History of Atmospheric Chemistry Modeling

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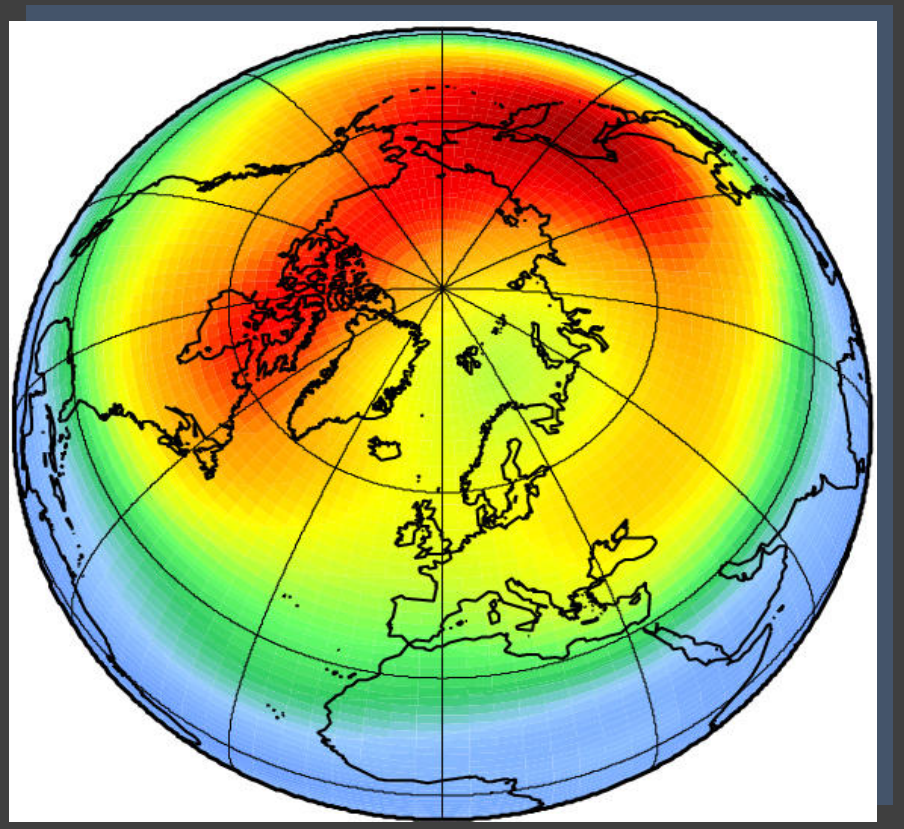
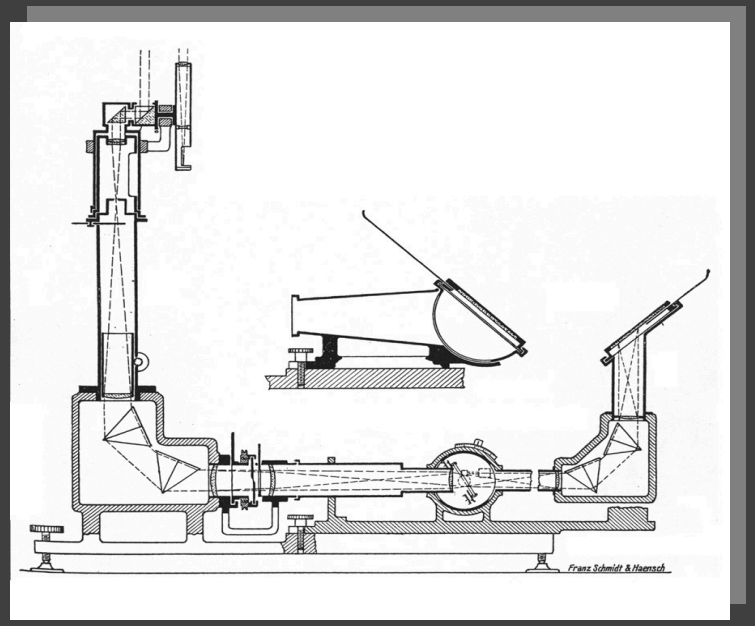
"The history of science is the history of failed models"

Introduction

- Progress in atmospheric science has resulted from the **complementarity** between observational approaches, laboratory studies and modeling.
- **Mathematical models** should be viewed as tools that are an integral part of **observational programs**.
- A prominent illustrative example is provided by the research on **stratospheric ozone**.
- Our historical voyage starts in **1920**.

