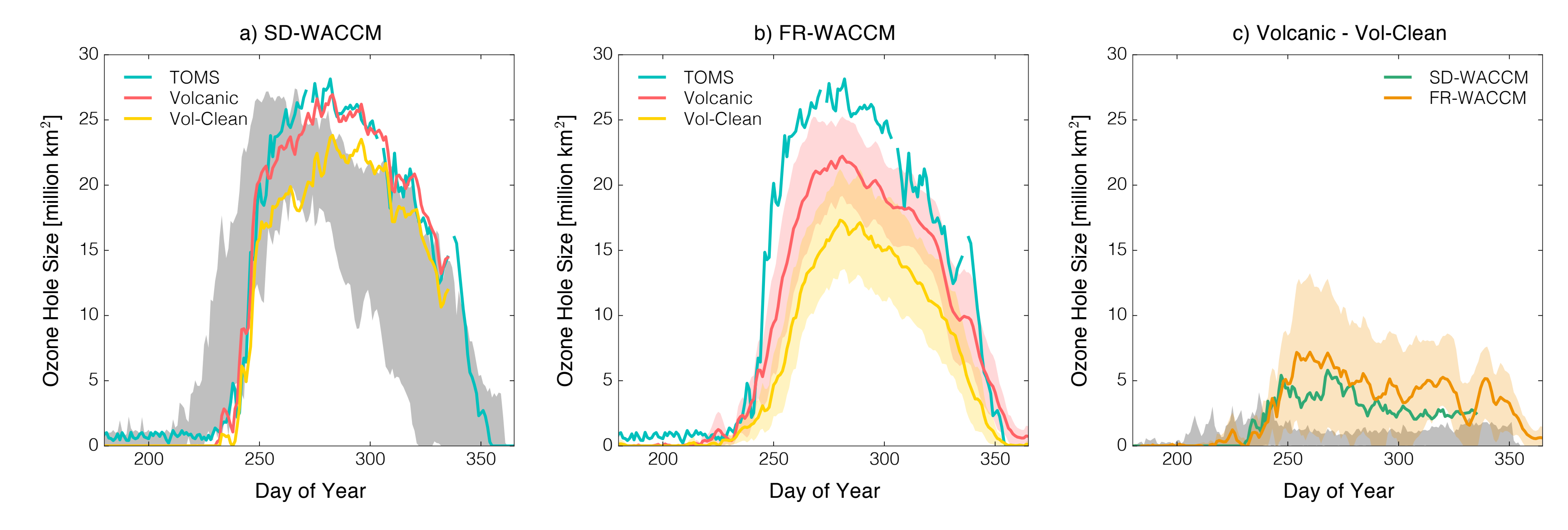
From Ivy et al, GRL, 2016

Calbuco Simulations with Free-Running Model



