Atmospheric Physics
UNIVERSITY OF TORONTO

The 2007 Noble Lecture Series

Atmospheric Chemistry and the Remote Sensing of the Global atmosphere March 26-30th 2007.

Lecture 1: Historical Perspectives: Atmospheric Chemistry and Remote Sensing

John P. Burrows
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University of Bremen, Bremen, Germany

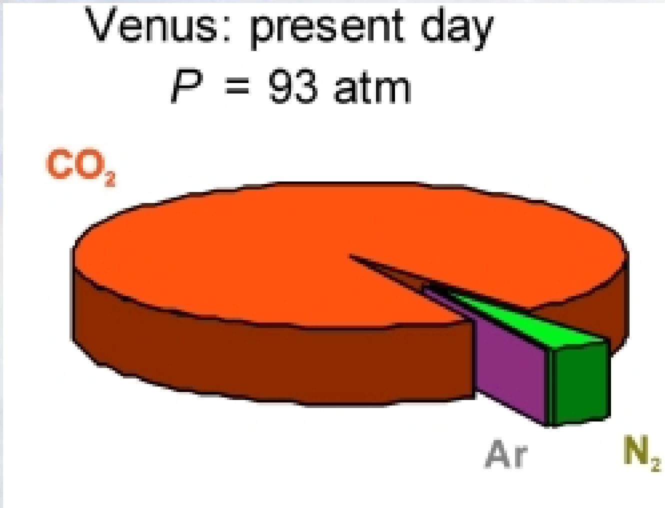
Lecture 1 : Content

Today's lecture addresses some of the milestones in our development of Atmospheric Chemistry and passive Remote Sensing using backscattered and reflected solar radiation.

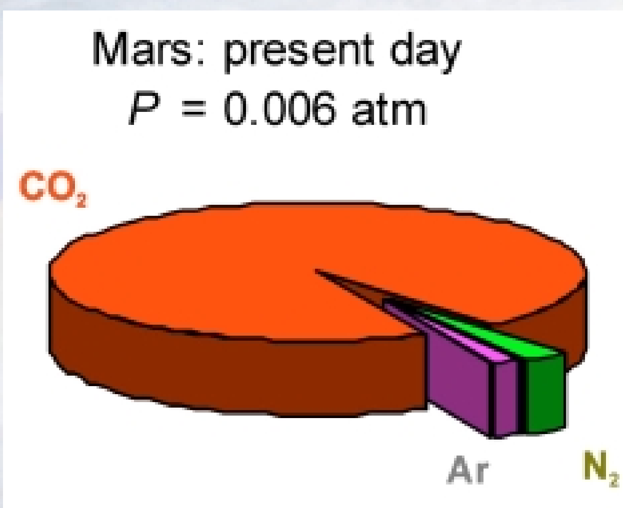
This lecture is based largely on „150 Years of Ozone Research“ By Guy Brasseur, NCAR. and „Origin of life and the Atmosphere“ By R. P. Wayne , University of Oxford

It is not complete but an interesting point for you to study more!

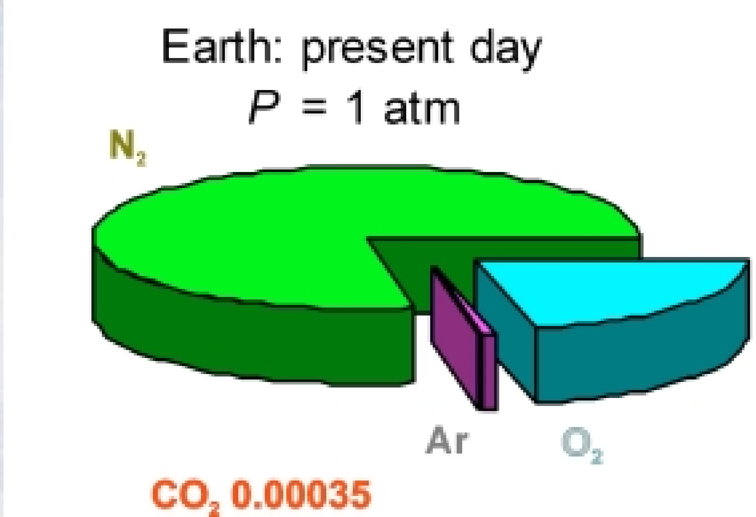
Planetary Atmospheres



Planetary Atmospheres



Planetary Atmospheres



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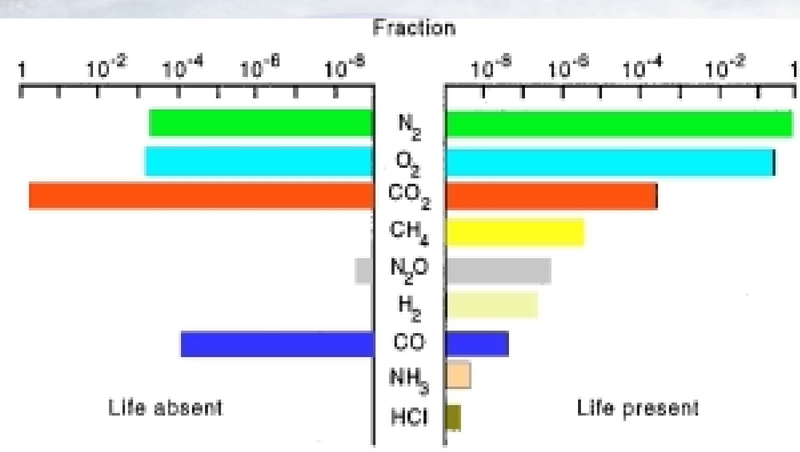
Earth's Atmosphere