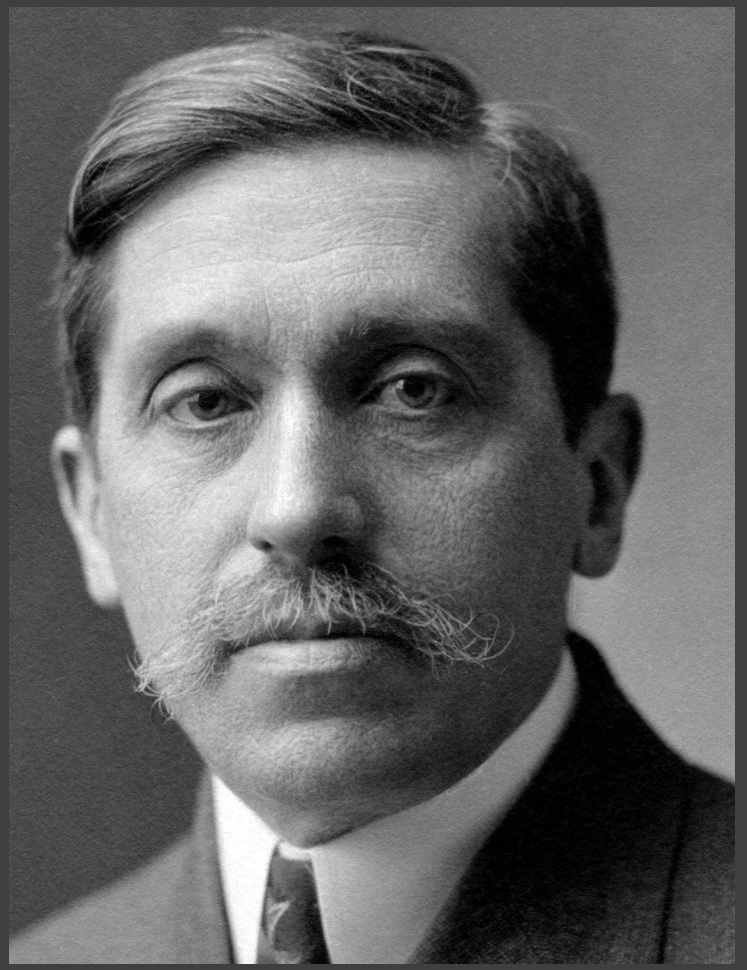


The 1920’s

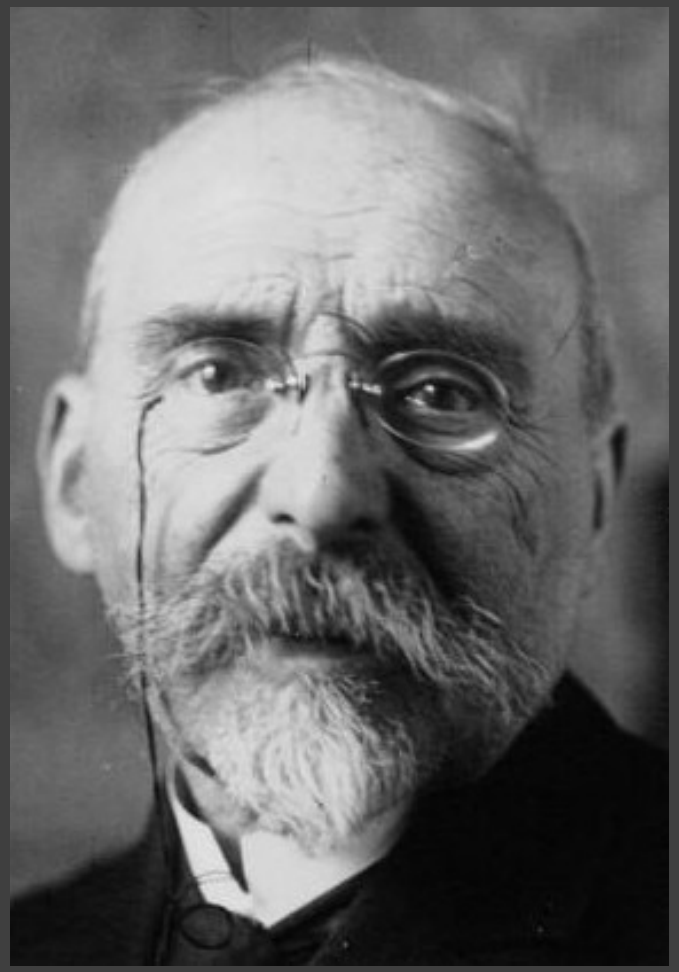


1920: Charles Fabry and Henri Buisson

In 1920, Charles Fabry and Henri Buisson at the University of Marseilles, France, by measuring the absorption of ultraviolet light in the atmosphere discover that the thickness of the ozone column at STP is only of the order of 3 mm.



Charles Fabry



Henri Buisson

The Dobson Ozone Photographic Spectrometer of Gordon Dobson at Oxford, UK.

Gordon Dobson

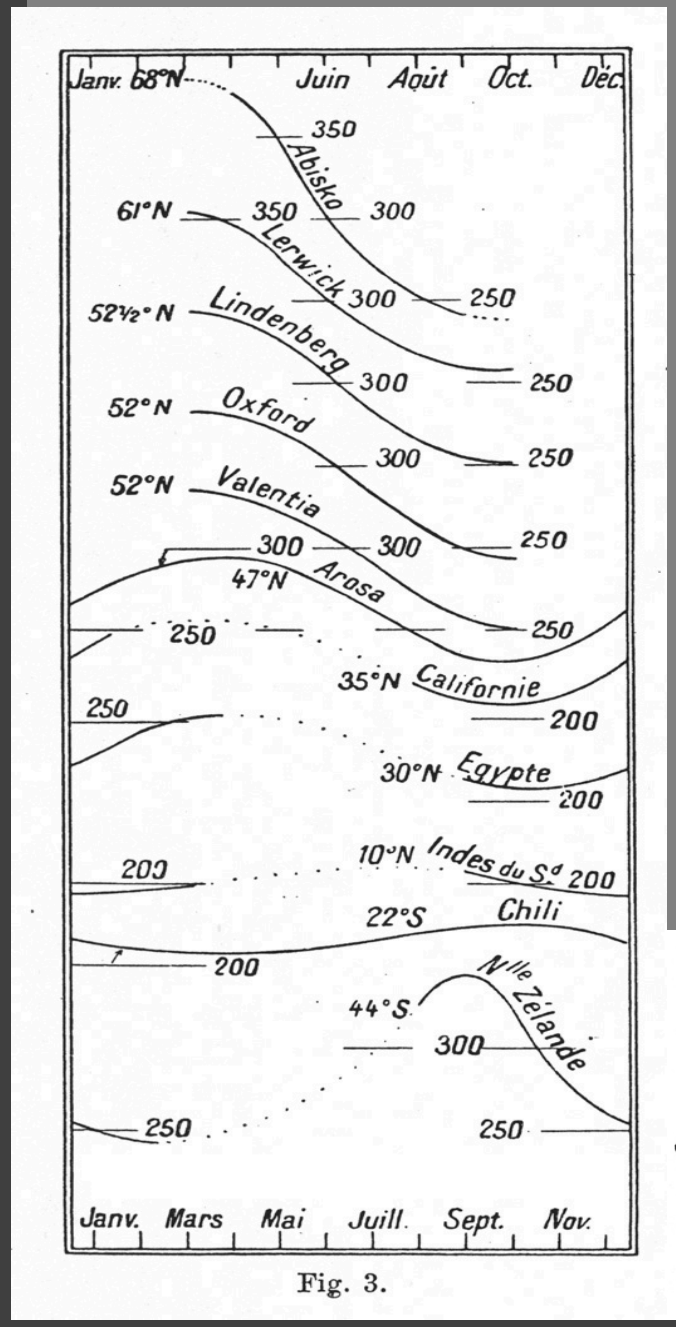
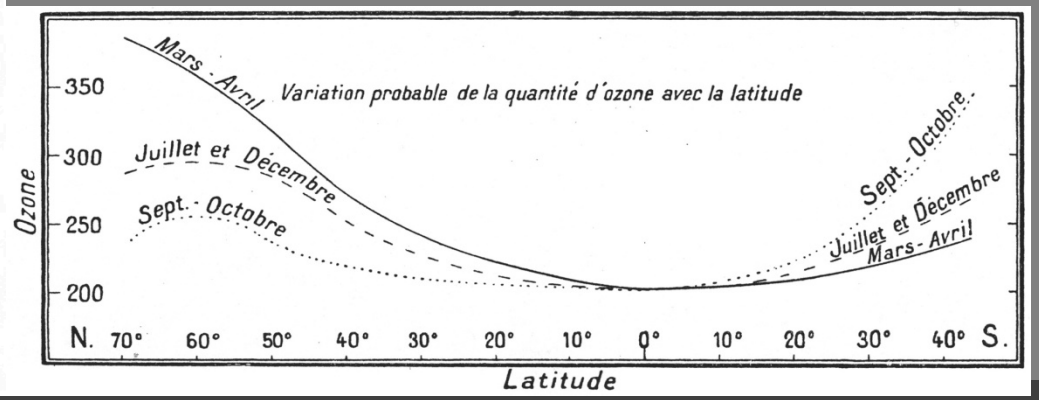
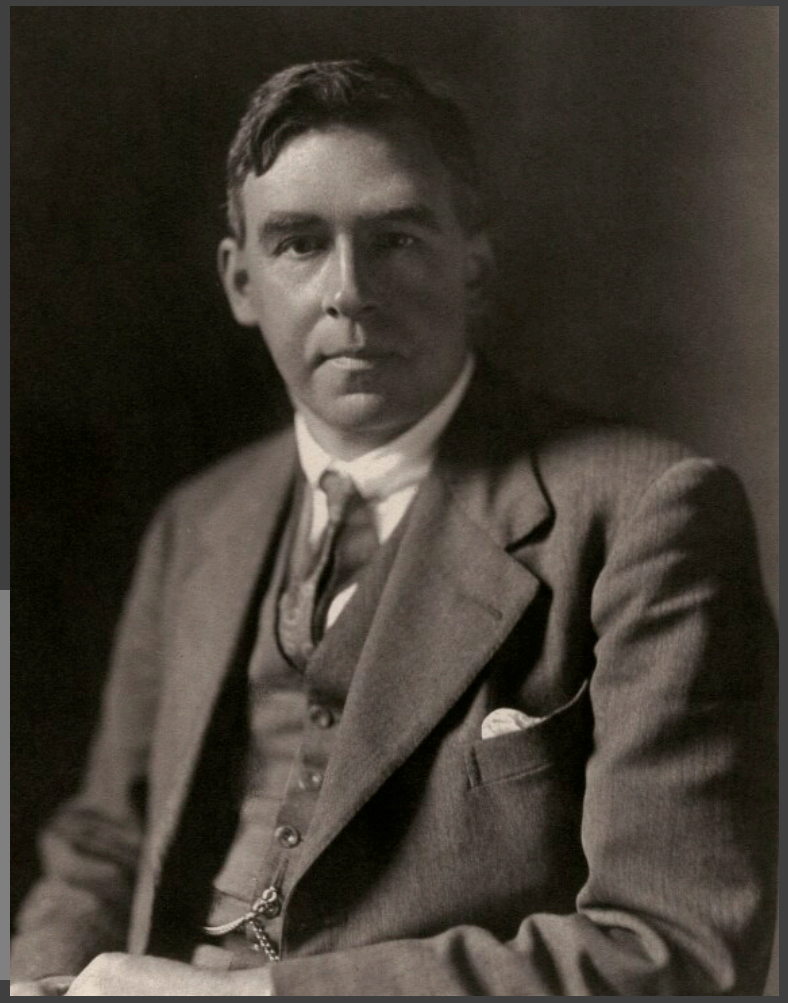


Fig. 3.