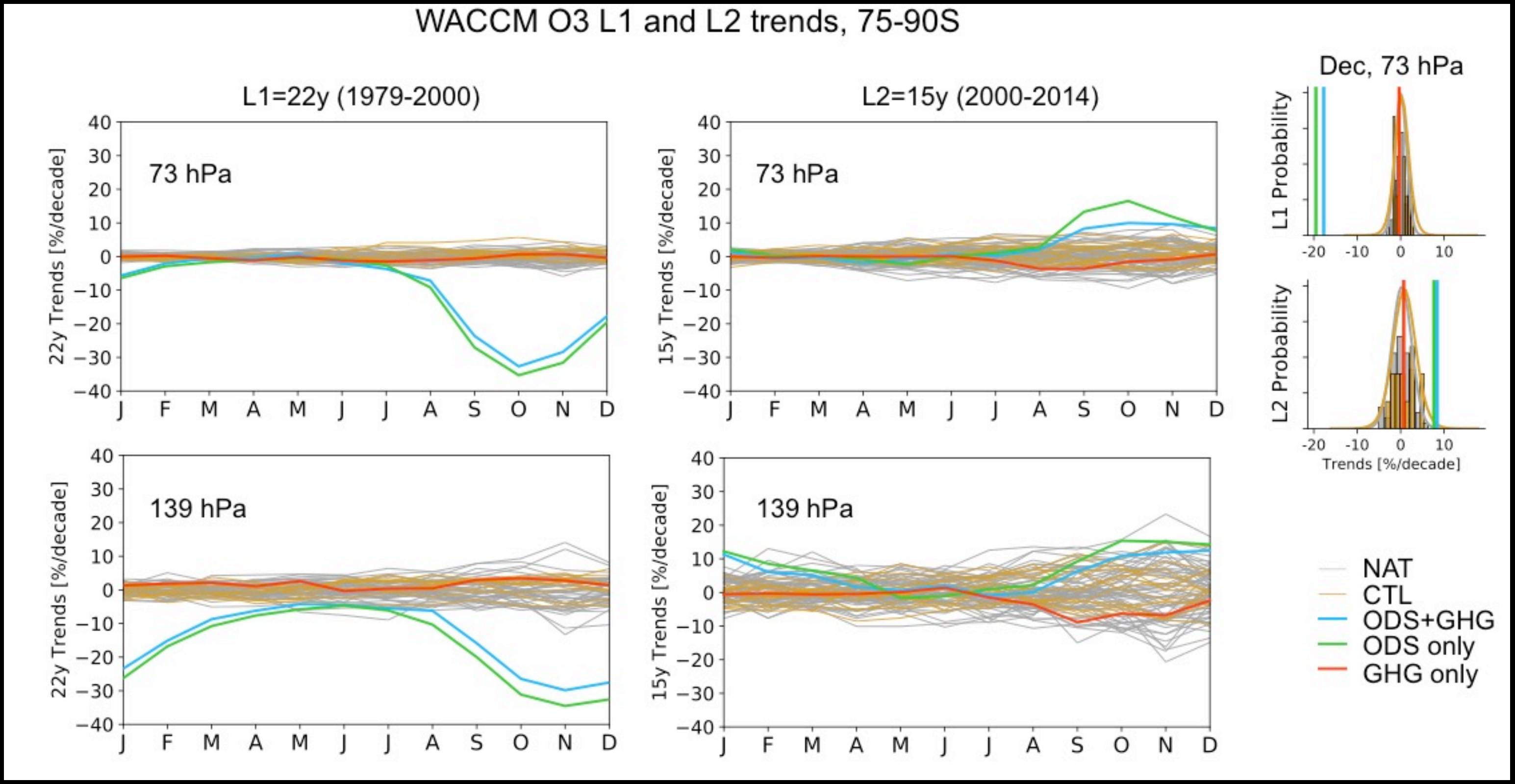
From Ivy et al, GRL, 2016

Calbuco Simulations with Free-Running Model



