# Chlorofluorocarbons, Stratospheric Ozone, and the Montreal Protocol:

## Anatomy of a Successful International Environmental Agreement

## Part I : Science of Ozone in the Stratosphere

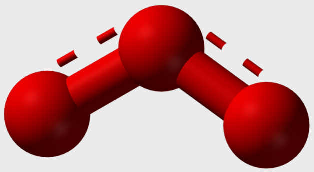

**Richard S. Stolarski    22 February 2012**

# Today we will learn:

- **Ozone in the Earth's stratosphere shields the surface from ultraviolet radiation**
- **Ozone is a renewable resource: it is being continuously created and destroyed**
- **Small emissions of chlorofluorocarbons can lead to buildup of parts per billion of chlorine because of their long lifetimes**
- **Parts per billion of chlorine can affect parts per million of ozone because of catalytic destruction processes**
- **Parts per million of ozone absorb virtually all of the radiation with wavelengths less than 300 nm (ultraviolet)**

# What is ozone?
# Why is it in the atmosphere?

- Ozone is a tri-atomic molecule of oxygen atoms



- Ozone is a powerful oxidizing agent, far stronger than $O_2$
- Ozone absorbs ultraviolet radiation

- Ozone is produced by the action of solar ultraviolet radiation on atmospheric molecular oxygen, $O_2$

# The smell of ozone was well-known in ancient history: but they did not know its source!

- **“Zeus thundered and hurled his bolt upon the ship and she quivered from stem to stern, smitten by the bolt of Zeus, and was filled with sulphurous smoke.” *Homer in the Odyssey***

- **“[Zeus] thundered horribly and dashed it to the ground in front of the horses of Diomedes, and a ghastly blaze of flaming sulphur shot up and the horses, terrified, both cringed away against the chariot.” *Homer in the Iliad***

**“Lightning and thunder are attended with a strong smell of sulphur, and the light produced by them is of a sulphurous complexion.” *Pliny***

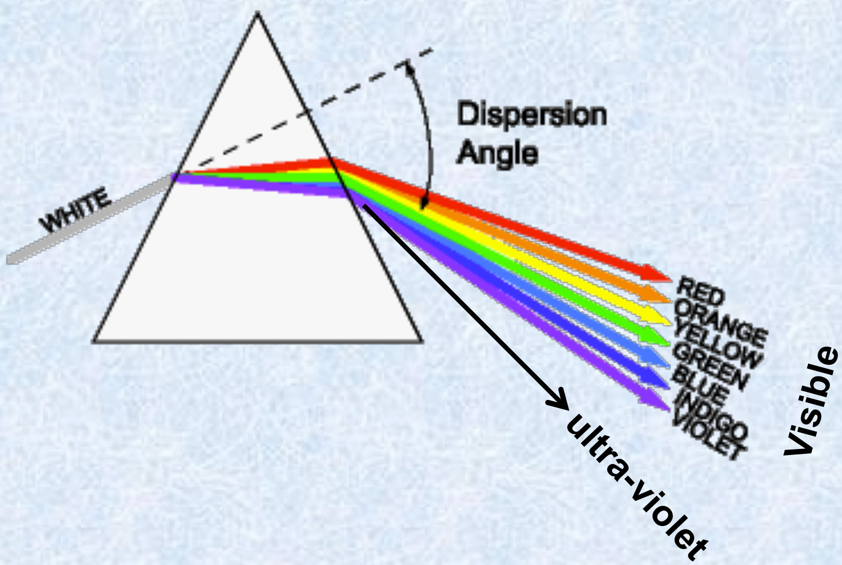
# Christian Friedrich Schönbein “discovered” ozone

- Christian Friedrich Schönbein in 1840 detected the same odor in an electrical discharge in his laboratory in Bern, Switzerland
- He recognized that the odor was not due to the electricity, but was due to the properties of a substance produced during the electrical process.
- He named this substance ozone (from ozein, Greek for "to smell").

Christian Friedrich Schönbein 1799–1868
The Discoverer of Ozone

# The Discovery of UV

- Johann Wilhelm Ritter uses a prism in 1801 to discover UV radiation
- Radiation beyond the violet darkened silver chloride!



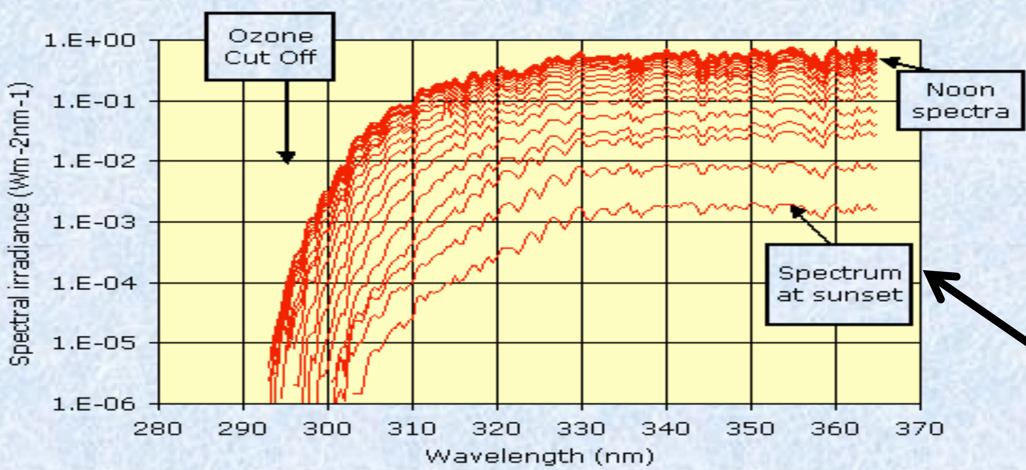

- One year earlier Herschel had discovered infrared radiation

Ritter

# Cutoff of the solar UV spectrum and the discovery of atmospheric ozone

**1879: Marie Alfred Cornú used newly-developed techniques for ultraviolet spectroscopy to measure the sun's spectrum.**

**To his surprise, the intensity of the sun's radiation dropped off rapidly at wavelengths below ~300 nm.**



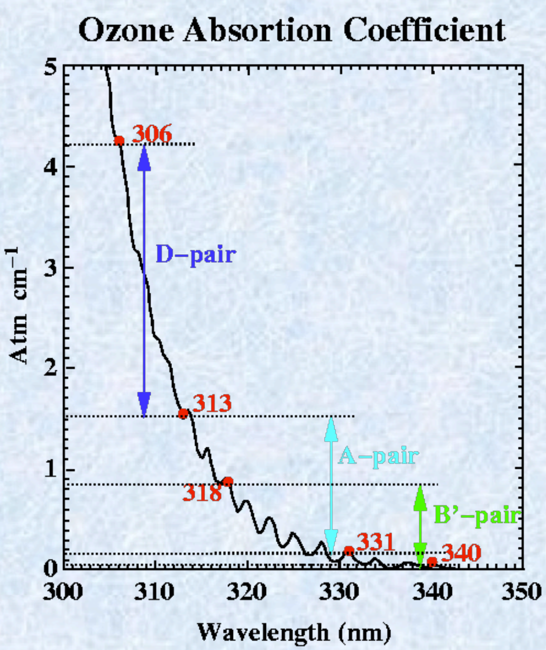


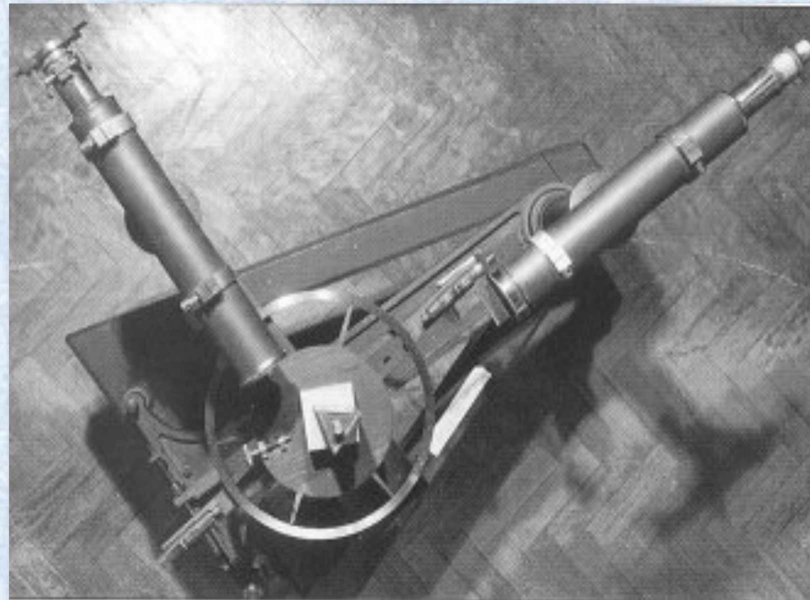
**Cornú**

**Modern spectral measurements**

# Hartley and the Identification of Atmospheric Ozone

- **1883: Hartley identified ozone as the substance absorbing uv from the sun at wavelengths less than 290 nanometers**

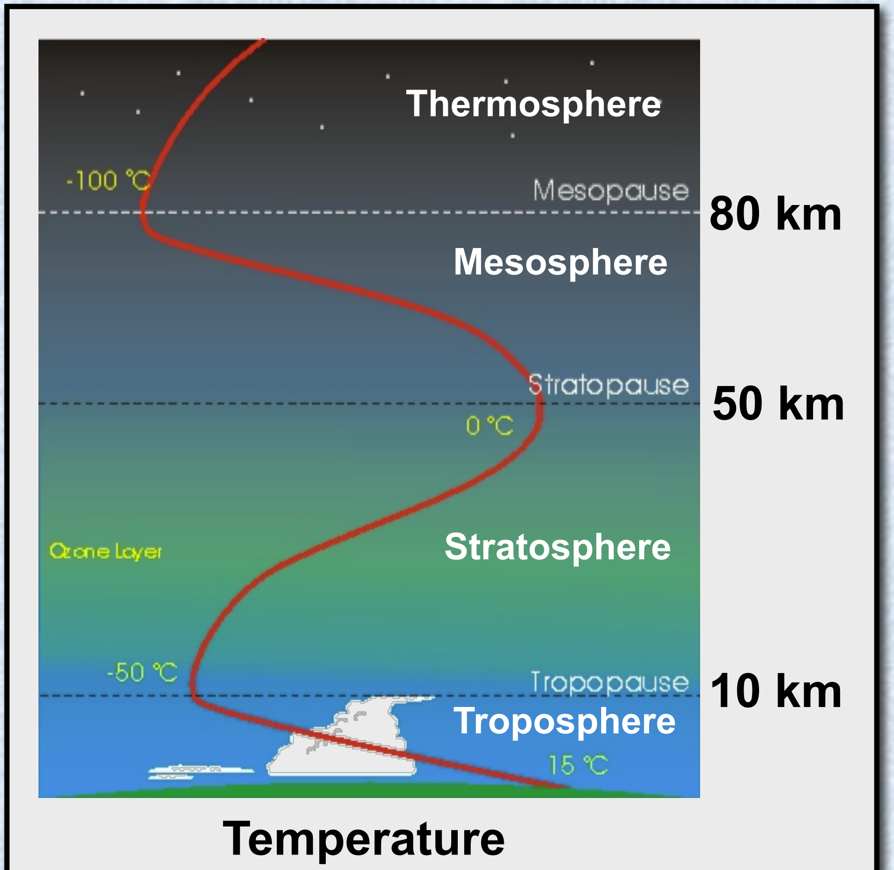


Hartley's Spectrometer
(note prism)