Determination of the Height of the Ozone Layer

In **1927-1928**, **Paul Götz** and **Dobson** deduce from spectrophotometric measurements made in Arosa, Switzerland, that the ozone layer is located near **40-50 km**.

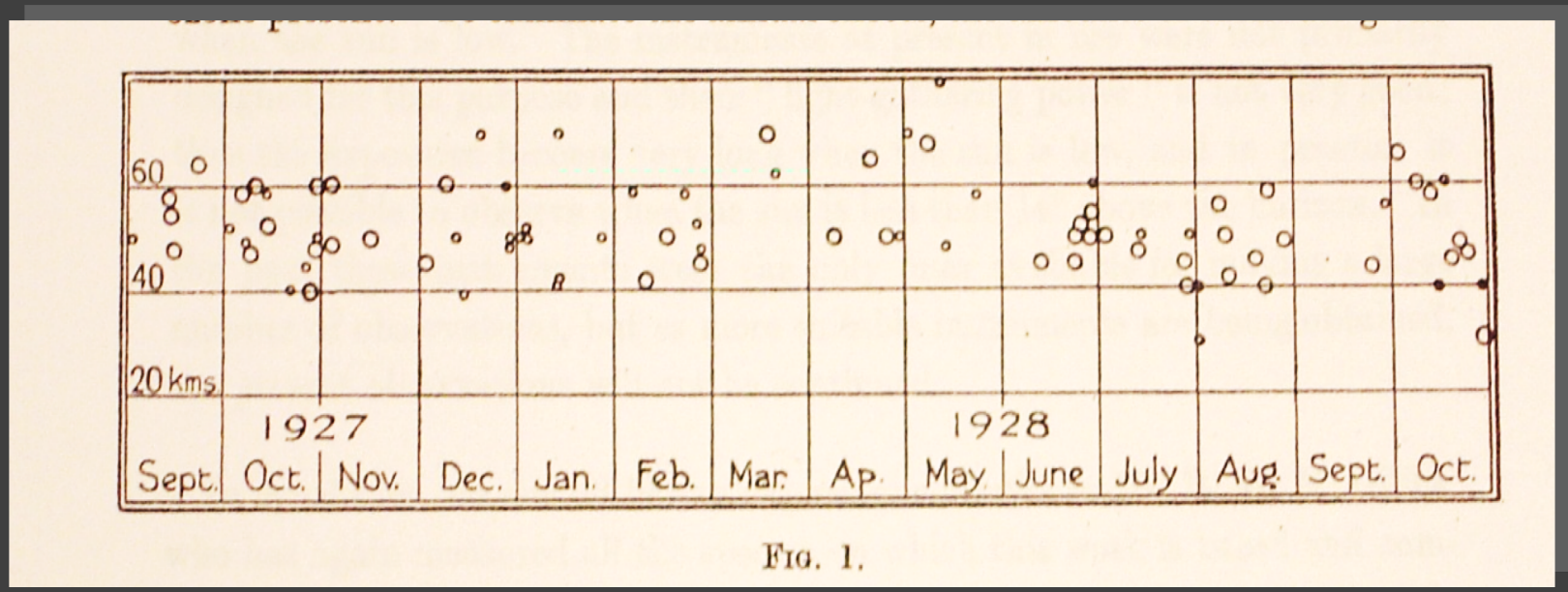
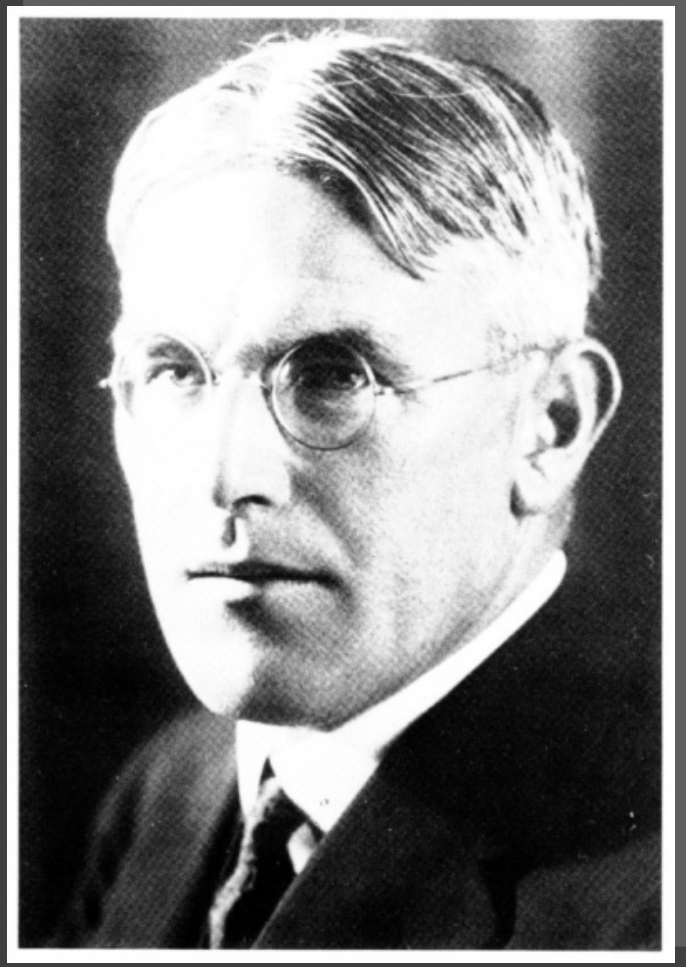


FIG. 1.