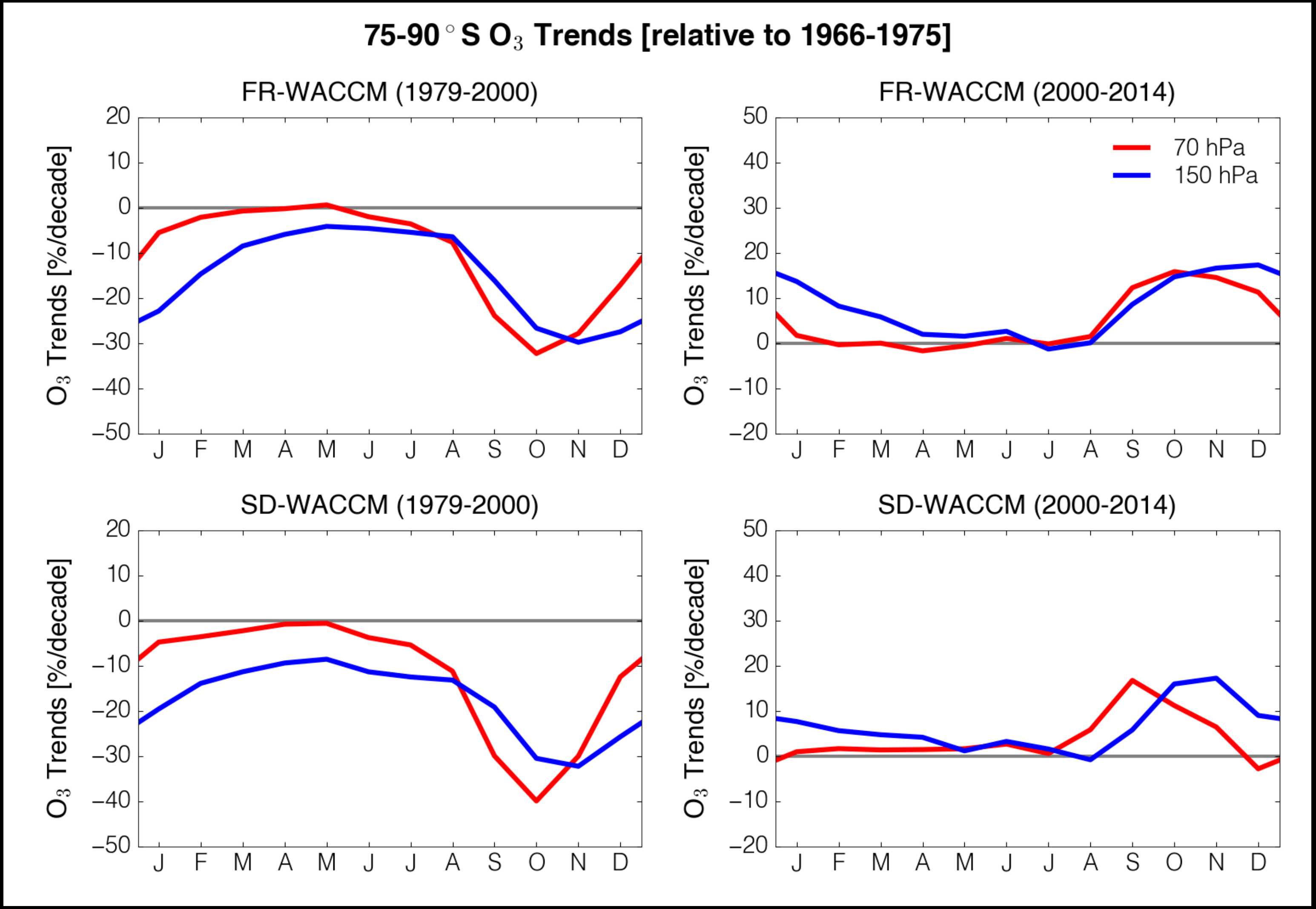
Cold conditions set the stage, but the record large hole required Calbuco