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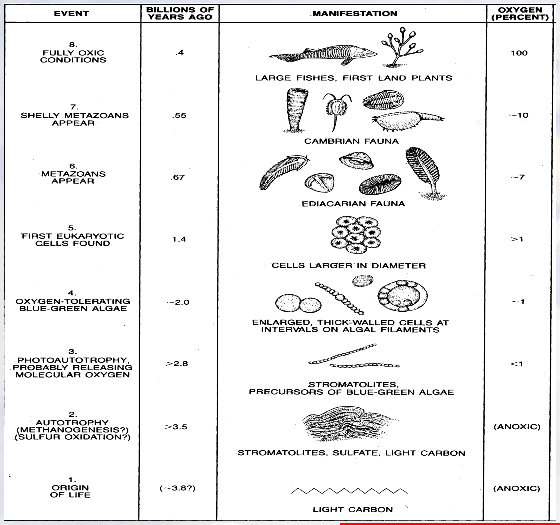
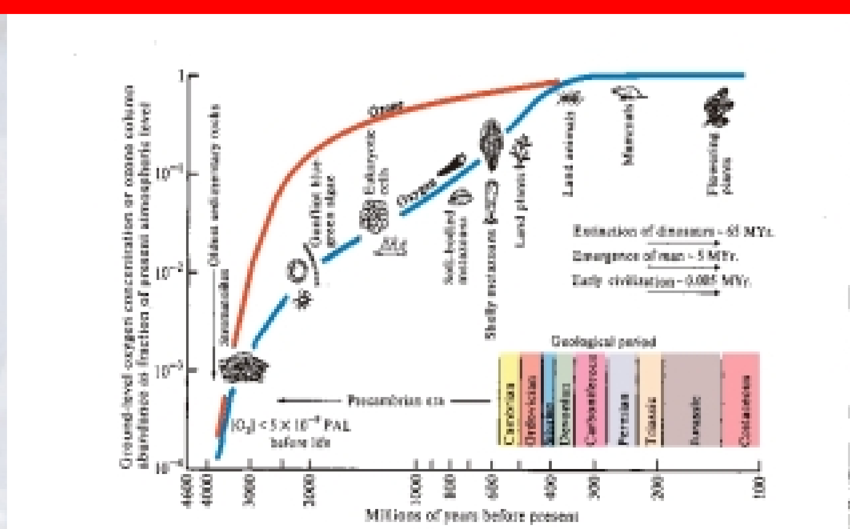
Biosphere Evolution



EVENT	BILLIONS OF YEARS AGO	MANIFESTATION	OXYGEN (PERCENT)
8. FULLY OXIC CONDITIONS	.4	LARGE FISHES, FIRST LAND PLANTS	100
7. SHELLY METAZOANS APPEAR	.55	CAMBRIAN FAUNA	~10
6. METAZOANS APPEAR	.67	EDIACARIAN FAUNA	~7
5. FIRST EUKARYOTIC CELLS FOUND	1.4	CELLS LARGER IN DIAMETER	>1
4. OXYGEN-TOLERATING BLUE-GREEN ALGAE	~2.0	ENLARGED, THICK-WALLED CELLS AT INTERVALS ON ALGAL FILAMENTS	~1
3. PHOTOAUTOTROPHY, PROBABLY RELEASING MOLECULAR OXYGEN	>2.8	STROMATOLITES, PRECURSORS OF BLUE-GREEN ALGAE	<1
2. AUTOTROPHY (METHANOGENESIS?) (SULFUR OXIDATION?)	>3.5	STROMATOLITES, SULFATE, LIGHT CARBON	(ANOXIC)
1. ORIGIN OF LIFE	(~3.8?)	LIGHT CARBON	(ANOXIC)

A Biogeochemical Atmosphere



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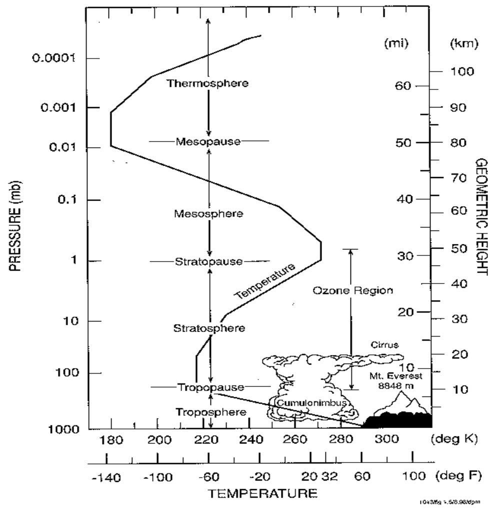
Temperature in the Atmosphere

Figure 1.5. Vertical profile of the temperature between the surface and 100 km altitude as as defined in the U.S. Standard Atmosphere (1976) and related atmosphere layers. Note that the tropopause level is represented for midlatitude conditions. Cumulonimbus clouds in the tropics extend to the tropical tropopause located near 18 km altitude.



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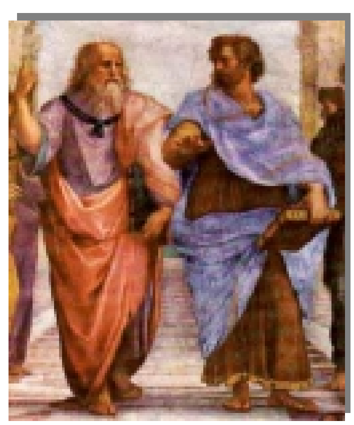
The History - The First Steps in Greece

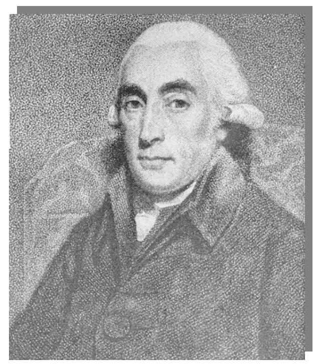
- Greek philosophers including Empedocles (5th century BC) believed that nature is composed of *earth, water, fire* and *air.*
- Aristotle (384-322 BC) realized that water was continuously recycled between the atmosphere and the ocean.



Fire-Air and Foul-air

- Leonardo da Vinci (1452-1519) in Italy and John Mayow (1641-1679) in Great Britain discovered that air is composed of "*fire-air*" that supports combustion and life, and "*foul-air*" that does not.
- *Carbon dioxide* is discovered around 1750 by Joseph Black (1728-1799).
- *Nitrogen* is identified several years later by Daniel Rutherford (1749-1819).

Joseph Black



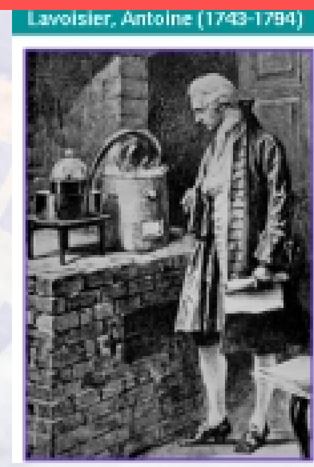
Oxygen

Priestley

"Fire-Air" was isolated in 1773 by Swedish chemist Carl Wilhelm Scheele (1742-1786), in 1774 by British scientist Joseph Priestley (1733-1804) and by French chemist Antoine-Laurent Lavoisier (1743-1794).

Oxygen

Lavoisier named this gas "oxygen" after the Greek *οξυς* (oxus: acid) and *γεινομαι* (geinomai: to generate). He was guillotined during the French Revolution, while Priestley, who was supporting the French Revolution, was on his to exile in America.