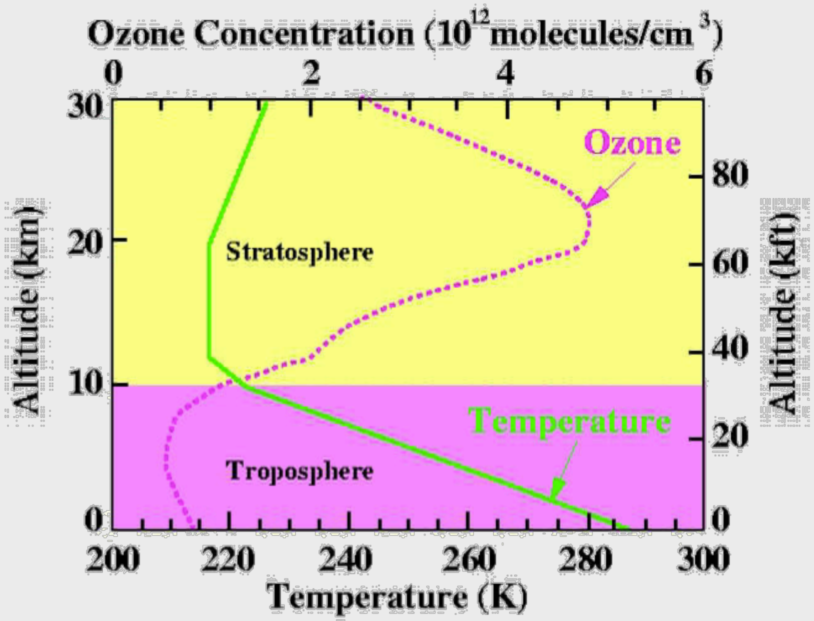
Sir Walter Noel Hartley

# Temperature Structure of the Atmosphere




1902: deBort discovers the stratosphere by ascending in a balloon with a thermometer

# Where is Ozone?




- Ozone is in a layer in the stratosphere
- Peak number density at about 20-25 km altitude
- Peak mole fraction at about 35 km altitude (~ 10 ppmv)

**Troposphere: lowest part of atmosphere where weather occurs (heated from below, unstable)**

**Stratosphere: above troposphere, permanent inversion layer (heated from above by $O_3$ absorption)**

# Ozone Photochemistry

## Odd Oxygen (O atoms + $O_3$ molecules)

### Chapman Theory 1930

| | |
|---|---|
| Initiation: | $h\nu + O_2 \text{ ---> } O + O$ <br> ($\lambda$ < 240 nm) |
| Propagation: | $O + O_2 + M \text{ ---> } O_3 + M$ <br> $h\nu + O_3 \text{ ---> } O_2 + O$ <br> (200 nm < $\lambda$ < 300 nm) |
| Termination: | $O + O_3 \text{ ---> } O_2 + O_2$ |

Sydney Chapman

**Ozone is continuously being made and destroyed in the atmosphere**

# Catalysis Accelerates Termination Reaction

**A catalytic agent speeds the rate of a reaction without being destroyed in the reaction**

**Example: Chlorine**

$Cl + O_3$ ---> $ClO + O_2$

$ClO + O$ ---> $Cl + O_2$

-------------------------------

$O + O_3$ ---> $O_2 + O_2$ net

**Fritz Weigert first studied the impact of chlorine on ozone decomposition his laboratory in 1907**

**Other examples are hydrogen, nitrogen, and bromine oxides**

# Fritz Weigert (1876-1947)

- Began his career in Nernst's laboratory in Berlin in 1905
- Did ozone photolysis experiments: published chlorine impact on ozone loss in 1907
- 1908 appointed lecturer in chemistry at Berlin University
- 1914 became professor of scientific photography and photochemistry at Leipzig
- Published many papers and books including "Optische Methoden der Chemie"
- 1936 fled Nazi Germany to England
- Took position on staff of Mount Vernon Hospital in Northwood
- Wrote a series of significant papers on the metabolism of chemical carcinogens

# Why are there oxides of hydrogen, nitrogen, chlorine, and bromine in the stratosphere?

They are generally reactive radicals form soluble compounds that will be washed out of the atmosphere when it rains

To get to the stratosphere, these reactive compounds need carriers that:

1. are not soluble
2. are unreactive
3. do not absorb visible light

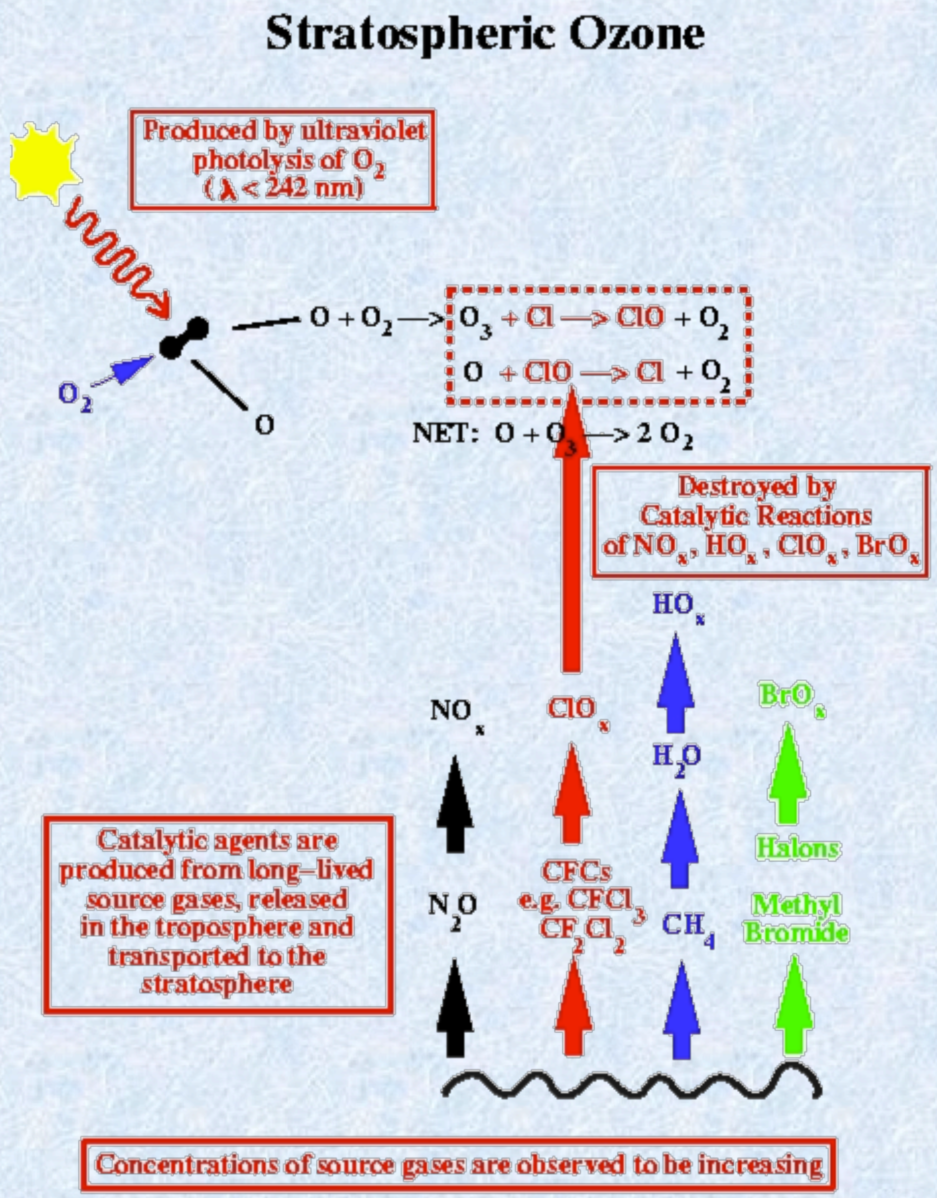
Nitrous Oxide ($N_2O$) …... → $NO_x$

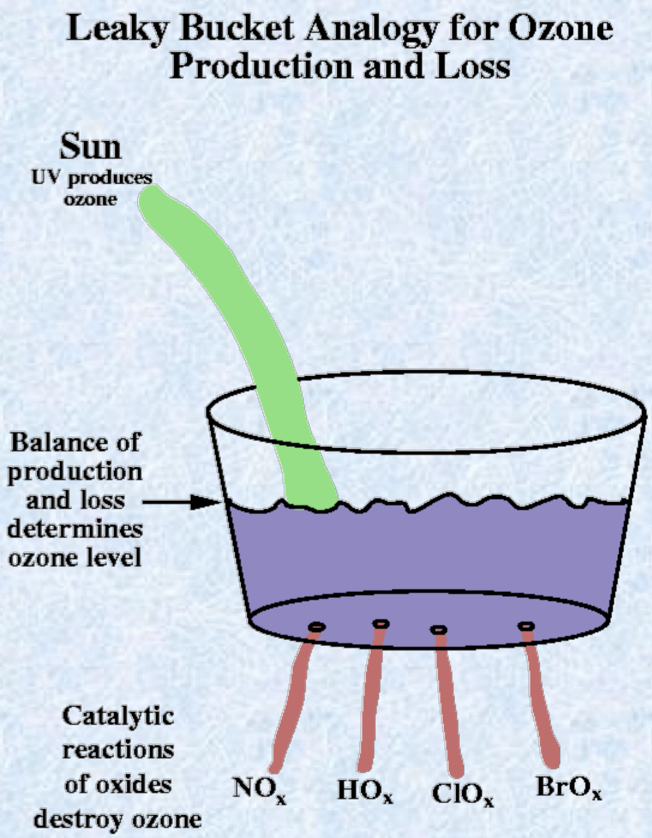
Methane ($CH_4$) …………. → $HO_x$

Methyl Chloride ($CH_3Cl$) → $ClO_x$

Methyl Bromide ($CH_3Br$) → $BrO_x$

# Biogeochemical Cycling of Elements and Stratospheric Ozone

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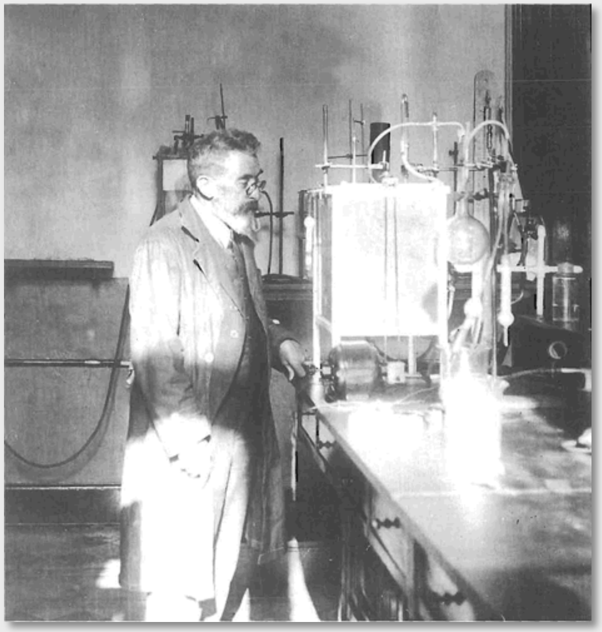
# Enter Chlorofluorocarbons (CFCs) !



**1898**
**Synthesis by Frederic Swarts, a Belgian fluorine chemist**

**1930**
**Process for industrial manufacture by Thomas Midgely**

Thomas Midgley with the single cylinder laboratory engine used to test fuel additives.