From Ivy et al, GRL, 2016

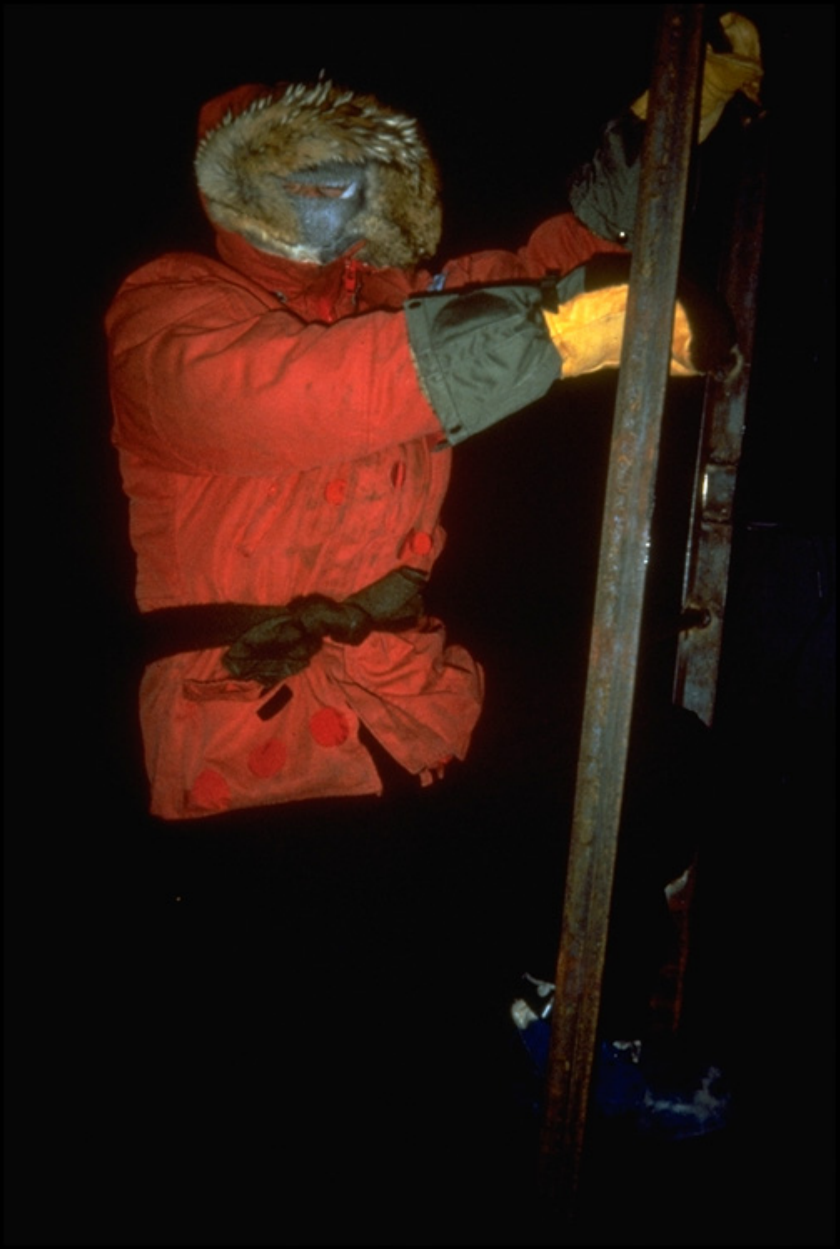


From Solomon et al., in press, JGR, 2017

Seasonal Cycles of Ozone Trends: Depletion and Healing