Noble Gases

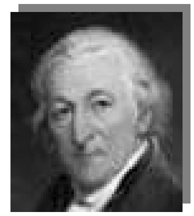
John William Strutt

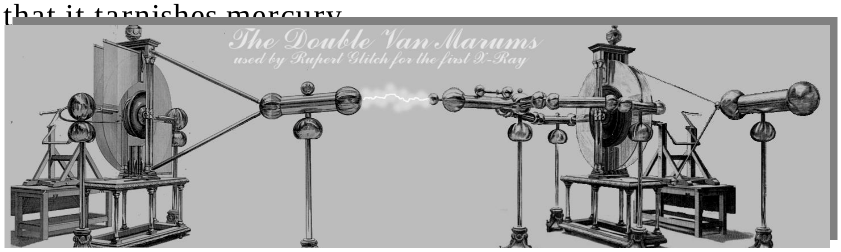
- John William Strutt known as Lord Rayleigh (1842-1919) and Sir William Ramsay (1852-1919) identified argon and other noble gases in the atmosphere.
- This discovery gave Ramsey the Nobel Prize for Chemistry in 1904.

William Ramsay

The Discovery of Ozone

- Dutch experimentalist Martinus van Marum (1750-1837) notes that the spark produced by a giant double plate-glass frictional electrostatic generator produced *"the odor of electrical matter."* He does not identify the gas generated by the spark, but notes that it tarnishes mercury.





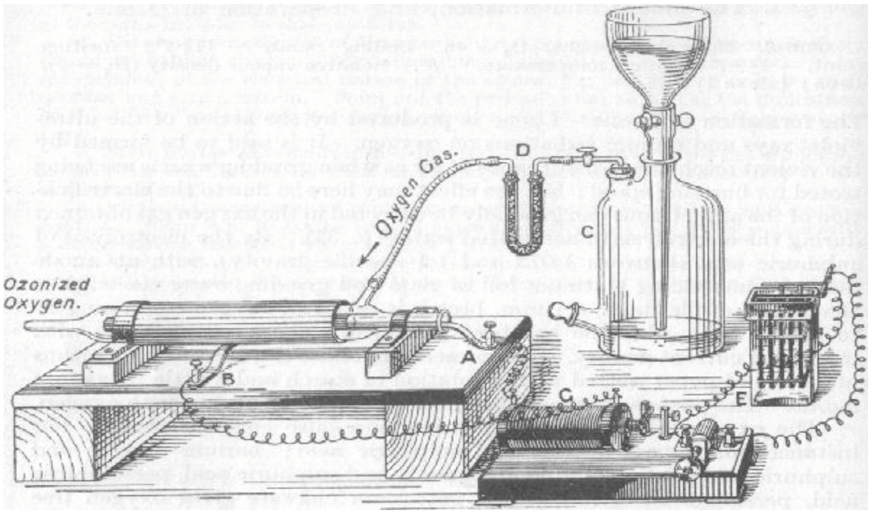
The Discovery of Ozone

- The gas discovered by van Marum remains un-named for 55 years, until in 1840, Christian Fredrich Sch**ö**nbein (1799-1868) detects the same peculiar odor in the oxygen liberated during the electrolysis of acidulated water.
- Schönbein names this gas "ozone" after the Greek word όζειν (ozein, to smell).

In a letter sent in 1840 to Francois Arago and submitted to the French Academy of Sciences, Schönbein suggests that ozone could belong to the chemical group of chlorine or bromine.

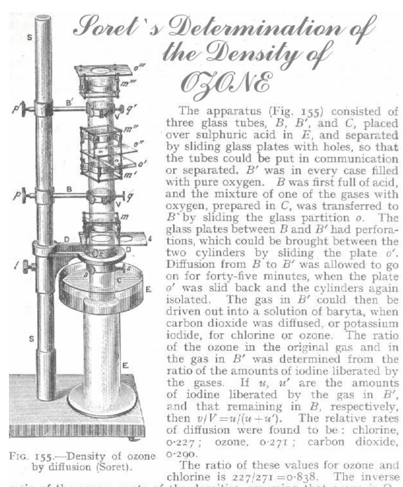
Ozonizer

In 1857 Werner Von Siemens designs an ozone generator



The Ozone Chemical Formula

- In 1845, Auguste de la Rive and Jean-Charles de Marignac (Geneva) suggest ozone is a form of oxygen.
- W. Olding (England), in his manual of chemistry (1861), suggests that the formula of ozone is O_3
- In 1868 Jean Louis Soret (Basel) determine the density of ozone gas using Graham`s law of diffusion. He establishes quantitatively that ozone is an allotropic form of oxygen: OOO or O_3 (oxygen dioxide).


Soret`s Determination of the Density of OZONE

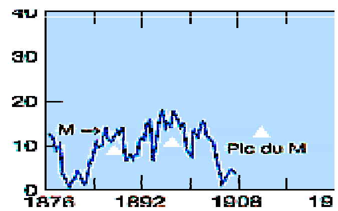
The apparatus (Fig. 155) consisted of three glass tubes, *B*, *B′*, and *C*, placed over sulphuric acid in *E*, and separated by sliding glass plates with holes, so that the tubes could be put in communication or separated. *B′* was in every case filled with pure oxygen. *B* was first full of acid, and the mixture of one of the gases with oxygen, prepared in *C*, was transferred to *B*` by sliding the glass partition *o*. The glass plates between *B* and *B′* had perforations, which could be brought between the two cylinders by sliding the plate *o′*. Diffusion from *B* to *B′* was allowed to go on for forty-five minutes, when the plate *o′* was slid back and the cylinders again isolated. The gas in *B′* could then be driven out into a solution of baryta, when carbon dioxide was diffused, or potassium iodide, for chlorine or ozone. The ratio of the ozone in the original gas and in the gas in *B′* was determined from the ratio of the amounts of iodine liberated by the gases. If u, u' are the amounts of iodine liberated by the gas in *B′*, and that remaining in *B*, respectively, then $v/V = u/(u+u')$. The relative rates of diffusion were found to be: chlorine, 0·227; ozone, 0·271; carbon dioxide, 0·290.

The ratio of these values for ozone and chlorine is 227/271 = 0·838. The inverse

FIG. 155.—Density of ozone by diffusion (Soret).