- **Came up with CFCs as a replacement for dangerous chemical in refrigerators, e.g. ammonia, sulfur dioxide**
- **Midgley also synthesized tetraethyl lead to reduce knocking in auto engines**

# The Curious Case of Thomas Midgley

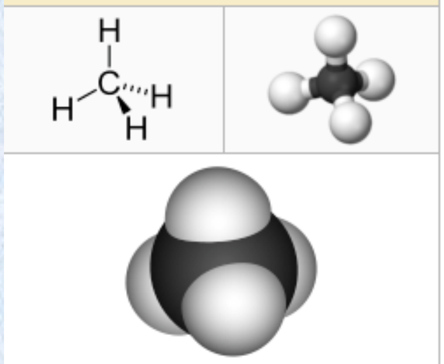
**Midgley became ill with polio and invented a mechanical bed to assist him: but he died of his own invention when he became entangled in the pulleys and strangled himself !**

# What are CFCs?

## (Chlorofluorocarbons)

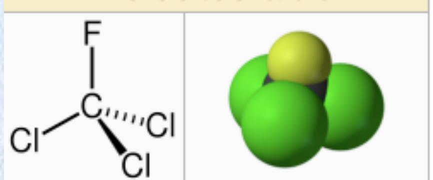
**Simplest CFCs are just methane ($CH_4$) with hydrogen replaced by halogen (chlorine or fluorine): e.g. CFC-11 ($CFCl_3$) or CFC-12 ($CF_2Cl_2$)**

**$CH_4$**



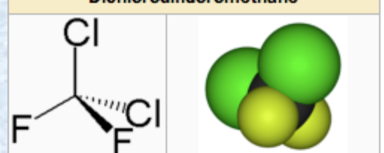
| Methane | |
|---|---|
| Other names | Marsh gas, firedamp |

**$CFCl_3$ (CFC-11)**



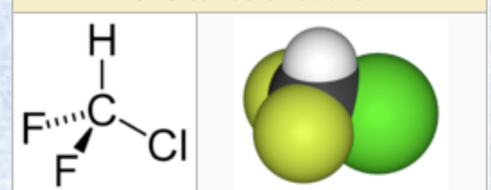
| Trichlorofluoromethane | |
|---|---|
| IUPAC name | Trichlorofluoromethane |
| Other names | Trichloro(fluoro)methane, Fluorotrichloromethane, Fluorochloroform, Freon 11, CFC 11, R 11, Arcton 9, Freon 11A, Freon 11B, Freon HE, Freon MF |

**$CF_2Cl_2$ (CFC-12)**



| Dichlorodifluoromethane | |
|---|---|
| IUPAC name | Dichlorodifluoromethane |
| Other names | Carbon dichloride difluoride, Dichloro-difluoro-methane, Difluorodichloromethane, Freon 12, R-12, CFC-12, P-12, Propellant 12, Halon 122, Arcton 6, Arcton 12, UN 1028 |

**$CHClF_2$ (HCFC-22)**



| Chlorodifluoromethane | |
|---|---|
| IUPAC name | Chlorodifluoromethane |
| Other names | Difluoromonochloromethane, Monochlorodifluoromethane, HCFC-22, R-22, Genetron 22, Freon 22, Arcton 4, Arcton 22, UN 1018 |

# How did we come to know about the importance of CFCs?

**Article**

*Nature* **249**, 810-812 (28 June 1974) | doi:10.1038/249810a0

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

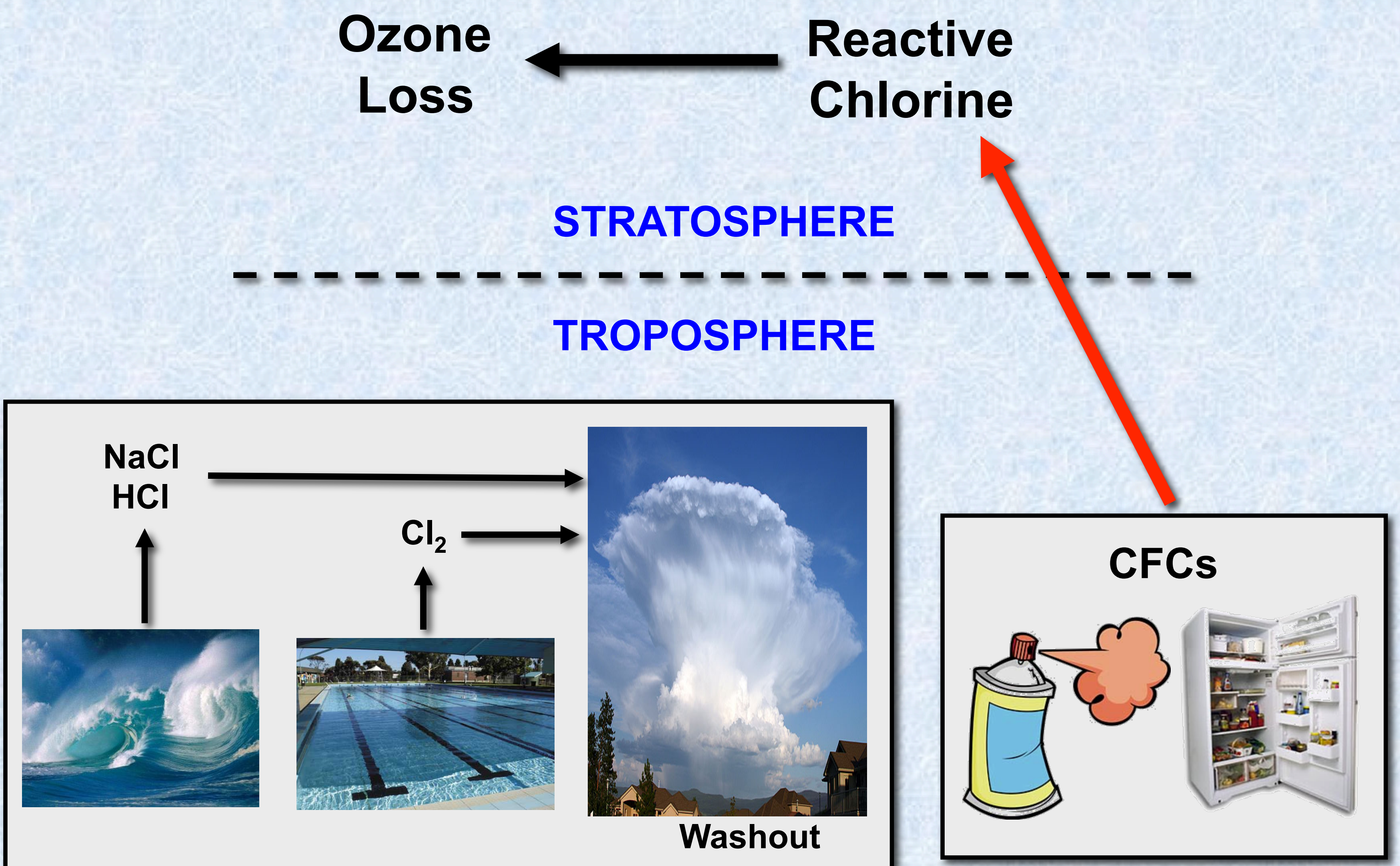
Mario J. Molina & F. S. Rowland

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

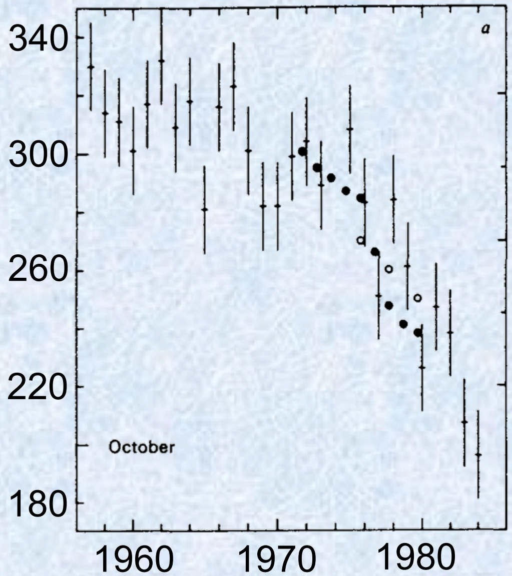
**Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the Chlorofluoromethanes in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

# Why are CFCs Important?

**They are carriers for chlorine to get to the stratosphere**



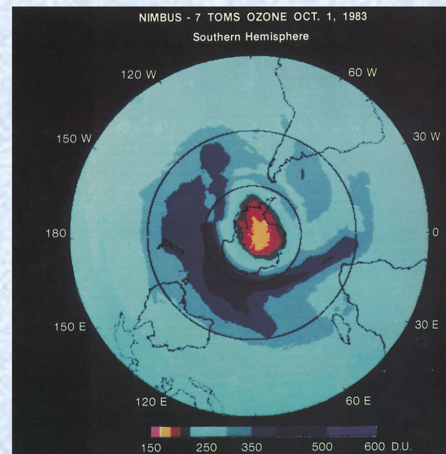
# Ozone Hole Discovery



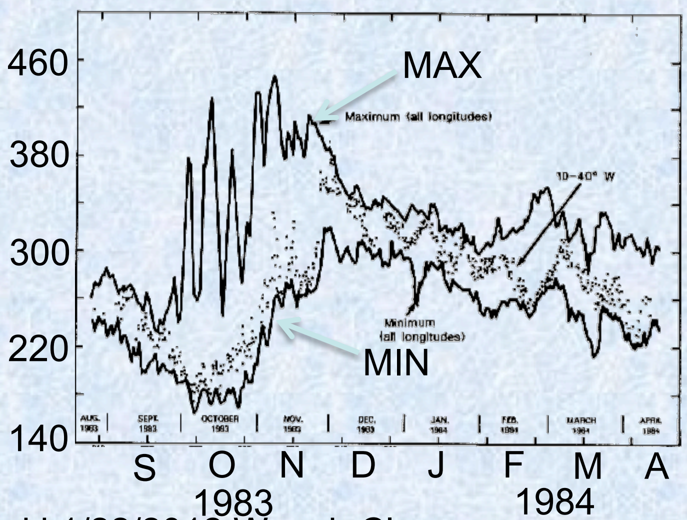


Farman, Gardiner, & Shanklin (1985)