Paul Götz

The First Ozone Conference in Paris (1929)

- At the first ozone conference in Paris, **Sydney Chapman,** a specialist of solar terrestrial relations, rather than invoking high-latitude auroral physics to explain Dobson observations, indicates that the formation of ozone probably results from the photolysis of molecular oxygen by solar ultraviolet radiation:

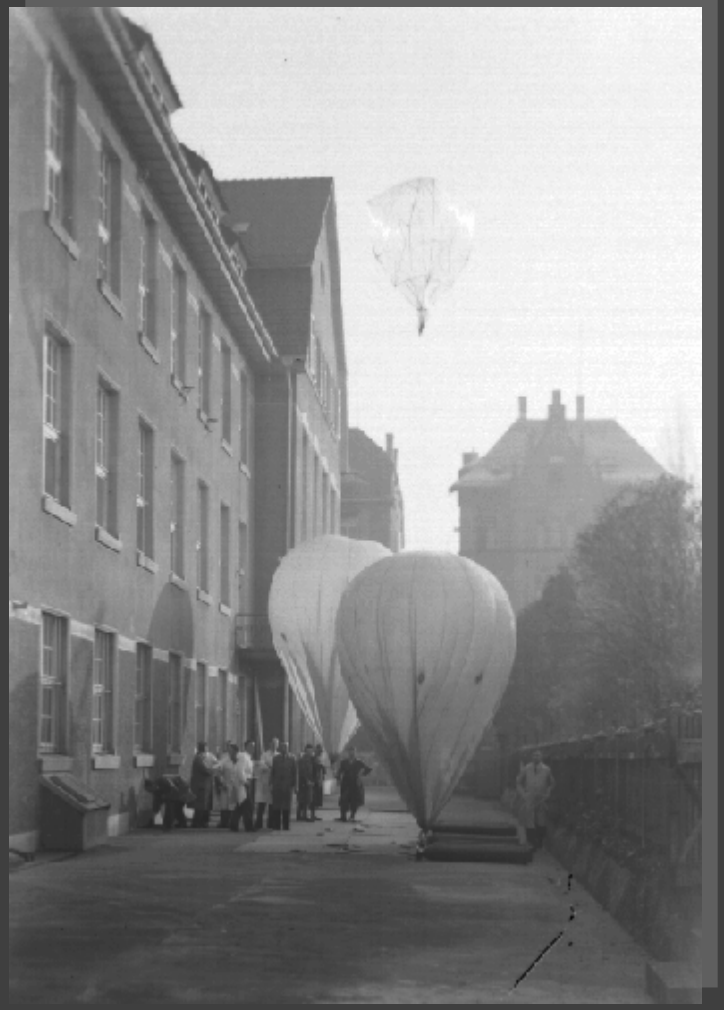
$$O_2 + UV \rightarrow O + O$$

- His theory does not explain the polar maximum in the ozone column.
- But his theory seems to confirm the early observations of Götz that the ozone layer is located near **40 km** altitude.

Sydney Chapman

The 1930’s

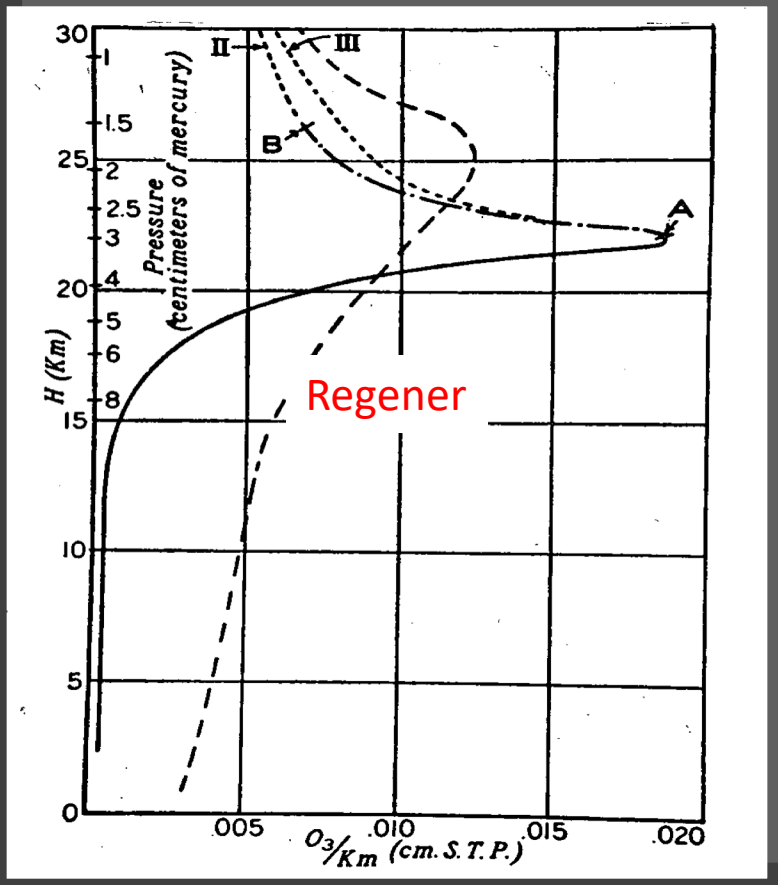
Height of the Ozone Layer



Erich Regener
1881-1955

Victor Regener
1913-2006

- **Erich Regener** and his son **Victor** who measure the solar ultraviolet absorption from a stratospheric balloon in **1934**, show that the ozone maximum is located near 25 km.



The Chapman Scheme (pure oxygen atmosphere) constitutes the basis for the first photochemical models of the atmosphere

- (1) $O_2 + h\nu \rightarrow O + O$ — Net production
- (2) $O + O + M \rightarrow O_2 + M$ — Recombination of O at high levels
- (3) $O + O_2 + M \rightarrow O_3 + M$ — Conversion of O into ozone
- (4) $O_3 + h\nu \rightarrow O_2 + O$ — Conversion of ozone into O
- (5) $O_3 + O \rightarrow O_2 + O_2$ — Net loss of O and ozone