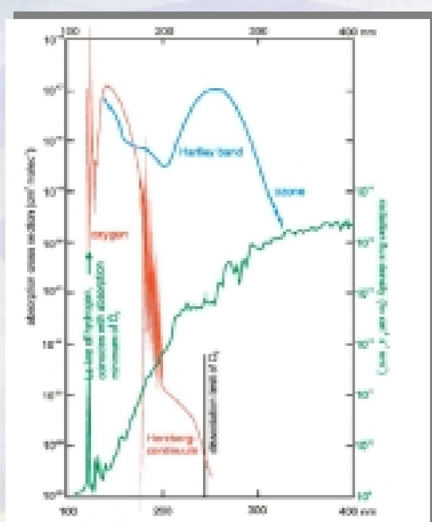
The First Atmospheric Observations of Ozone

- In 1858 André Houzeau (Rouen, France) develops a quantitative method (involving a mixture of iodine and arsenic) to measure ozone, and discovers that ozone is present in air.



- French Chemist Albert Levy uses this chemical method to observe the abundance of ozone almost continuously from 1877 to 1907 at the municipal Observatory of Parc Montsouris in Paris.

The Optical Properties of Ozone



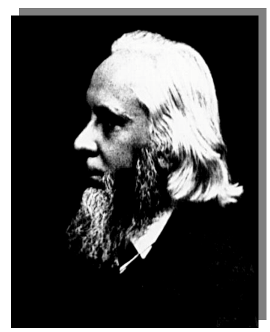
The Optical Properties of Ozone

- In 1879, Marie Alfred Cornu observes a sharp cutoff (300 nm) in the ultraviolet (UV) solar spectrum.
- In 1881, Walter Noel Hartley measures the ozone absorption cross section in the laboratory and recognizes that this UV cutoff is produced by the presence of ozone in the atmosphere.
- In 1913, John William Strutt (Lord Rayleigh) shows that the UV absorption does not happen in lower atmosphere

Alfred Cornu
Professor at
Ecole Polytechnique
in Paris

The Optical Properties of Ozone

- In 1890, William Huggins reported several absorption bands in the observed spectrum of star Sirius between 320 and 360 nm.
- In 1917, these bands were atributed by A. Fowler and R. J. Strutt to the presence of ozone in the atmosphere.
- In 1920 at Marseilles, France, Charles Fabry and Henri Buisson used UV absorption properties to deduce that the thinckness of atmospheric ozone was of the order of 3 mm STP



W. Huggins

The Optical Measurement of Ozone

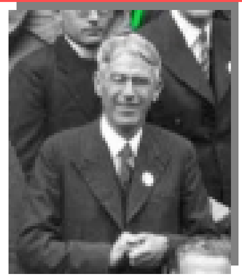
G.M.B. Dobson

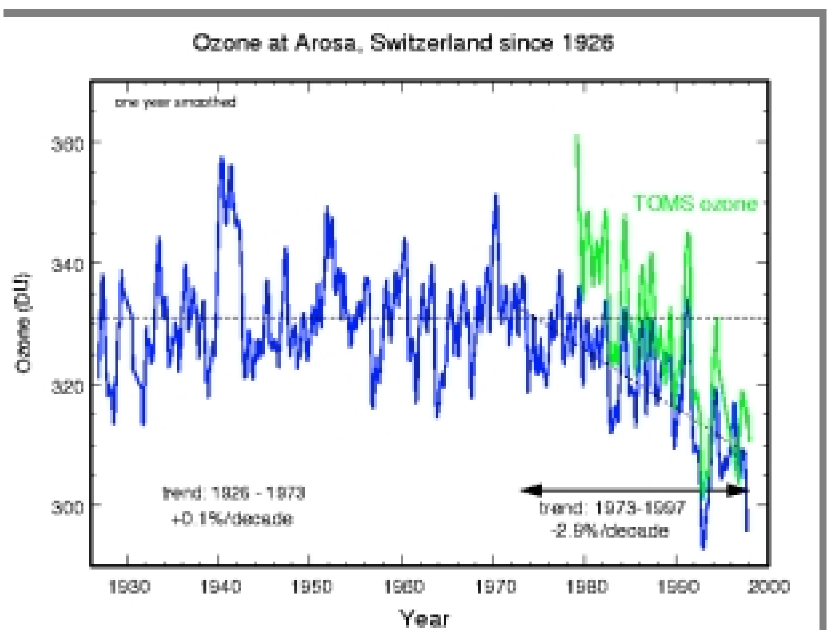
- In the 1920’s the British scientist, G.M.B. Dobson (Oxford University) developed a spectrophotometer that for many years remained the only accurate method to measure the ozone column abundance.
- This instrument was installed at different locations, which led Dobson to estimate the latitudinal and seasonal evolution of the ozone column.
- Dobson also discovered a strong influence of atmospheric dynamics on ozone.

The Dobson Ozone Spectrophotometer

Ozone Observations

- Paul Götz during a Spitzbergen expedition in 1929 (by inverting Dobson spectrophotometer measurements at high solar zenith angles) shows that the maximum ozone concentration is located near 25 km altitude.
- Götz and Hans Dütsch conducted systematic ozone observation in Arosa, Switzerland since 1926.





The Ozone Conferences

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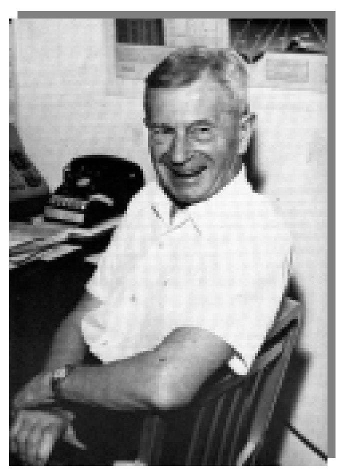
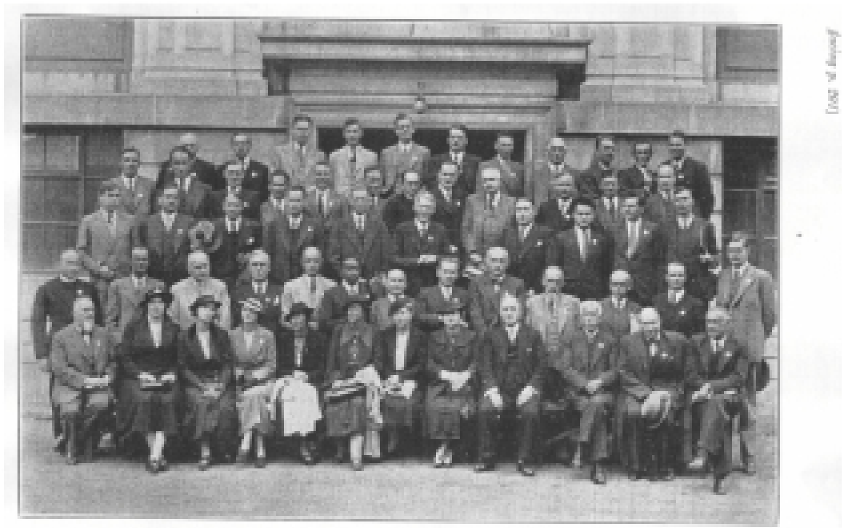
The First Ozone Conference in Paris (1929)

- The first ozone conference takes place in Paris in 1929, and is co-chaired by Dobson and Fabry.
- Sydney Chapman presents the first photochemical theory of ozone, and suggests that the formation of ozone results from the photolysis of molecular oxygen.
- On the basis of the photochemical parameters available at that time, he suggests that the ozone layer is located near 45 km altitude.