**Discovered (1985) at the British Antarctic Survey station at Halley Bay from measurements begun during the IGY**




**Original TOMS ozone hole map produced by Don Heath and PK Bhartia in 1985**



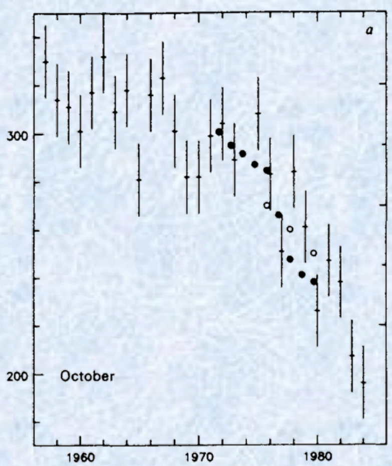

**Satellite measurements (1986) showed that Halley Bay was in best location for seeing ozone hole**

# The Antarctic Ozone Hole

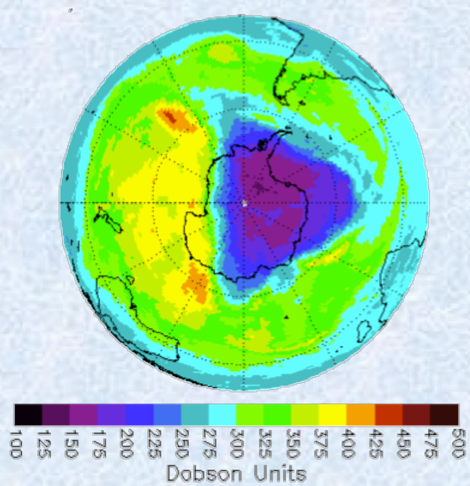
Discovery → Mapping → Smoking Gun

Theories

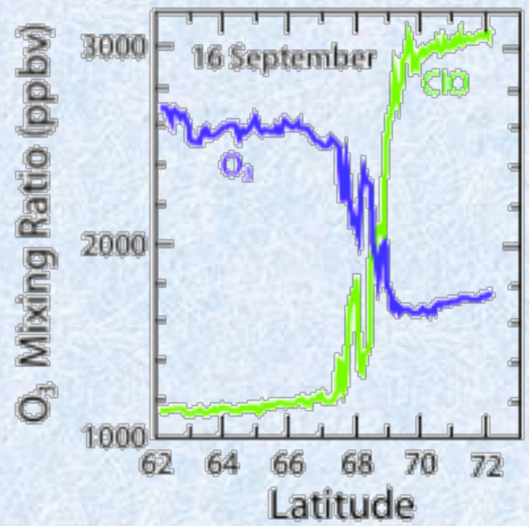
**1985**




**1986**

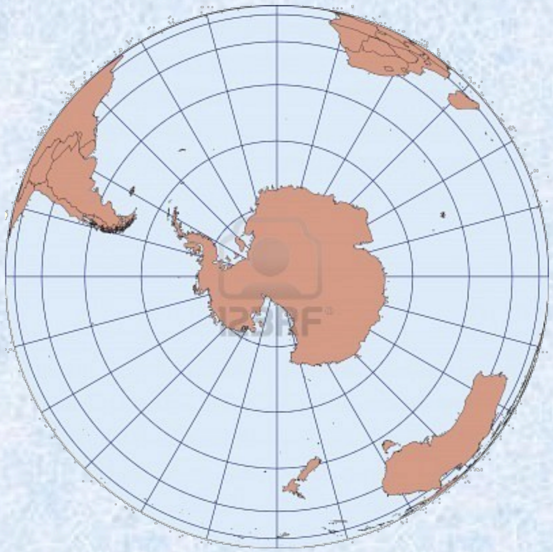



**1987**



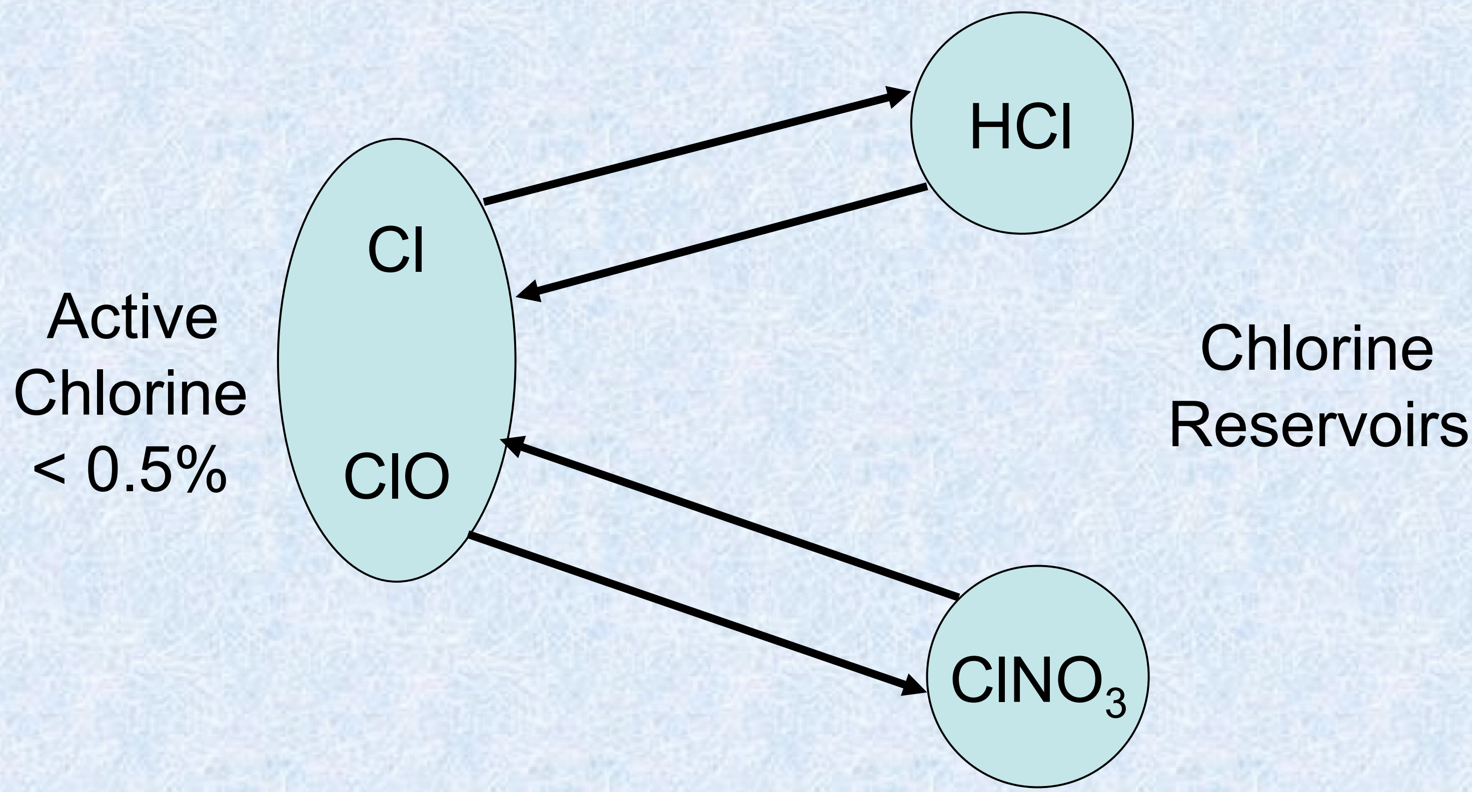

**Progress was very rapid because the ideas that formed the pieces of the puzzle were in place, some measurements had been started years before, and new measurement techniques had been, or were being developed.**

# Chemistry in the Antarctic What's Different?



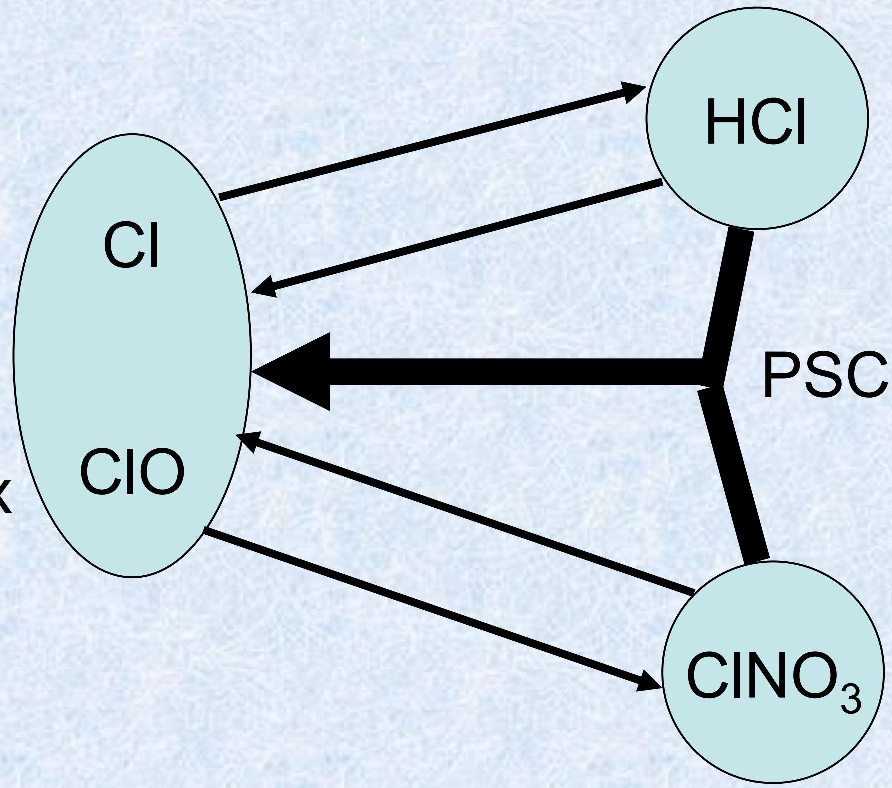
- Region is isolated by polar vortex winds (circumpolar ocean, few mountain ranges)
- Temperature gets very cold in polar night (radiation to space)
- Polar stratospheric clouds form (despite low humidity of stratosphere)
- Reactions on cloud surfaces convert chlorine reservoirs to active radicals
- Sun comes up, rapid ozone destruction begins

# Chlorine Photochemistry (normal)



# Chlorine Photochemistry (polar)

Active
Chlorine
Increases
By 50 to 100x




PSC Reactions
Drain
Chlorine
Reservoirs

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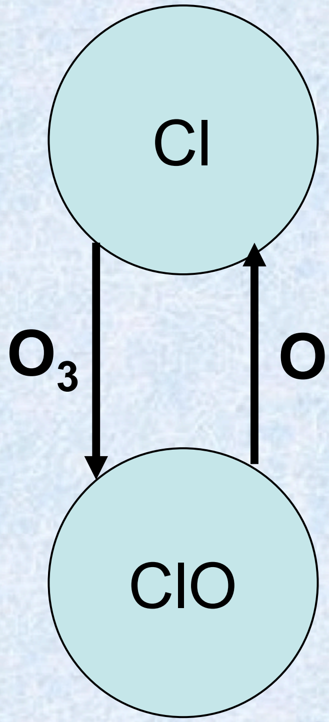
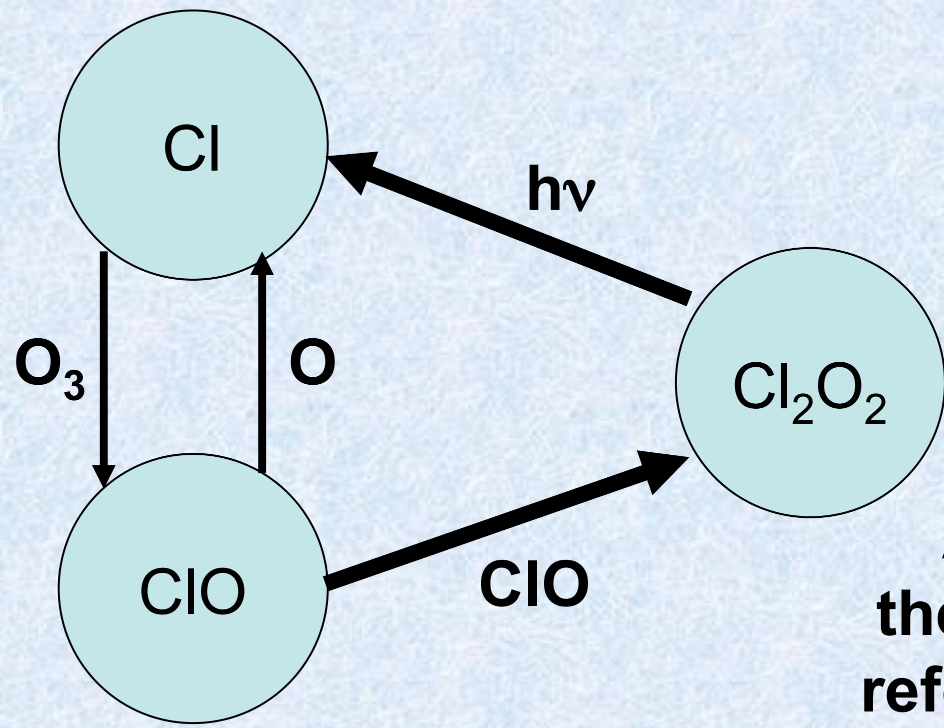
# Chlorine Photochemistry (normal)