From Solomon et al., in press, JGR, 2017



Spectroscopy

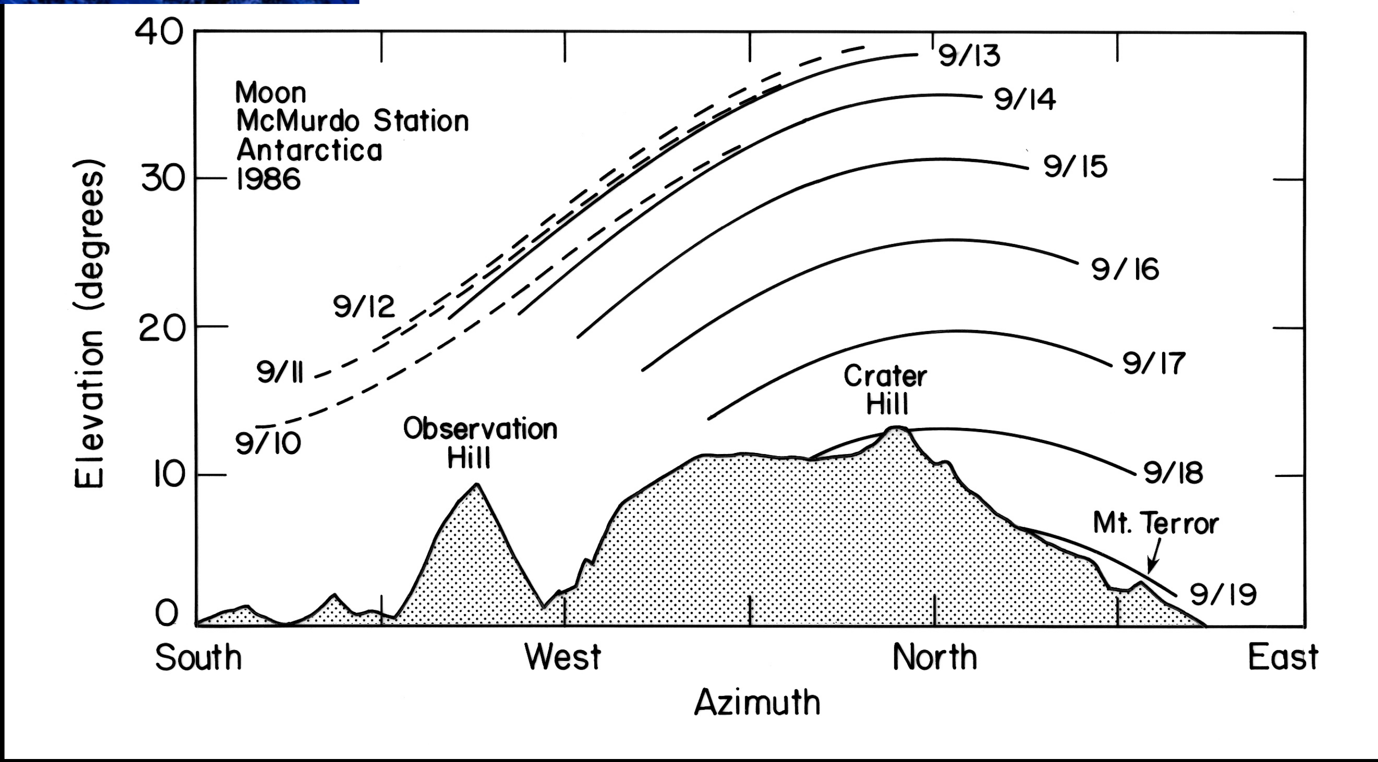
Measurements of chlorine dioxide at McMurdo Station, Antarctica