The Second Ozone Conference (Oxford, 1936)



Conference on Atmospheric Ozone, Oxford, September 9th–11th, 1936

The Second Ozone Conference (Oxford, 1936)

M.O. 403.

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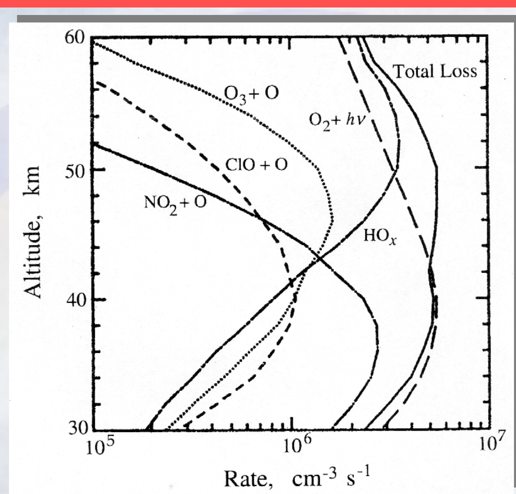
Conference on Atmospheric Ozone

Oxford: September 9th—11th, 1936

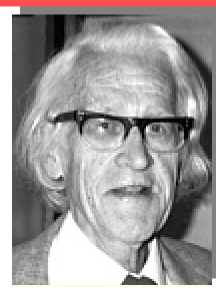
The band of workers on the problems of atmospheric ozone is not large; it was nearly fully represented at last month's Ozone Conference,* attended by about 60 members, and this 60 included a

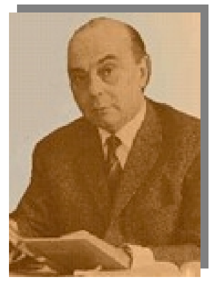
The Second Ozone Conference (Oxford, 1936)

The Photochemical Theories



Ozone and Hydrogen



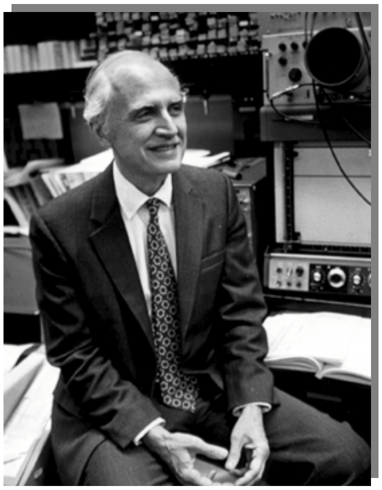


- Sir David Bates (Belfast) and Baron Marcel Nicolet (Brussels), working together at Caltech in Pasadena, suggest that hydrogen radicals (H, OH, HO_2) produced by photolysis of water vapor and methane provide a major ozone destruction mechanism in the *mesosphere.*
- J. Hampson in Canada suggests that similar processes can destroy ozone in the *stratosphere.*

Ozone and Nitrogen

- Paul Crutzen shows that the major ozone loss in the stratosphere is provided by a catalytic cycle involving the presence of nitric oxide (NO)
- Nitric oxide is produced in the stratosphere by oxidation of nitrous oxide (N_2O)

The Impact of Aviation

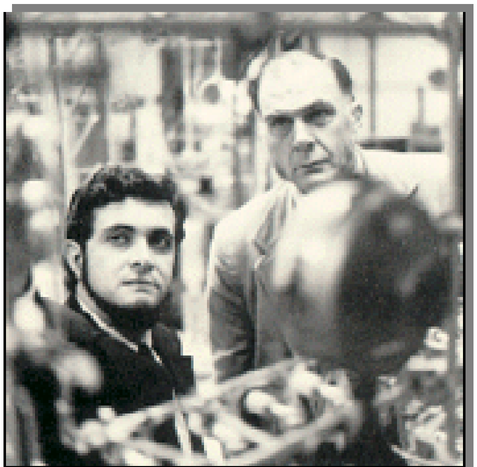


- In 1971, Harold Johnston (University of California at Berkeley) suggests that the nitrogen oxides to be released by a projected fleet of supersonic aircraft could produce substantial ozone depletion. Paul Crutzen also pointed out that the impact of aircraft could be damaging.
- An intensive research program, the Climatic Impact Assessment Program (CIAP) is sponsored by the US Department of Transportation (1972-1974).

Ozone and Chlorine

- At a scientific conference in Kyoto, Japan in 1974, Richard Stolarski and Ralph Cicerone, then at the University of Michigan, suggested that chlorine could also catalytically destroy ozone in the stratosphere.
- They note that large amounts of chlorine are released during volcanic eruptions

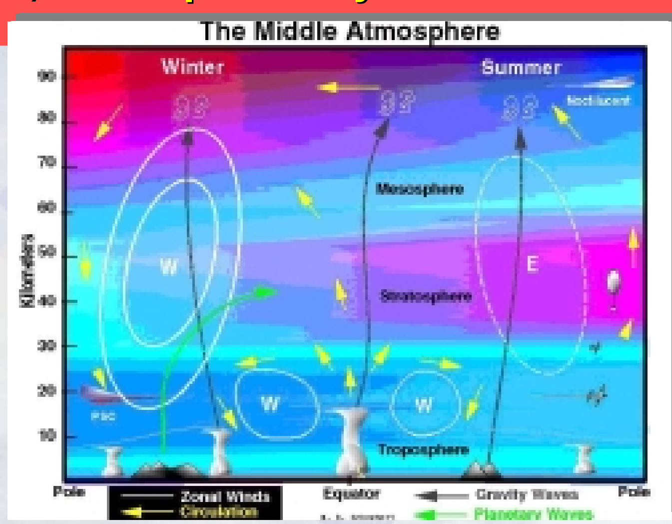
Chlorofluorocarbons and Ozone



Mario Molina and F. Sherwood Rowland

- In 1972 Jim Lovelock pointed out that the amount of CF_3Cl ad CF_2Cl_2 was about the same as that produced.
- In 1974, Mario Molina and Sherry Rowland at the University of California, Irvine, show that industrially manufactured chloro-fluorocarbons could provide the major source of stratospheric chlorine and therefore are a major threat to the ozone layer.