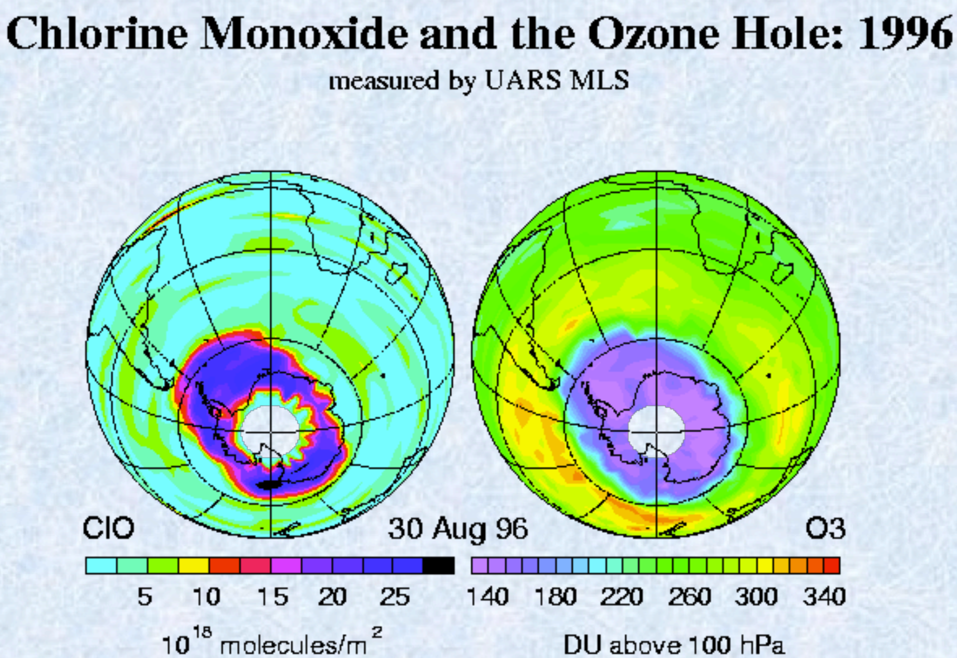

**Catalytic destruction is limited by the availability of oxygen atoms**

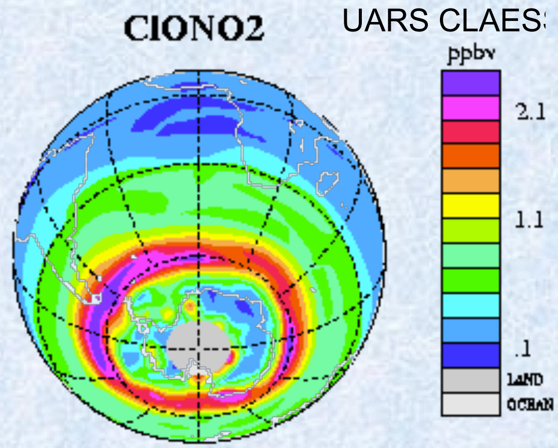
# Chlorine Photochemistry (Polar)

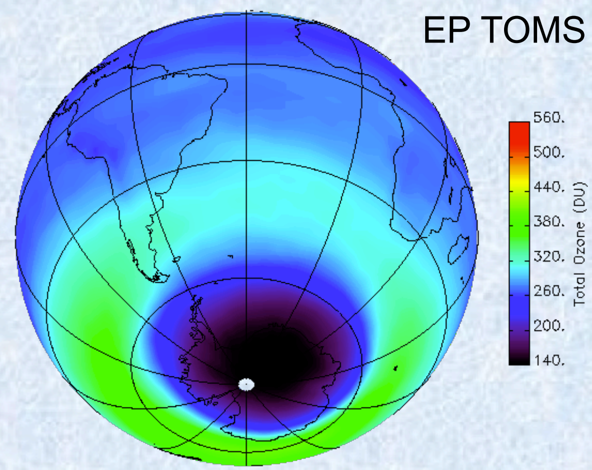


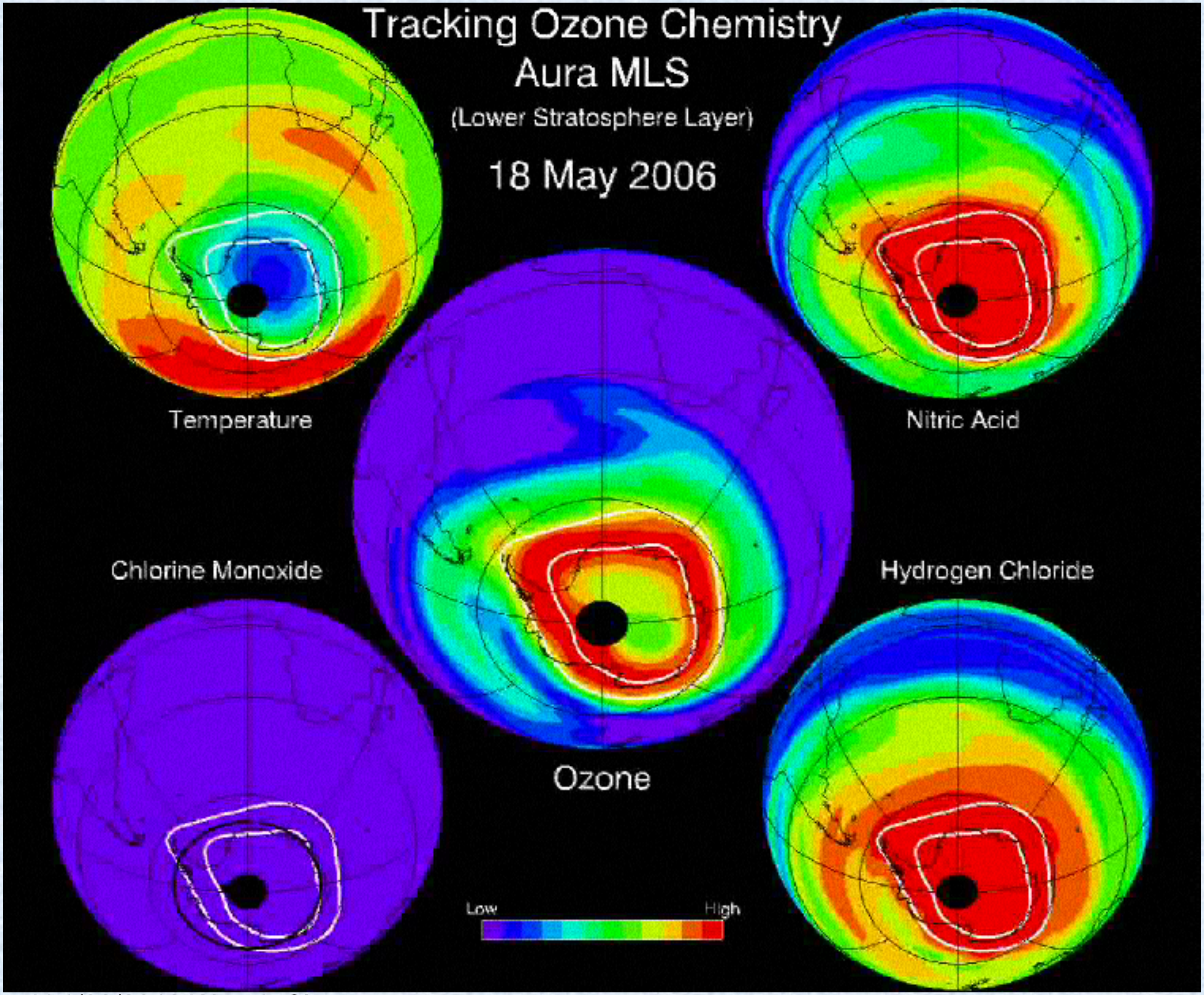

**At High ClO the self-reaction reforms Cl atoms without atomic oxygen**

# Satellite Measurements of the Ozone Hole



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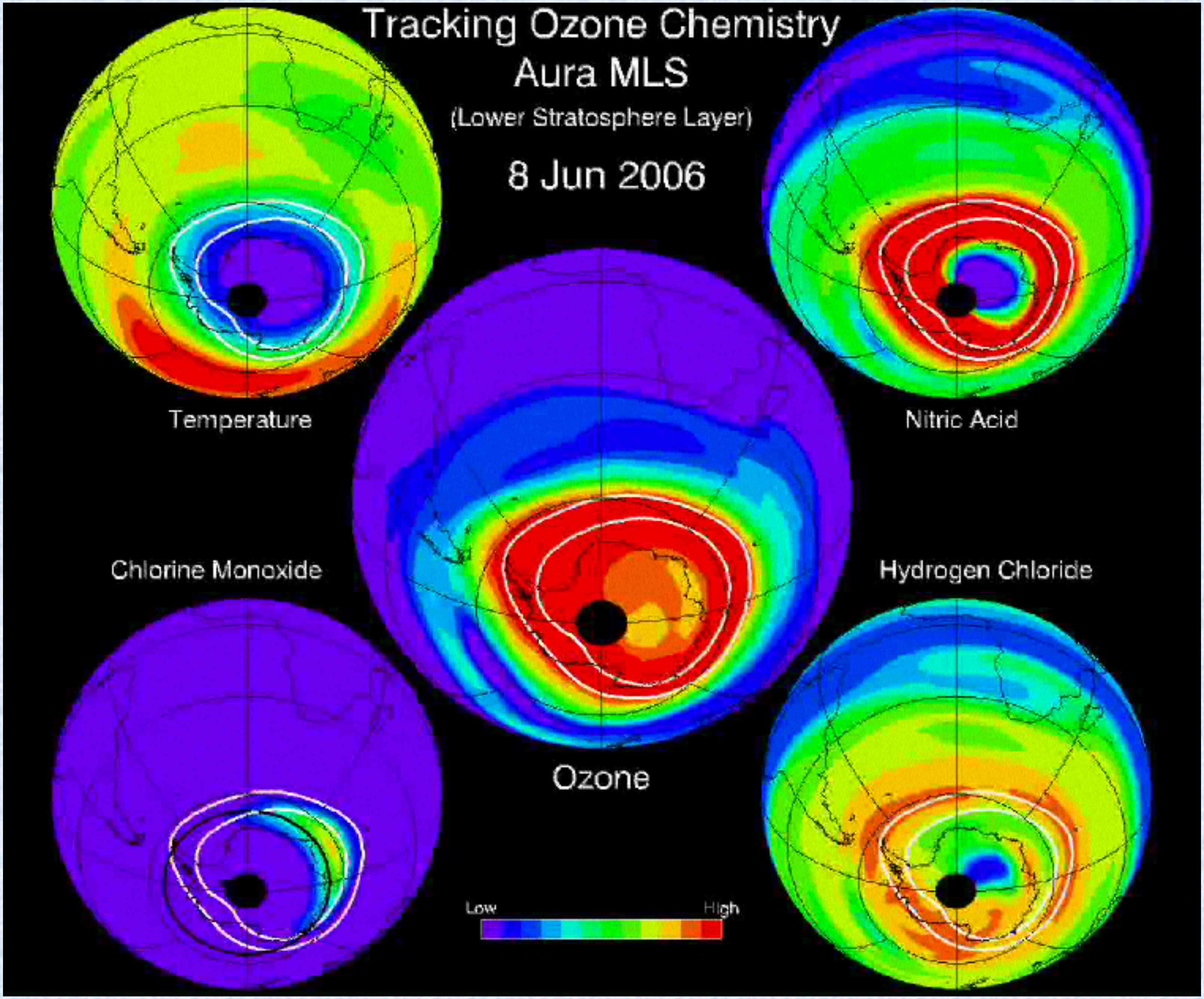