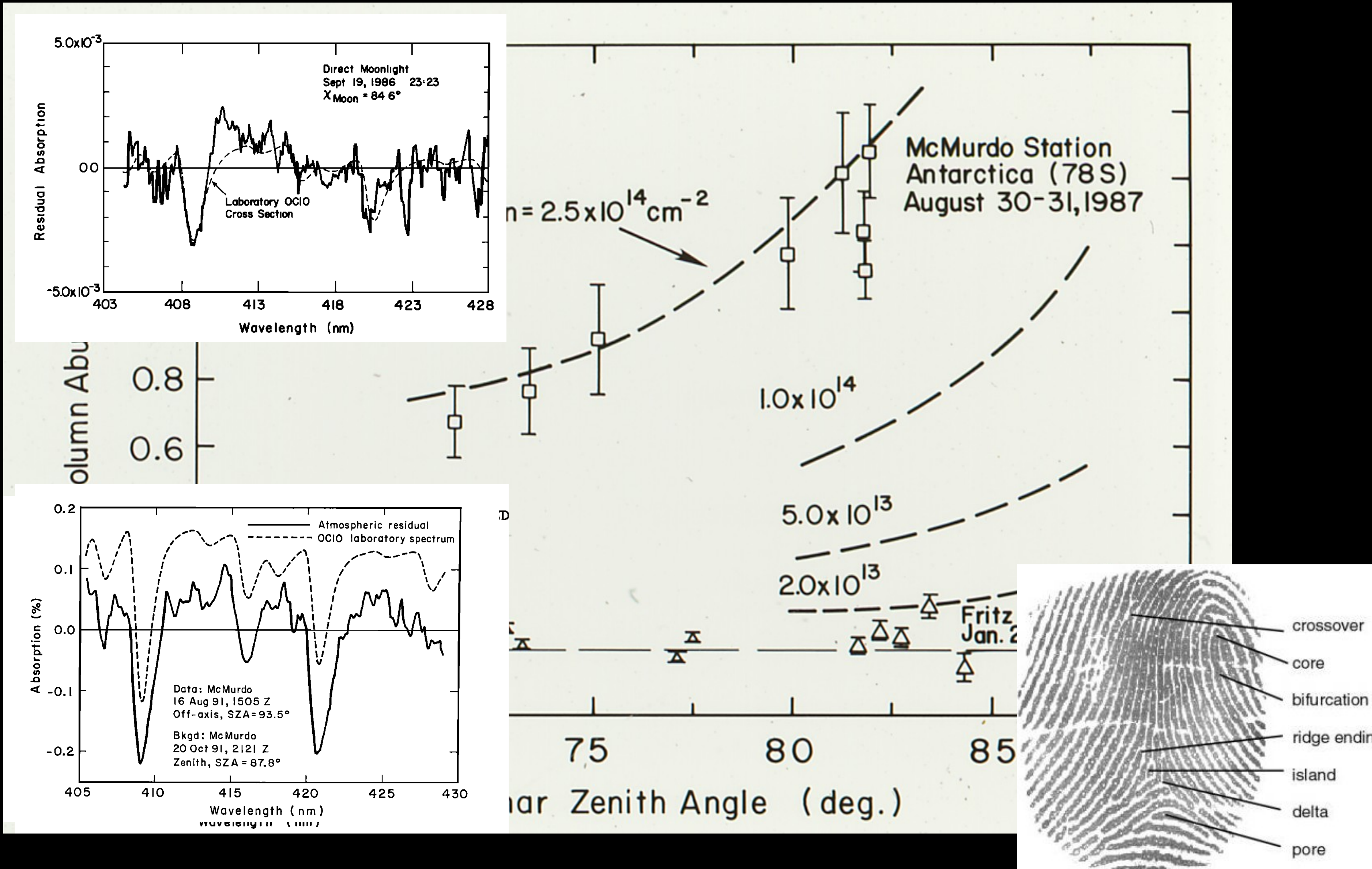
Temperature = -40° C

Windspeed = 50-80 km/hour

Using the moon to best advantage:

Path Length =1 when overhead
= 2 at 60˚
= 3 at 70˚

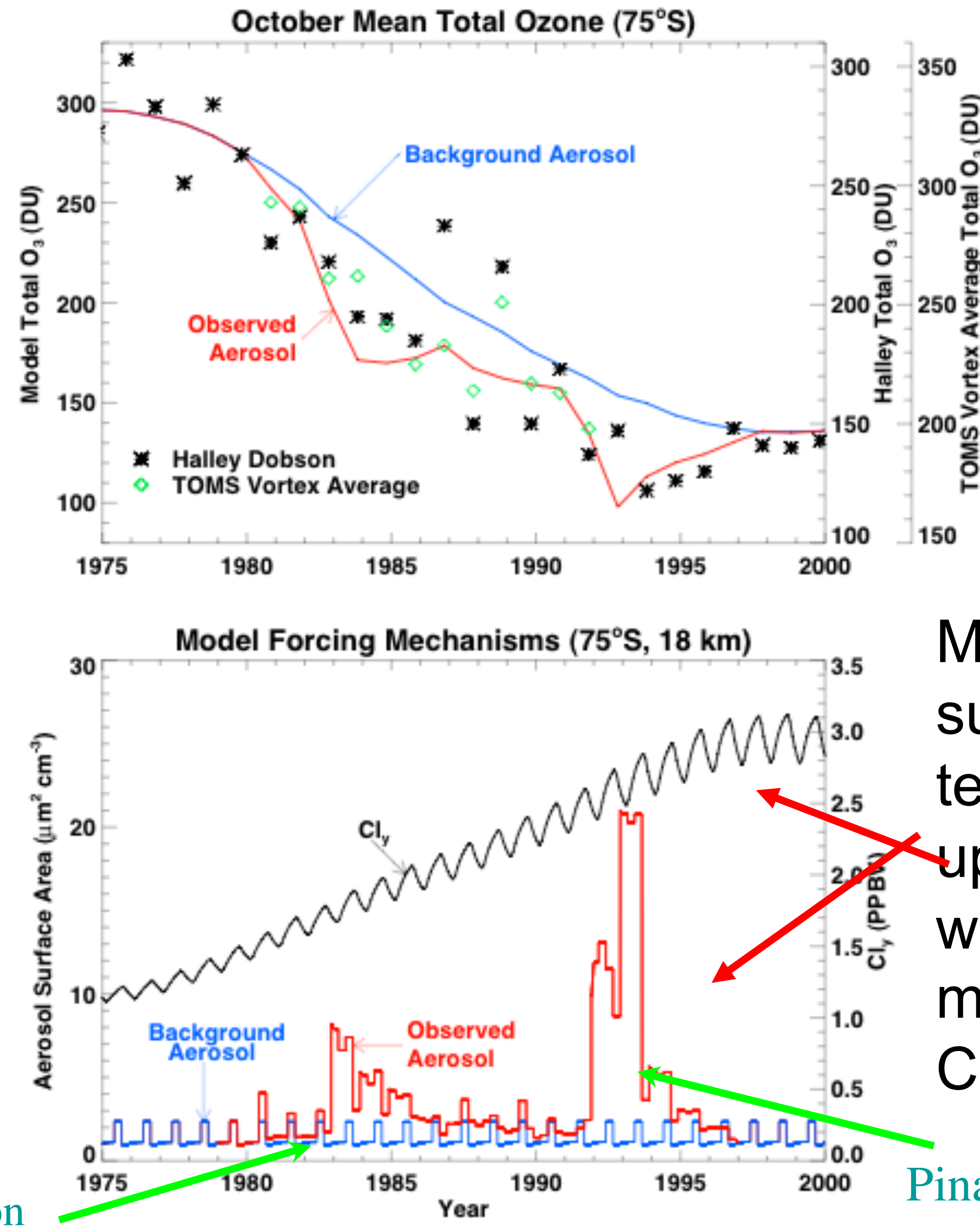




OClO observed as a function of lunar angle through the nights in Antarctica (about 100x greater than gas-phase chemistry!).

Liquid aerosol effects on ozone depletion can be readily seen in the Antarctic record and played a significant l role in the 'onset' after the Chichon eruption [Shanklin was right in the letter to NASA]

(Portmann, Solomon et al., JGR, 1996)