1936: Wulf and Deming develop the first model of stratospheric ozone

THE THEORETICAL CALCULATION OF THE DISTRIBUTION OF PHOTOCHEMICALLY-FORMED OZONE IN THE ATMOSPHERE

By Oliver R. Wulf and Lola S. Deming

Absorption cross section of O_2 and O_3

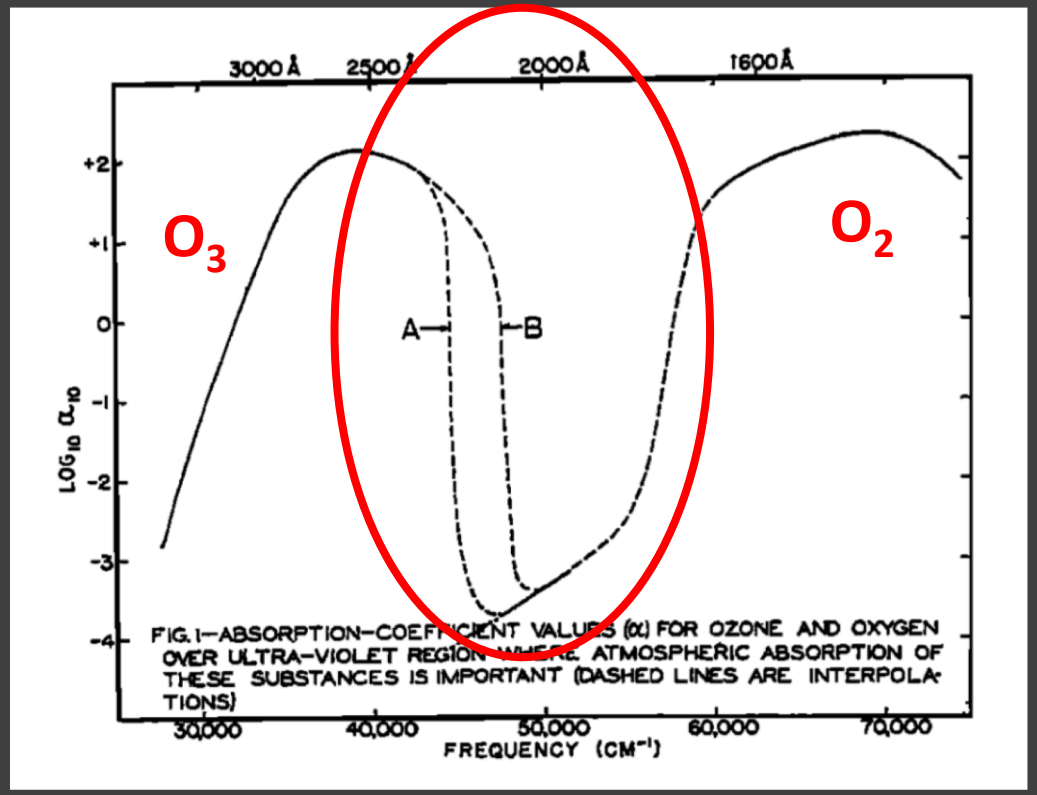
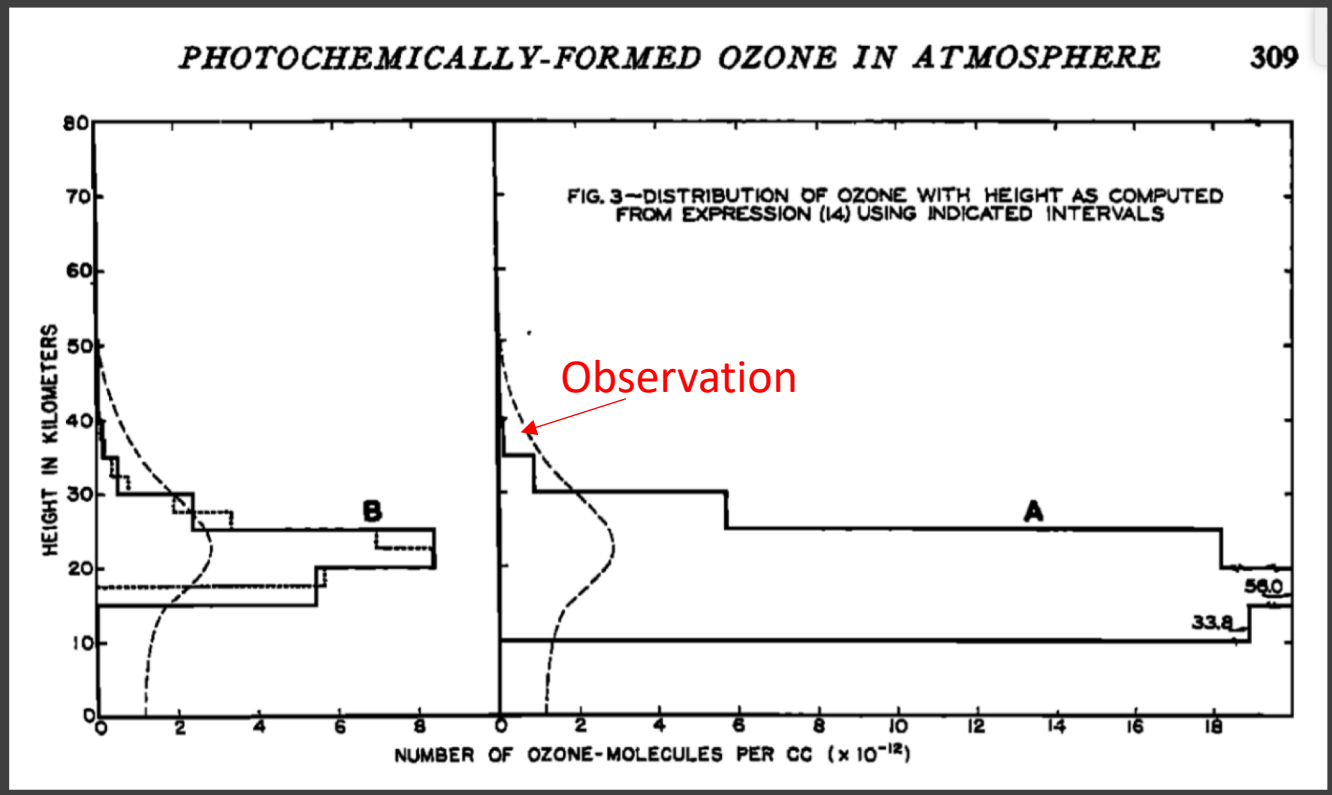


FIG. 1—ABSORPTION-COEFFICIENT VALUES (α) FOR OZONE AND OXYGEN OVER ULTRA-VIOLET REGION WHERE ATMOSPHERIC ABSORPTION OF THESE SUBSTANCES IS IMPORTANT (DASHED LINES ARE INTERPOLATIONS)

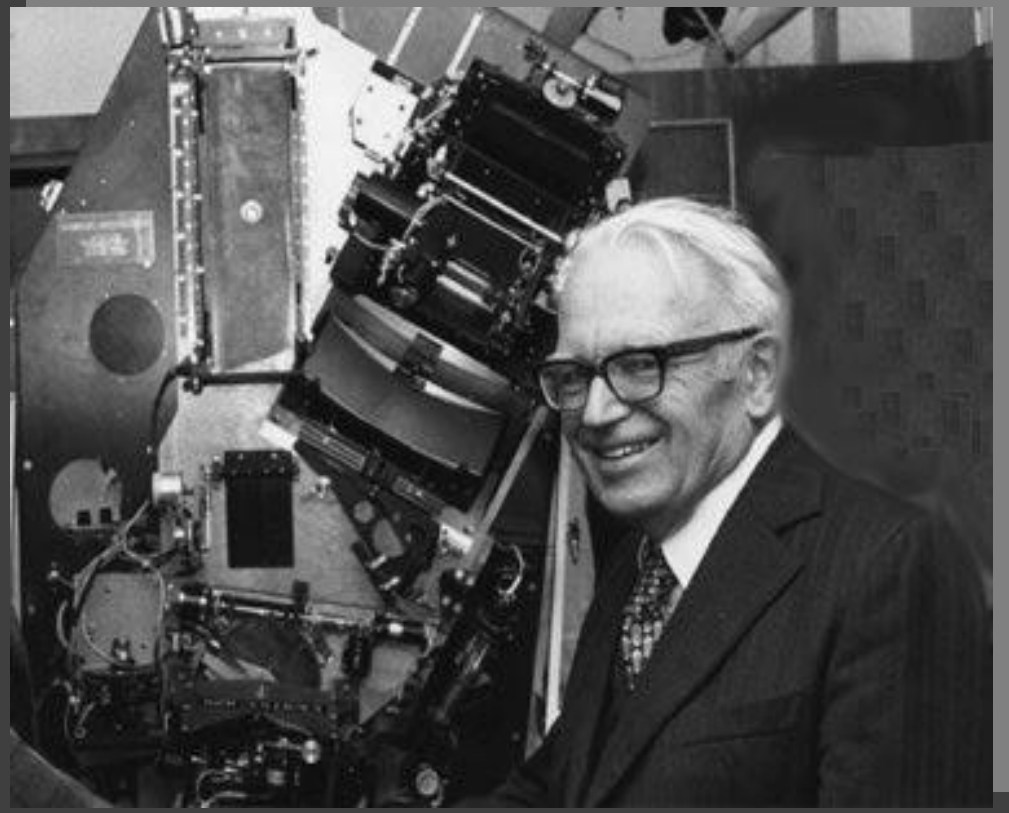
Calculated vertical distributions
The dashed curve refers to the observations



Ozone Production in the Stratosphere

In 1953, **P. Brix** and **G. Herzberg** show that the photolysis of oxygen (and therefore the photochemical production of ozone) is possible for radiation beyond 200 nm, and is therefore taking place down to the lower stratosphere.