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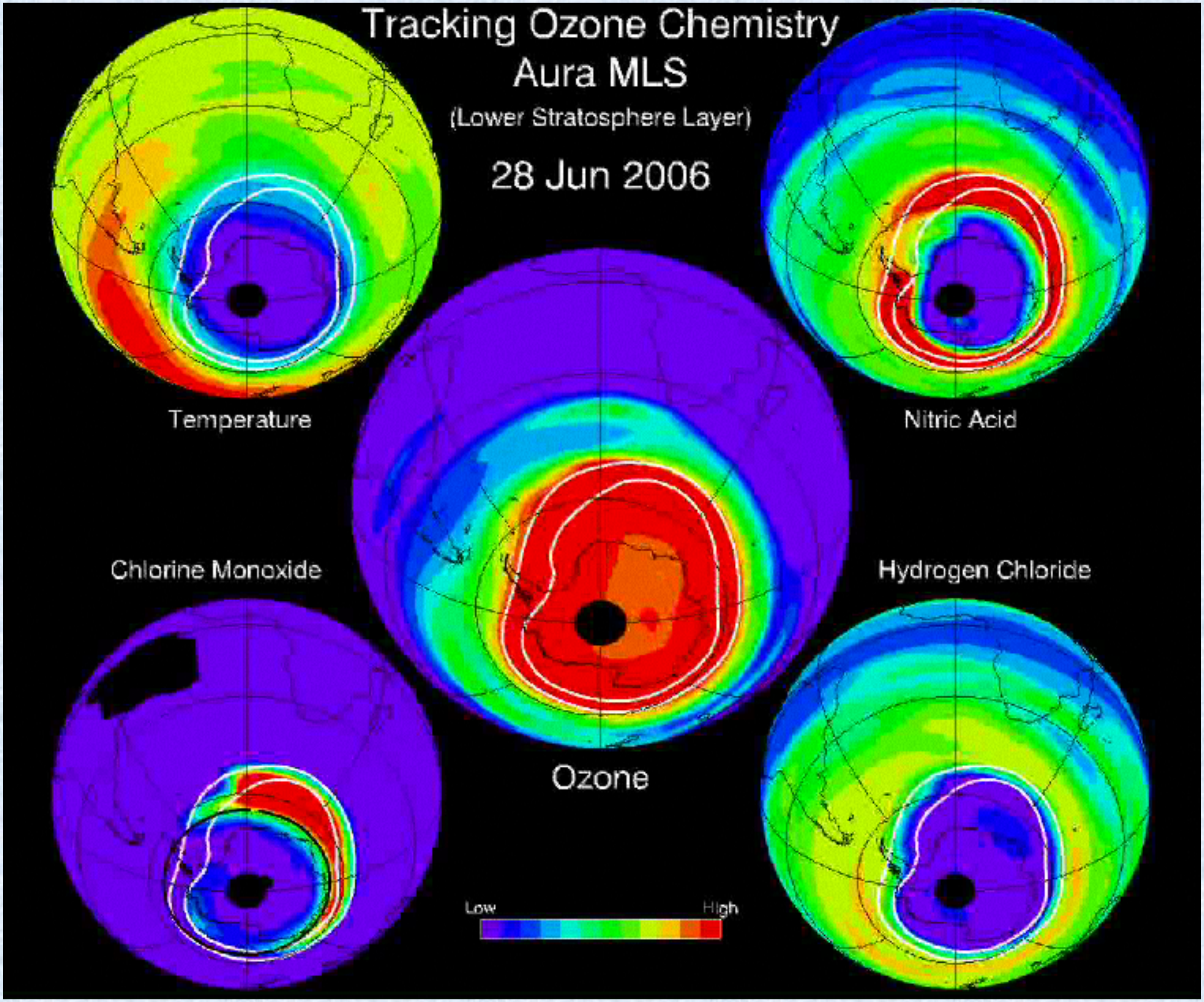
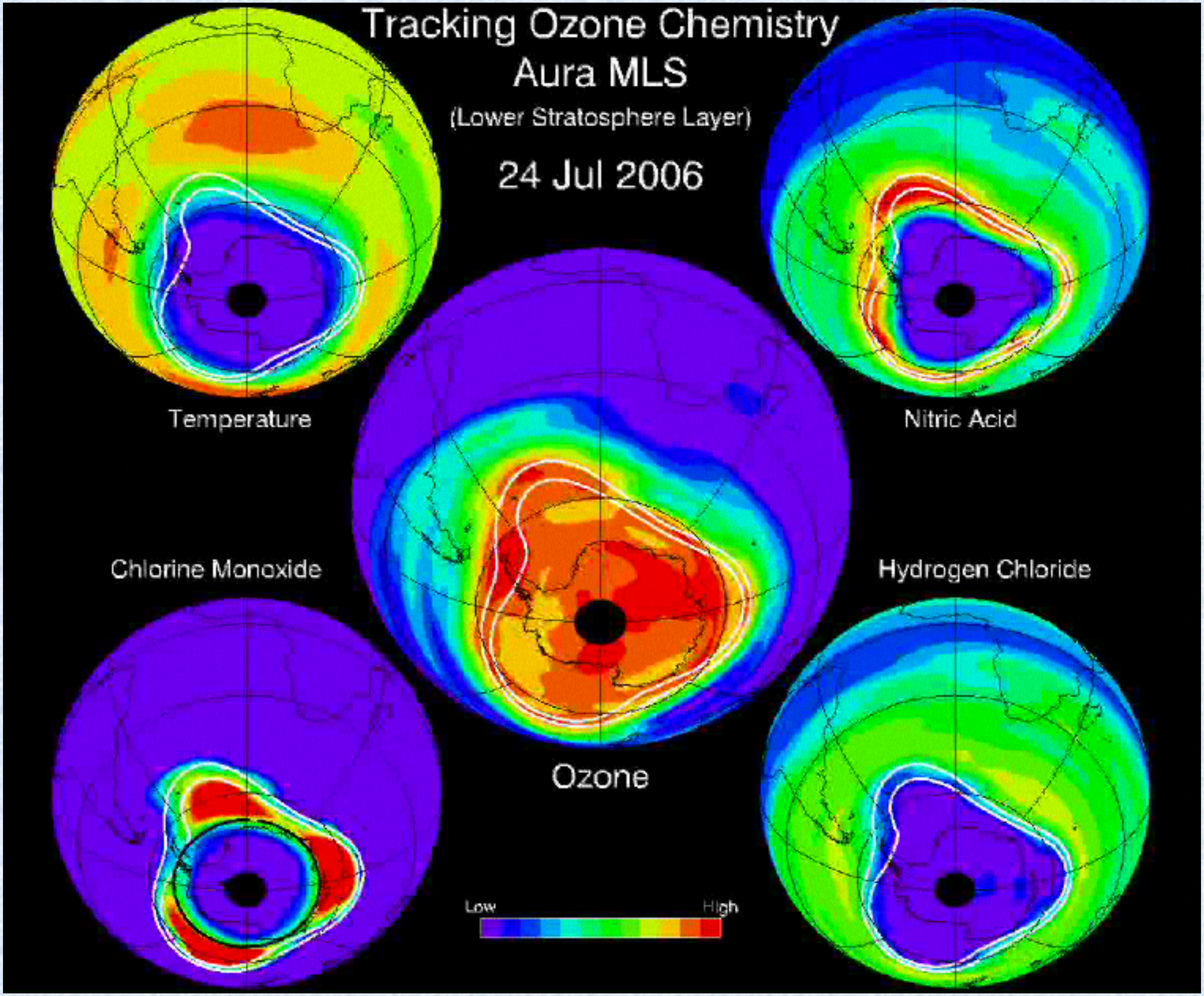

Tracking Ozone Chemistry
Aura MLS
(Lower Stratosphere Layer)
28 Jun 2006
Temperature
Nitric Acid
Chlorine Monoxide
Hydrogen Chloride
Ozone
Low
High

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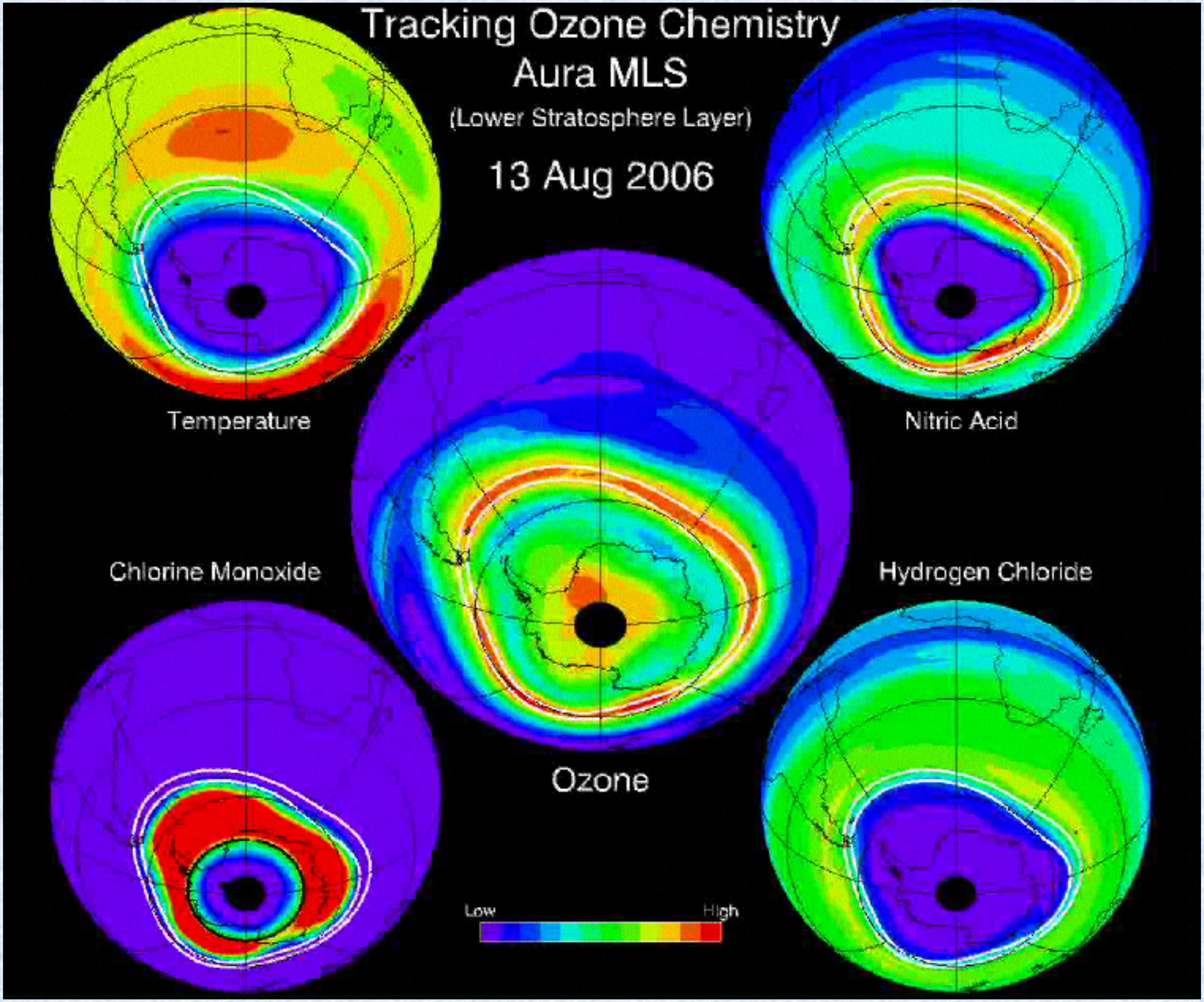