More surface teams up with more Cly

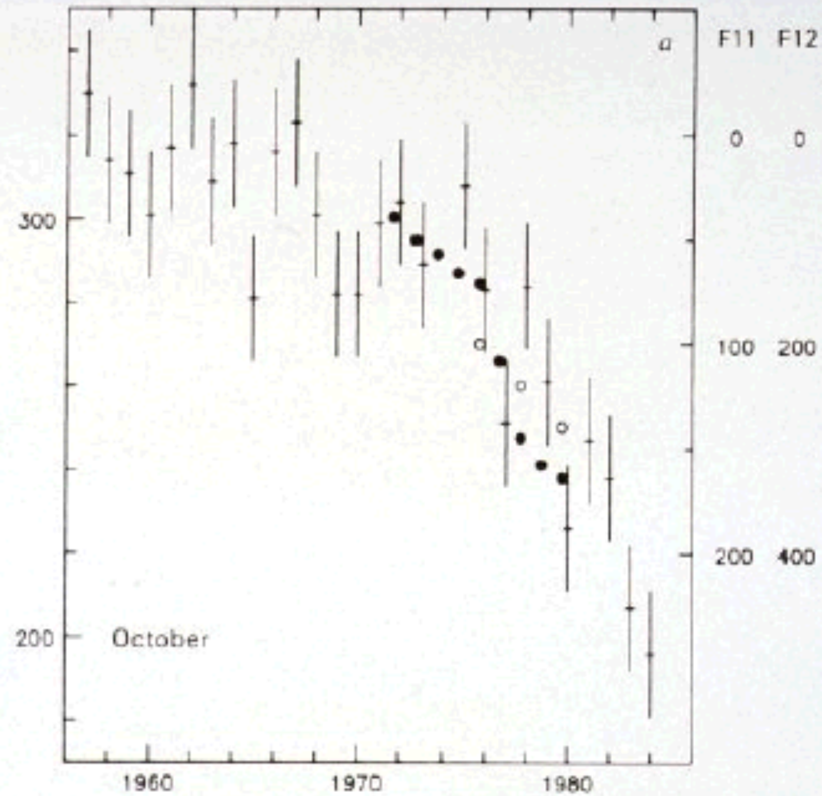
El Chichon

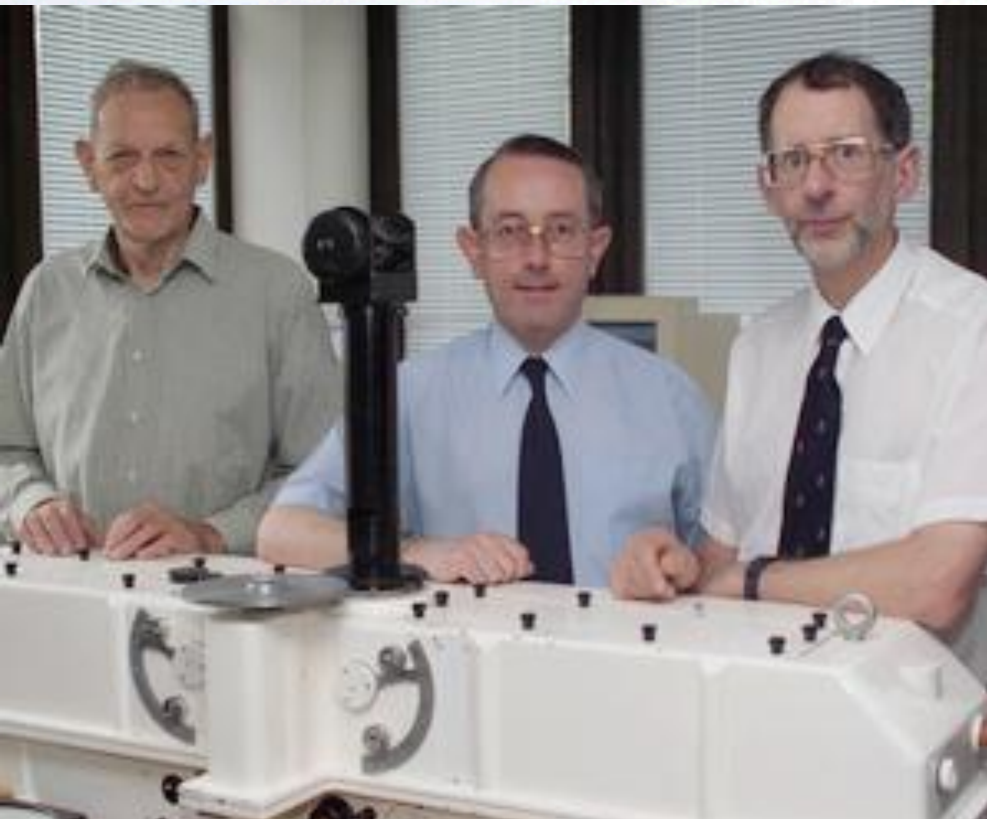
Pinatubo

Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction

J. C. Farman, B. G. Gardiner & J. D. Shanklin

British Antarctic Survey, Natural Environment Research Council, High Cross, Madingley Road, Cambridge CB3 0ET, UK





Recent att
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observation
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is apparent
considered.

The Response of NASA

National Aeronautics and
Space Administration

Goddard Space Flight Center
Wallops Flight Facility
Wallops Island, Virginia 23337

NASA

001429

NOV 29 1983

Reply to Attn of: 1001

British Antarctic Survey
Attention: Mr. Jonathan D. Shanklin
High Cross Madingley Road
Cambridge, England CB3 OET

Subject: Request for Ozone Data

Your request of October 10, 1983, for ozone data has been forwarded to Mr. Alfred C. Holland (Code 963) of the Applications Directorate at this Facility. Our group is no longer involved in this activity.

Mr. Holland may be reached at telephone (804) 824-3411, extension 328.

Harvey C. Needleman, Head
Balloon Projects Branch

25th Anniversary
1958-1983