G. Herzberg



The late 1940’s and the 1950’s

1948-1949:
Rocket Observations of Ozone up to 70 km

A-20 ROCKET BORNE OZONE SPECTROMETER

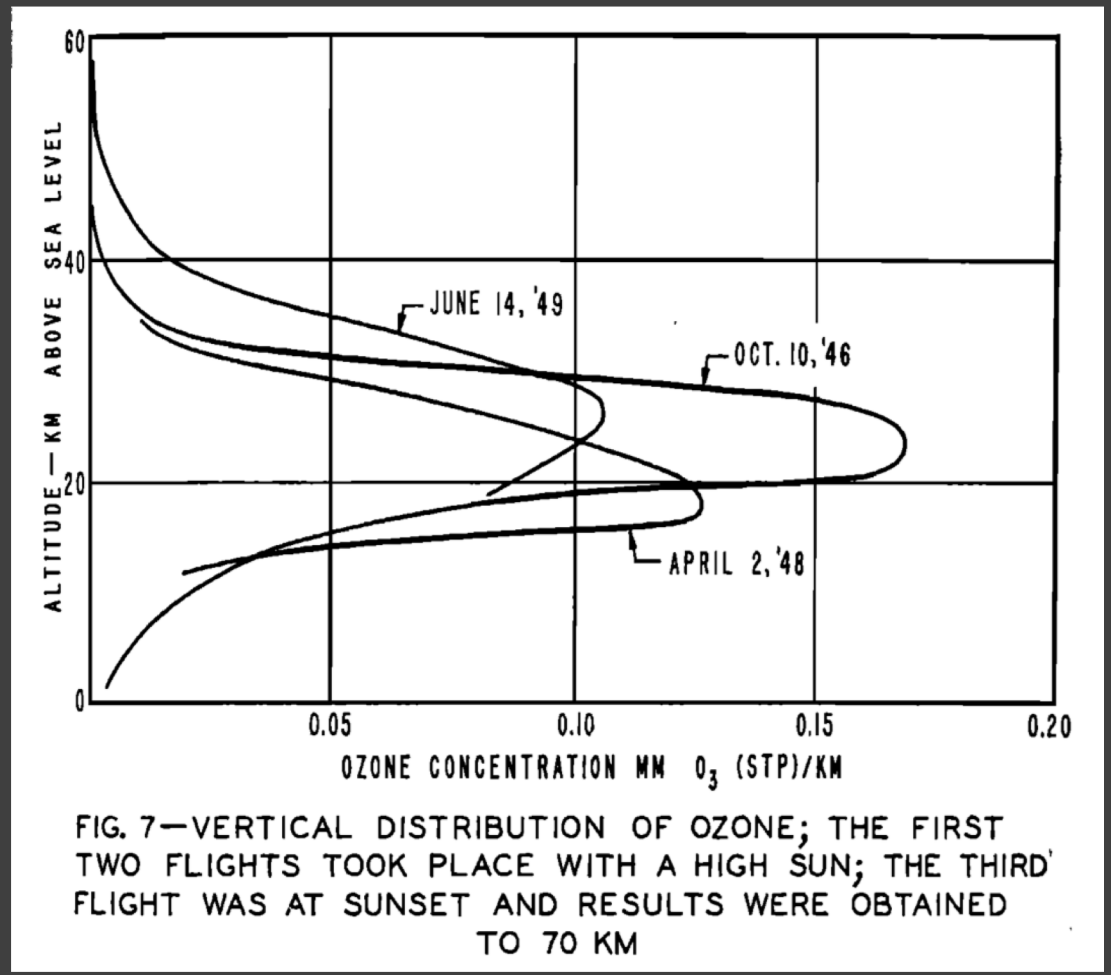


FIG. 7—VERTICAL DISTRIBUTION OF OZONE; THE FIRST TWO FLIGHTS TOOK PLACE WITH A HIGH SUN; THE THIRD FLIGHT WAS AT SUNSET AND RESULTS WERE OBTAINED TO 70 KM

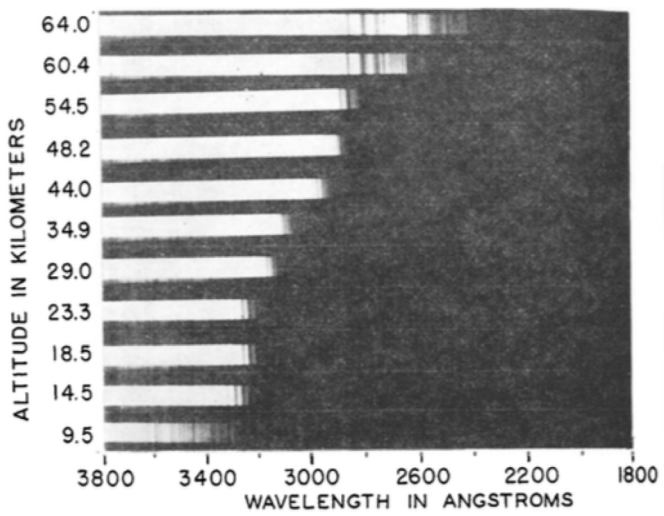


FIG. 4—A SERIES OF SOLAR SPECTRA OBTAINED WITH SPECTROGRAPH B, SHOWING THE EXTENSION TOWARD SHORTER WAVELENGTHS AS THE ROCKET ASCENDED