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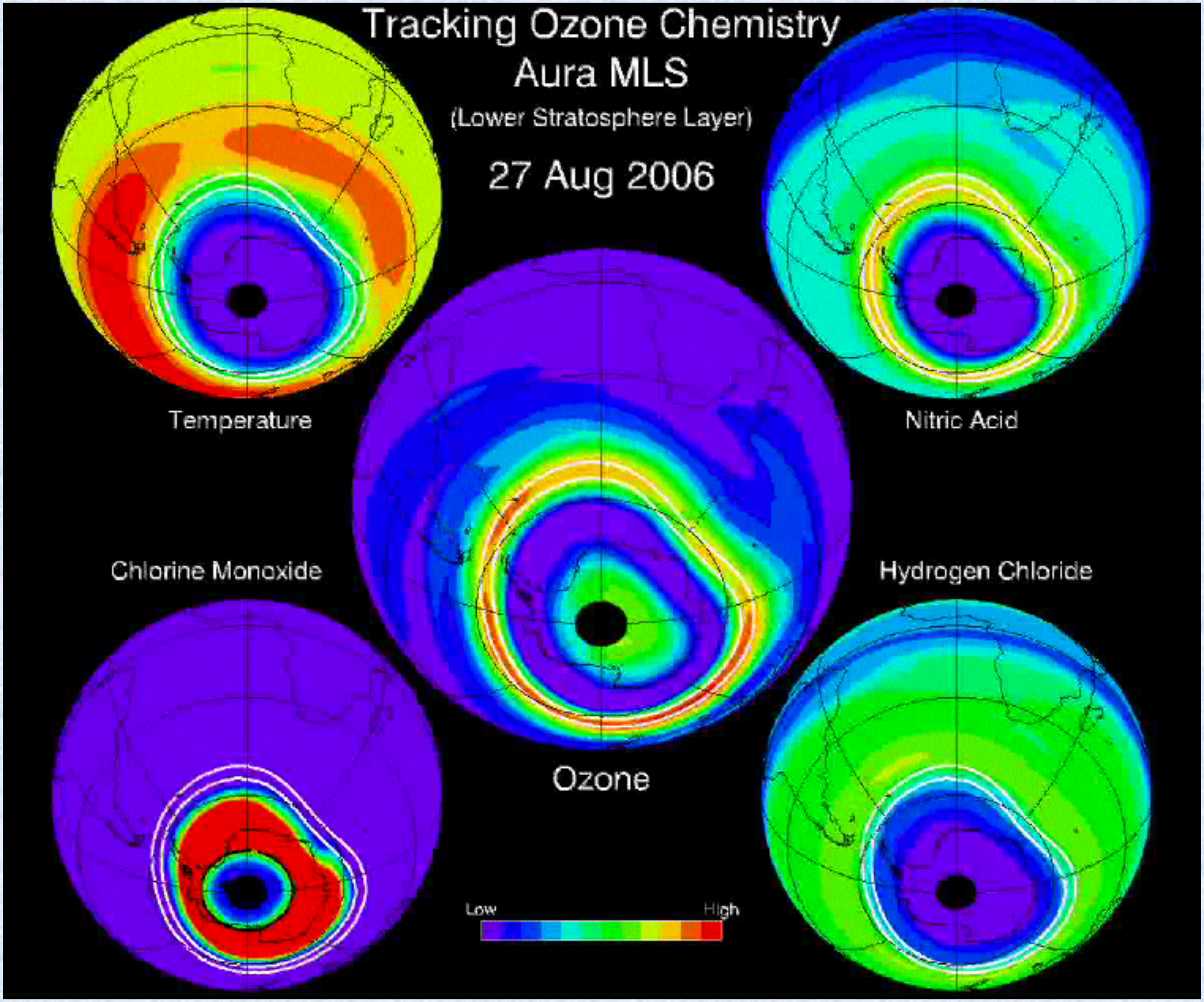


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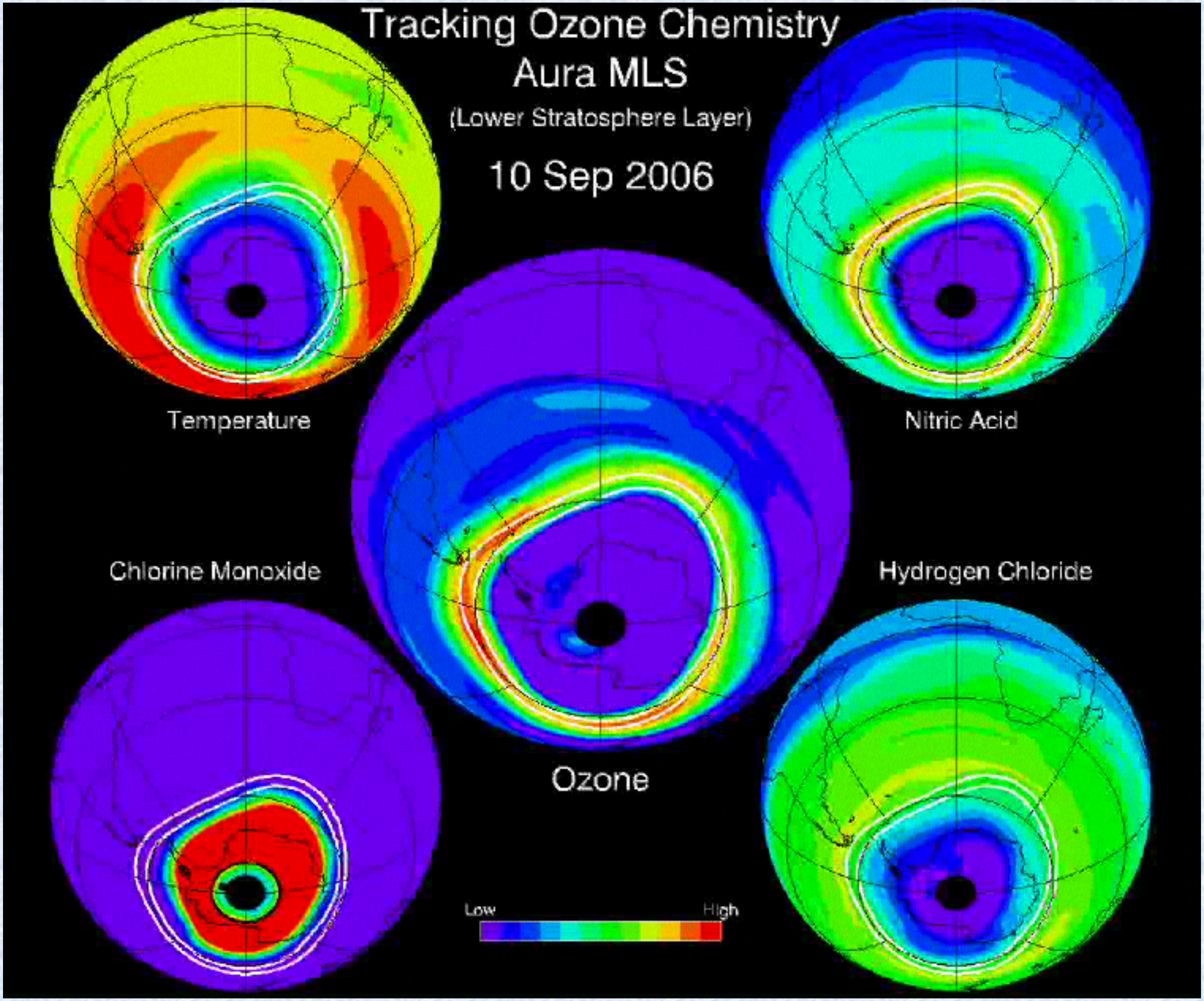


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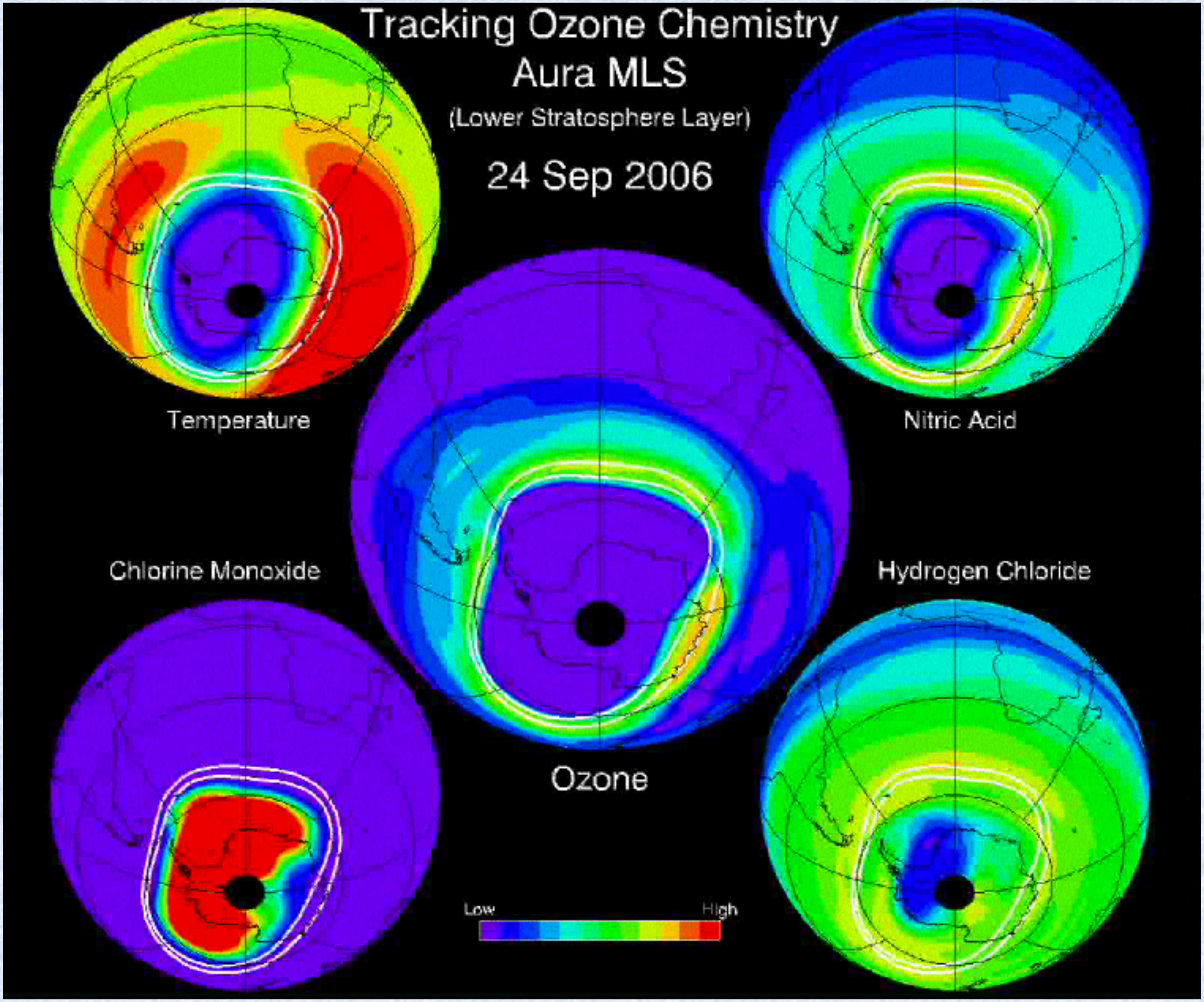