Ozone, Atmospheric Dynamics and Transport



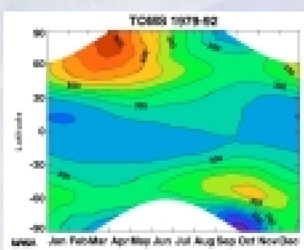
The Meridional Circulation

Alan Brewer

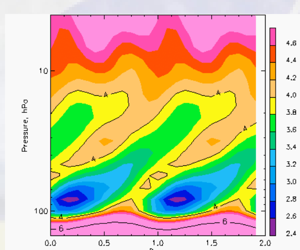
- By observing water vapor and ozone in the atmosphere, Alan Brewer and G.M.B. Dobson derive the meridional circulation in the stratosphere.
- Subsequent theoretical studies showed that the meridional circulation is produced by the momentum deposited by wave breaking, and explain, for example, the very cold temperatures observed at the tropopause and at the summer mesopause.

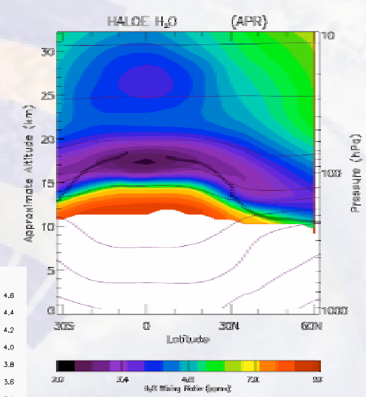
G.M.B. Dobson

The Brewer-Dobson Circulation, Ozone and Water Vapor



TOMS





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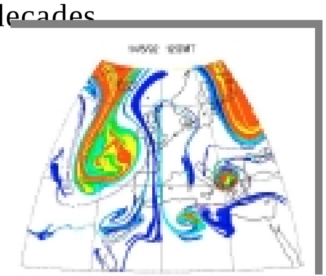
Middle Atmosphere Dynamics

James R. Holton

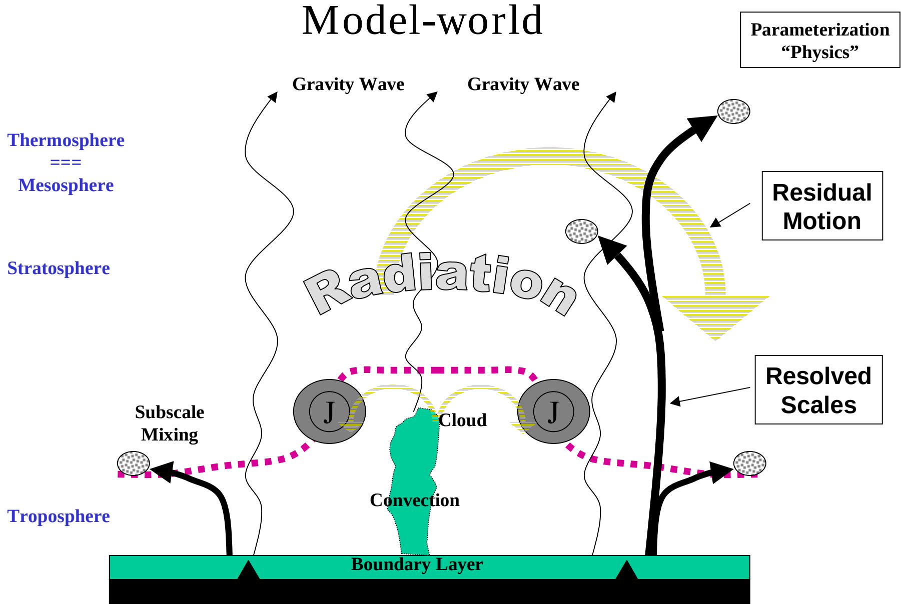
Michael McIntyre

- Major advances in our understanding of middle atmosphere dynamics, including Rossby, gravity and tropical waves, stratospheric warmings, wave-mean flow interactions and the meridional circulation, the quasi-biennial oscillation, dynamical barriers, cross-tropopause exchanges have been made in the last decades.

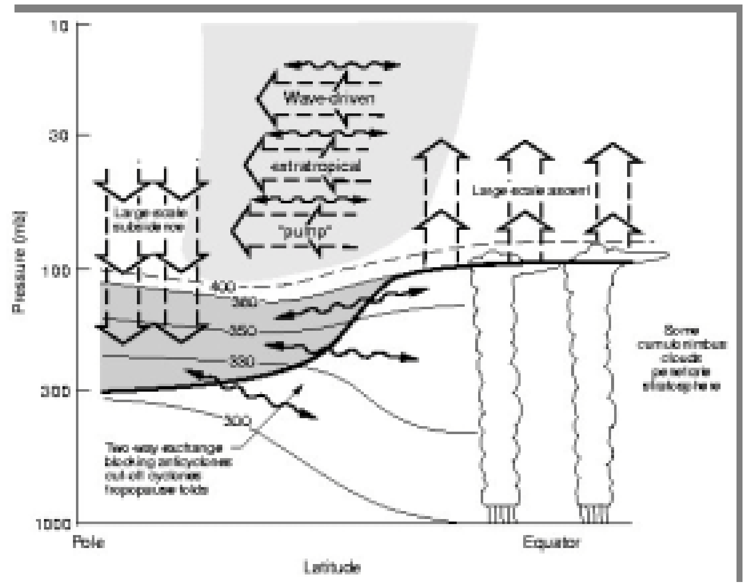
Key contributions were made by **Jim Holton, Michael McIntyre** and many others.



Model-world

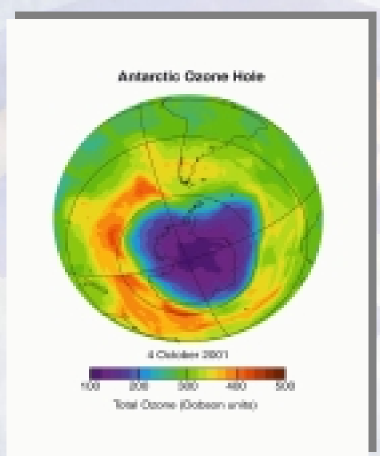


From R. Rood



From Holton et al.