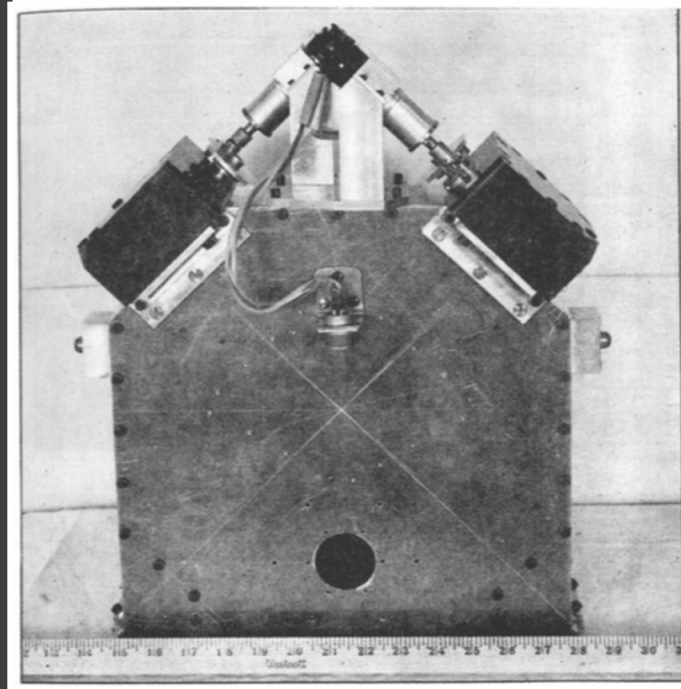
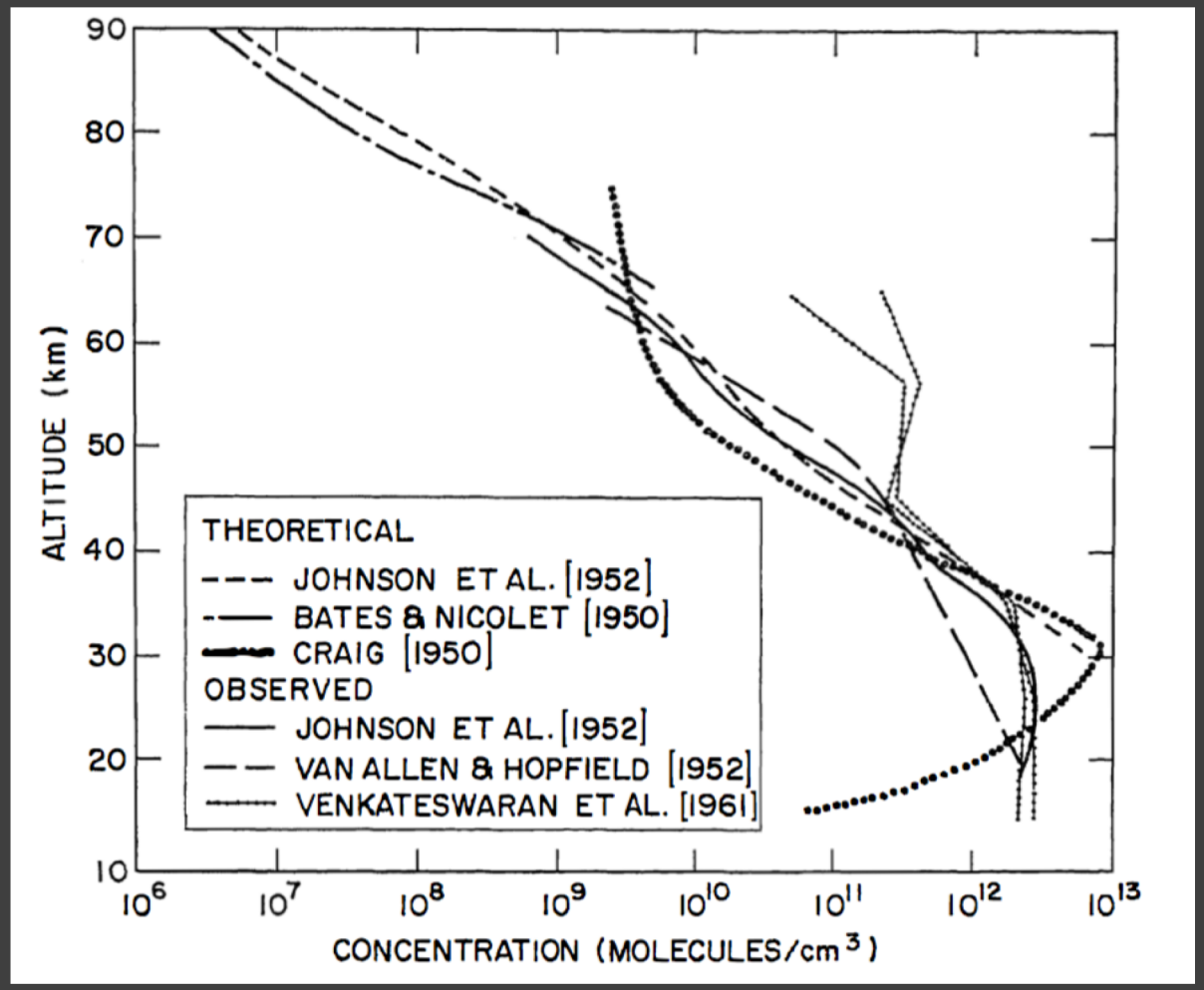
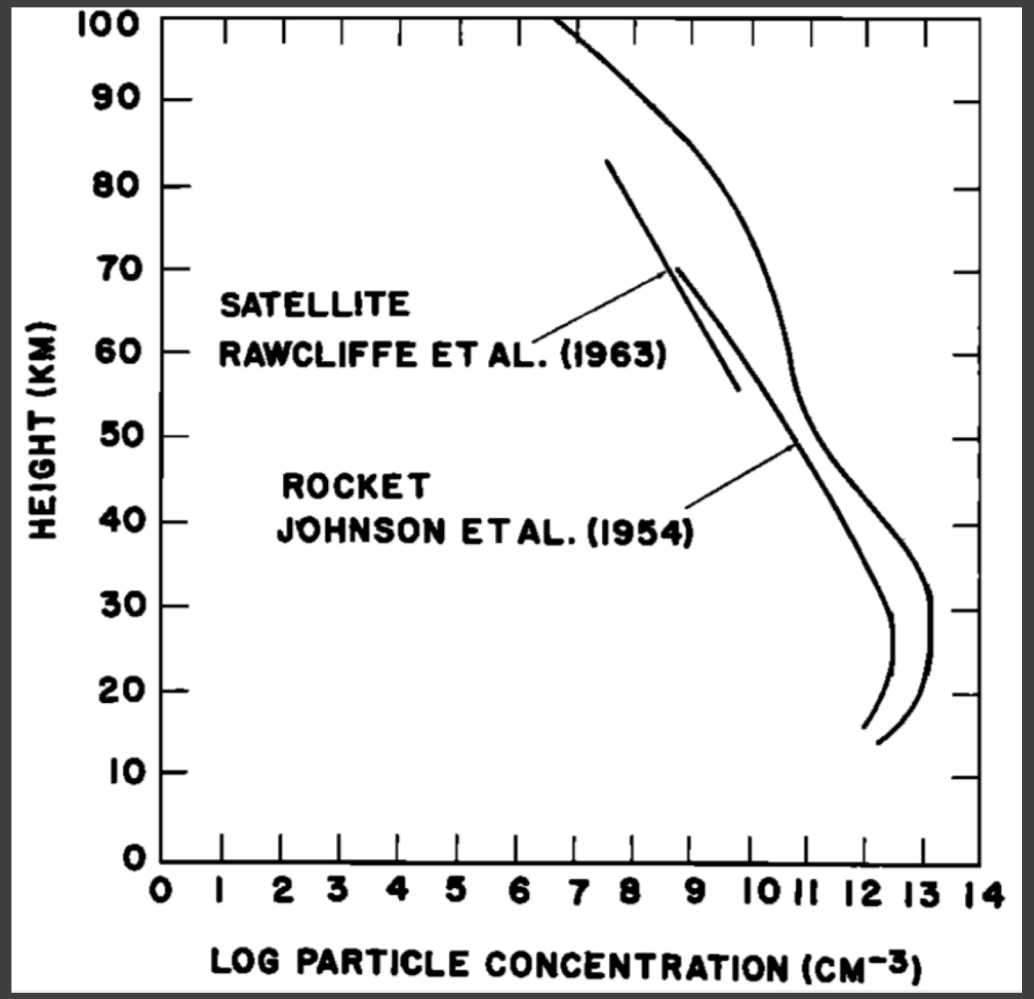


FIG. 3—SPECTROGRAPH B ASSEMBLED AND READY FO INSTALLATION IN THE ROCKET; THE TWO SLITS CAN BE SEEN AT THE SIDES DIRECTLY BELOW CAMERAS; THE HOLE NEAR THE BOTTOM IS THE PORT THROUG WHICH THE AIR WAS EVACUATED