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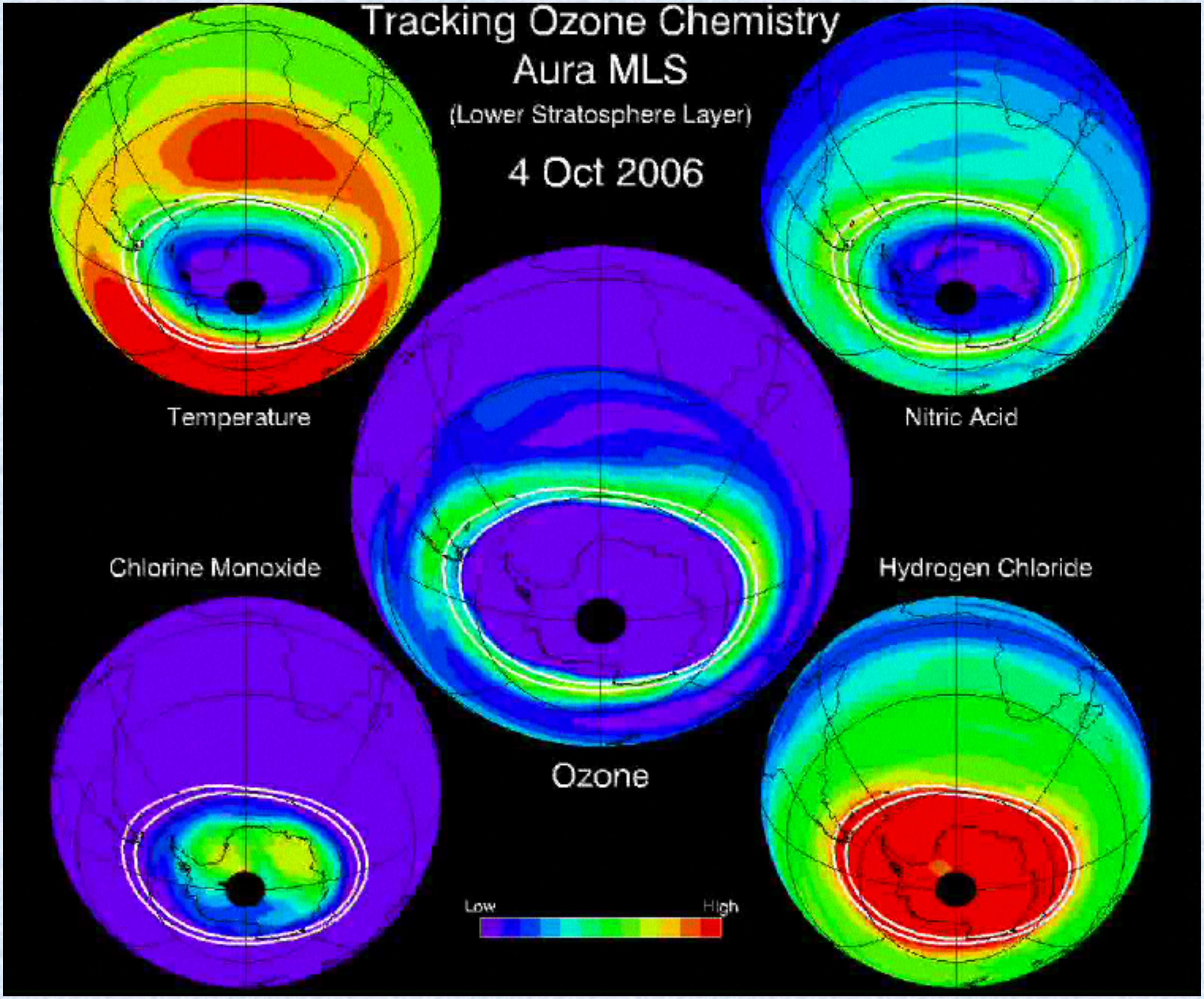
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Aura MLS
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Temperature
Nitric Acid
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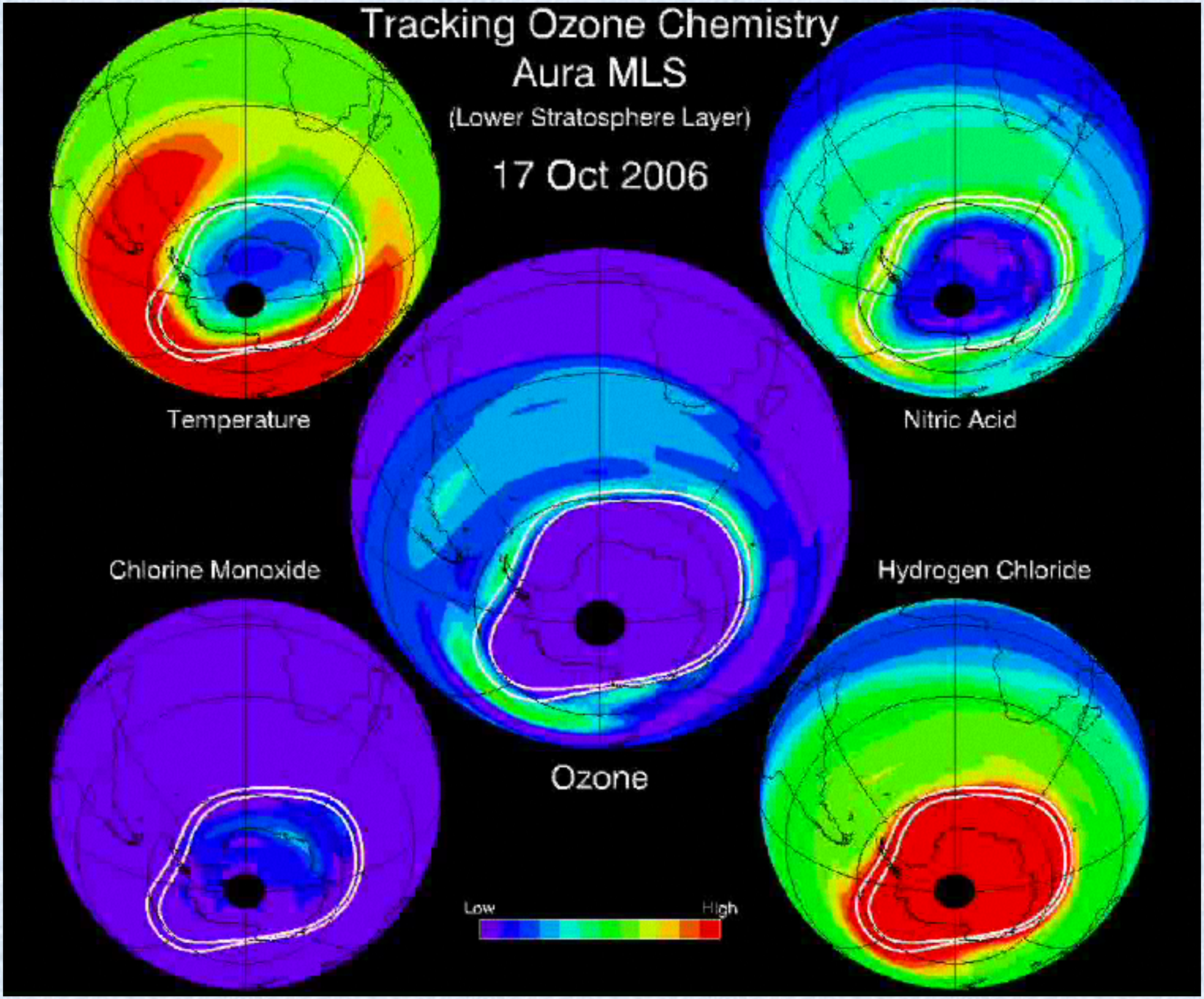


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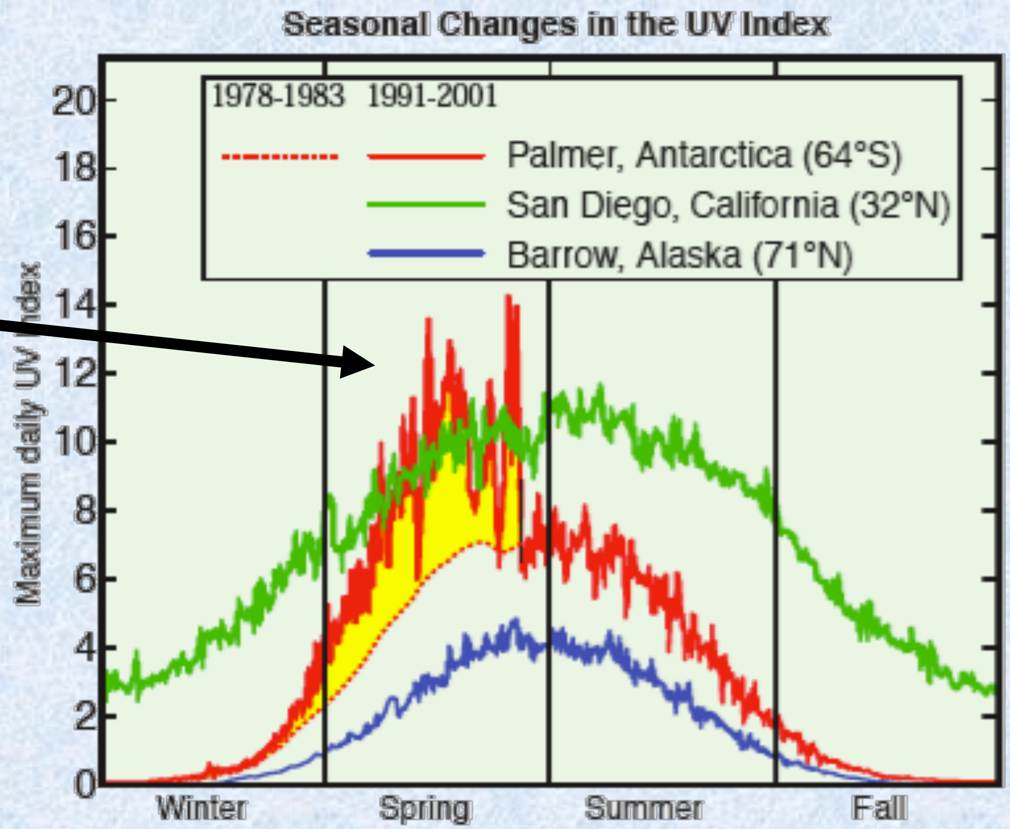
# Does the Ozone Hole Matter?

When ozone hole passes over Antarctic peninsula (and southern part of South America) UV index can be larger than low latitude regions like San Diego

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# Summary

- Ozone shields the surface from ultraviolet radiation
- Ozone is a renewable resource
- Chlorofluorocarbons have long lifetimes
- Parts per billion of chlorine can affect parts per million of ozone
- Parts per million of ozone absorb virtually all of the UV

**Next time**

**The Montreal Protocol**