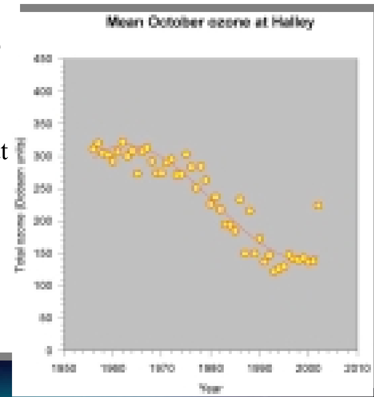
The Ozone Hole

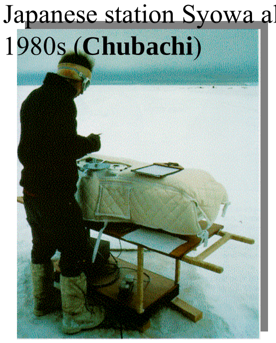


The Ozone Hole: A challenge for the scientific community

In 1985 publication of the Observations made at the British Antarctic station of Halley Bay (**Farman**, Gardener and Shartner) during the 1970's and 1980's show a dramatic decrease in the ozone column that is not simulated by atmospheric models.

Japanese station Syowa also showed O3 loss in 1980s (**Chubachi**)



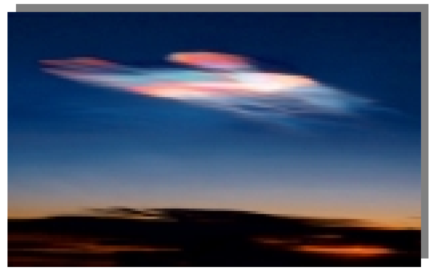


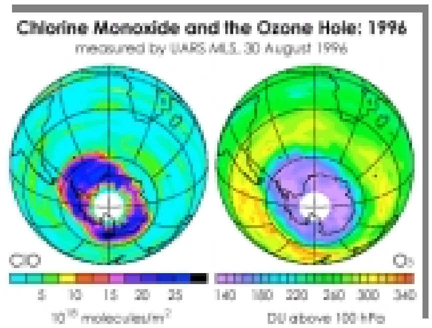
Halley Station

The Explanations

- Early theories to explain the observed ozone hole refer to dynamical perturbations and solar variability.
- Susan Solomon and colleagues suggest that chlorine can be activated on the surface of polar stratospheric cloud (PSC) particles observed over Antarctica, and can destroy most of the lower stratospheric polar ozone in a few weeks.
- Considerable experimental work is initiated to study heterogeneous chemical processes

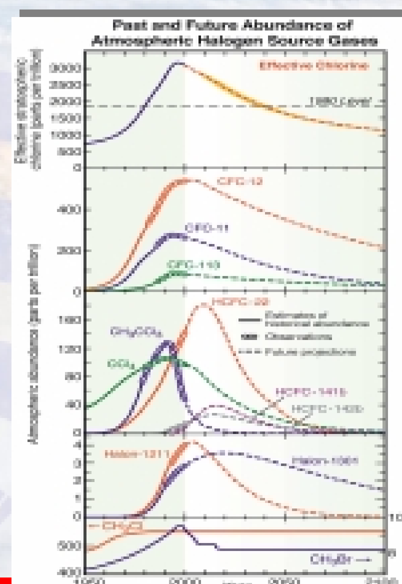
The Antarctic
Ozone Hole





- The most efficient catalytic reaction cycle responsible for the ozone hole is discovered by Mario Molina.
- Airborne field campaigns and space observations confirm that anthropogenic chlorine is responsible for the formation of the ozone hole.
- Substantial ozone destruction is also observed in the Arctic.

A Success Story



The international protocol signed in Montreal, Canada in 1987, and the subsequent amendments, lead to a phase-out of the most ozone-damaging chlorofluorocarbons.

The ozone hole is predicted to disappear around year 2050.

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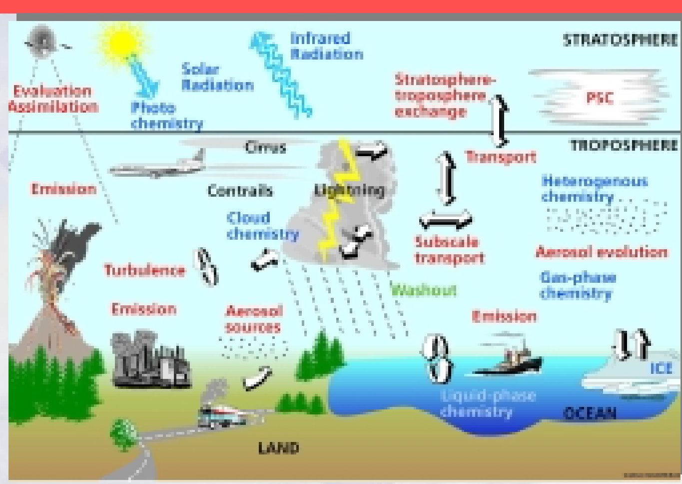
Paul Crutzen, Mario Molina, and Sherry Rowland receive the 1995 Nobel Prize in Chemistry for their seminal discoveries concerning the chemistry of ozone

Tropospheric Ozone



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The Photochemistry of Tropospheric Ozone

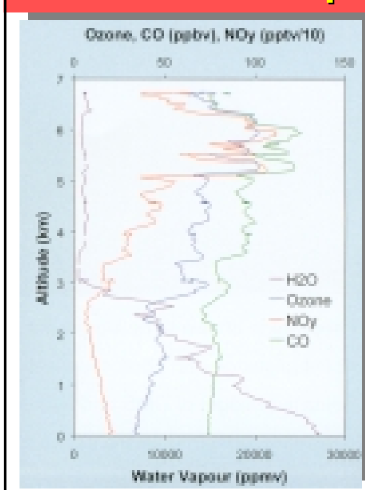
•In the early 1950’s, Dutch biogeochemist **Arie Haagen-Smith** working in California suggests that the formation of urban ozone (Los Angeles smog) results from the action of sunlight on reactive hydrocarbons and nitrogen oxides released by oil refineries and automobiles.

•In the early 1970, **Paul Crutzen** as well as **William Chameides** show that similar mechanisms affect tropopsheric ozone at the global scale.

Arie Haagen-Smith

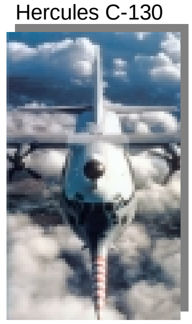
The role of ozone and of the OH radical in the ***oxidizing power*** of the atmosphere is recognized.

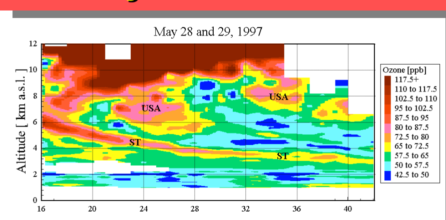
Field campaigns to investigate tropopsheric photochemistry



Vertical Profiles from ACSOE campaign, summer 1996

Hercules C-130

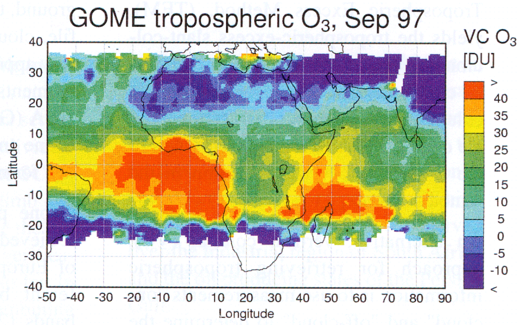




Lidar Observations

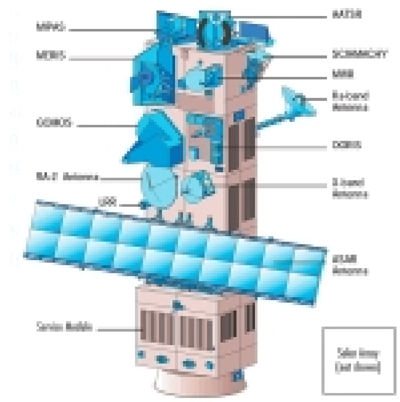
Shadoz in the tropics

Tropospheric ozone from satellites



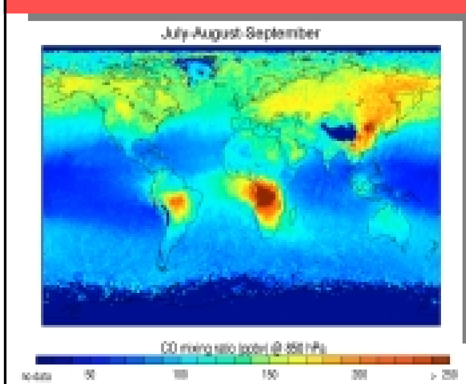
GOME: Global ozone monitoring experiment (on ERS-2)

A. Richter and J. Burrows, Uni Bremen



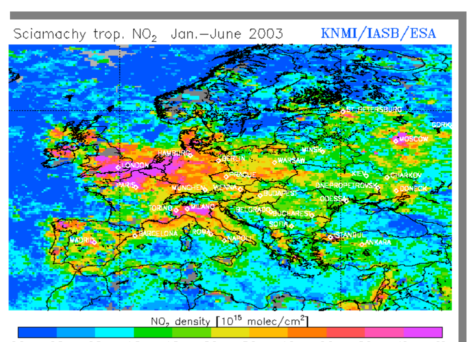
Envisat: launched February 2002

Air Quality is Monitored from Space

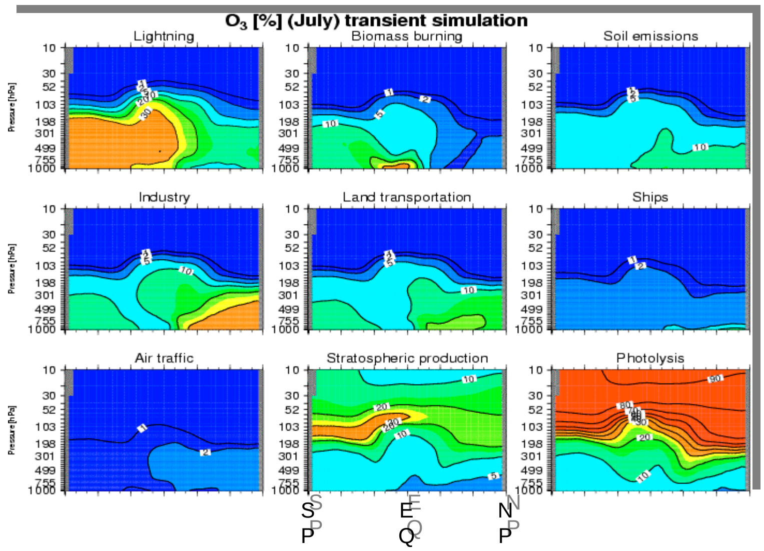


CO from MOPITT

NO_2 from Sciamachy



Modeling the global budget of tropospheric ozone

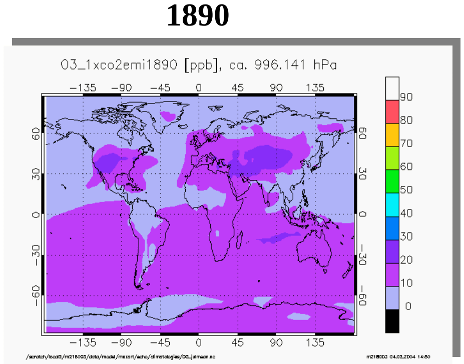


Grewe, Dameris, Fichter, Sausen et al., 2002, DLR

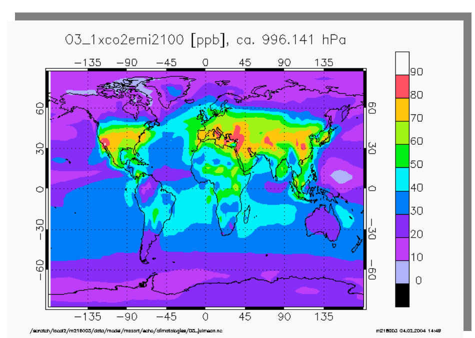
Modeling Global Changes in the Chemical Composition of the Tropopshere

Changes in the emissions of ozone precursors have led to substantial changes in tropospheric ozone levels, particularly in the industrialized world. It will continue to do so in the future, particularly in Asia and in the southern hemisphere.

1890



2100



Surface ozone (ppbv) in July - MOZART-2 Model

Summary and Conclusions

1 Much Progress has been in the past 150 years

2 Atmospheric Chemistry Matured

3 However driven by Serendipity

4 New Challenge : Chemistry and Climate