In the 1960, the vertical distribution of ozone is known up to the mesosphere

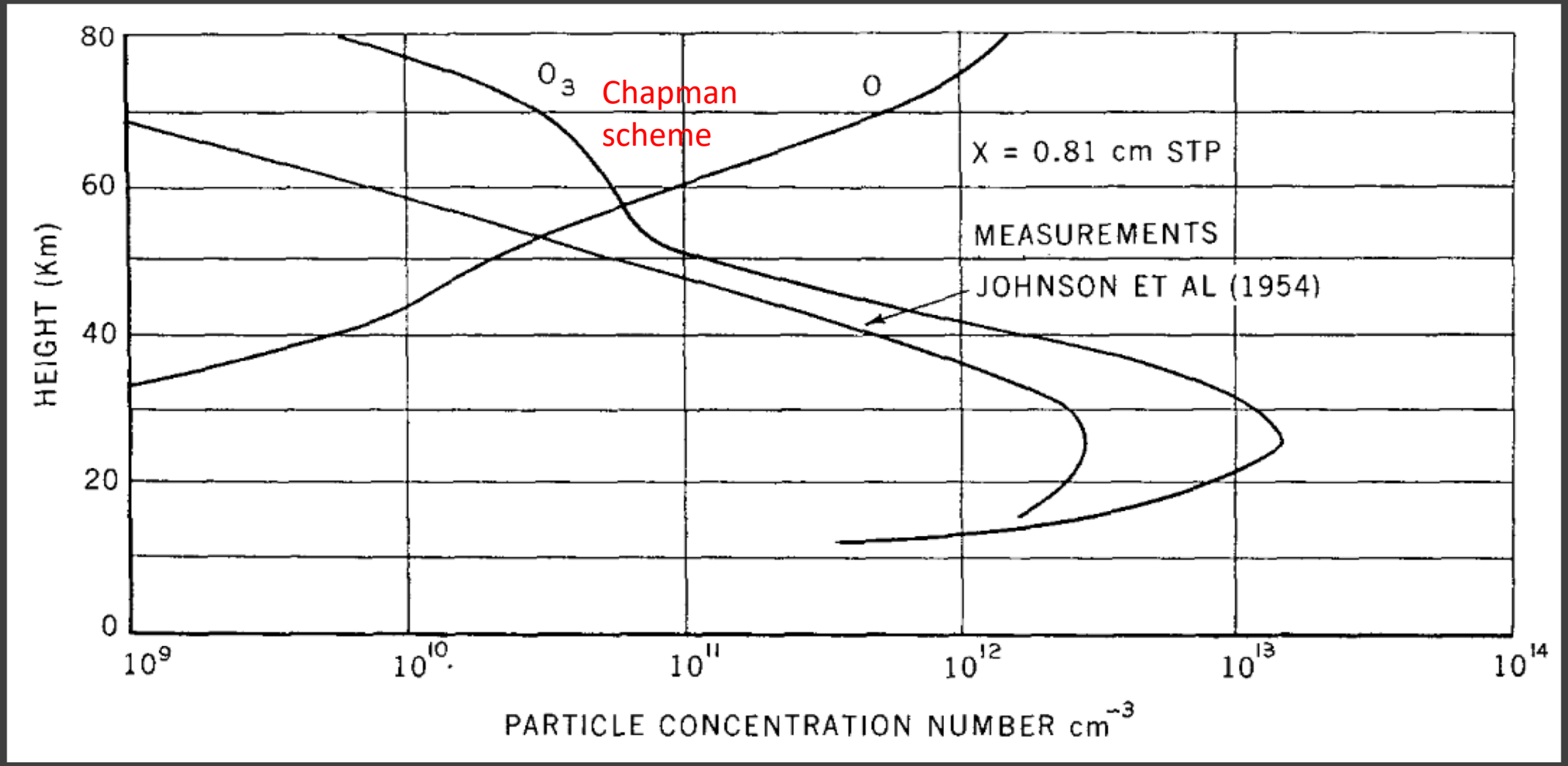
(Rocket and satellite measurements)





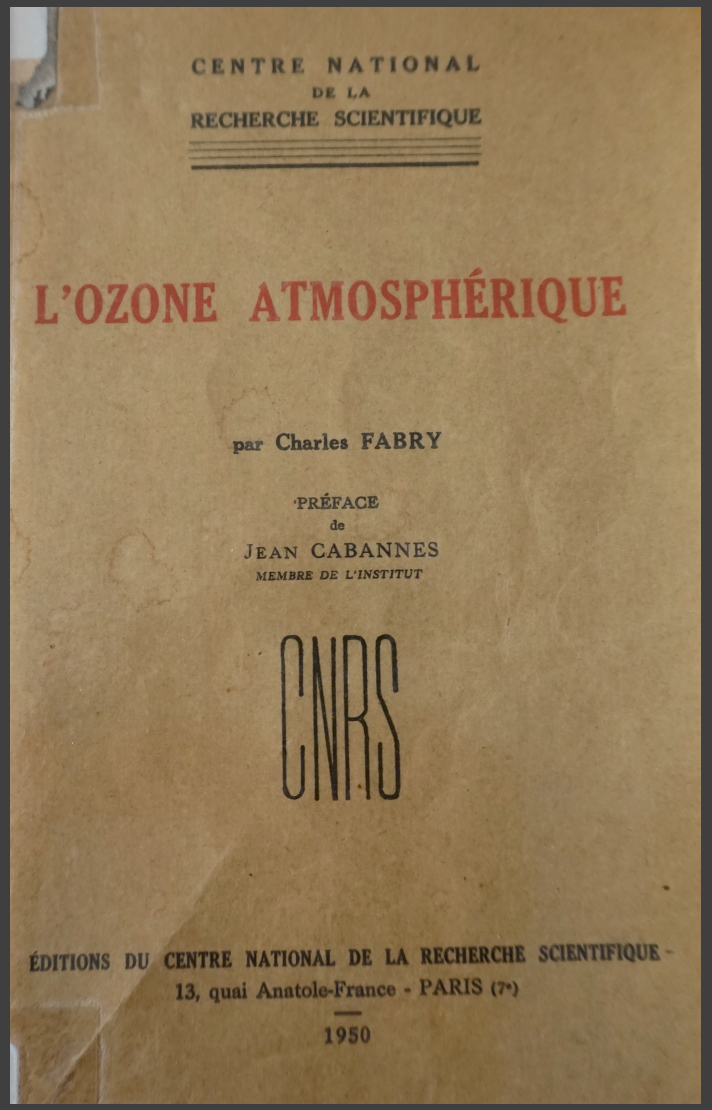
The Chapman Scheme overestimates the ozone concentrations

"The ozone problem"



1945: Fabry does not believe in the photochemical theory

« It is certain that the purely ultraviolet theory does not fit well with the facts observed in northern regions after the polar night. [...] Looking at the state of the matter, one gets the impression that we have not yet been able to pinpoint the crucial point of the problem, and that discoveries remain to be made, important not only for the theory of ozone, but perhaps also for general physics.»



1950: Catalytic Ozone Destruction by Hydrogen Radicals

- 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.*

- $O_3 + H \rightarrow OH + O_2$
- $O + OH \rightarrow H + O_2$

$OH + O \rightarrow H + O_2$

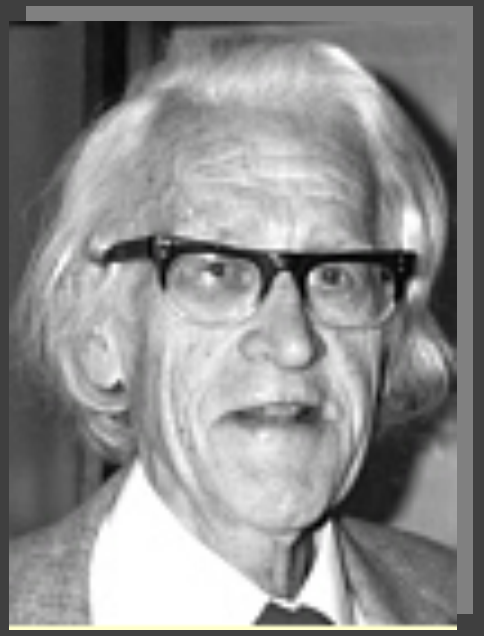
$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + O \rightarrow OH + O_2$

- $O + O_3 \rightarrow O_2 + O_2$ (net)

$O + O \rightarrow O_2$ (net)

Bates



Nicolet

The 1960’s

1960's:
The models based on the Chapman theory considerably overestimate ozone in the entire mesosphere and stratosphere.

The correction introduced by Bates and Nicolet (1950) did not reduce the bias in the stratosphere.

Barrie Hunt indicates that the reaction $O_3 + O(^1D)$ could be of importance in the atmosphere, but notes that the photochemical O_3 problem is left unresolved.

The Need for a Modified Photochemical Theory of the Ozonosphere

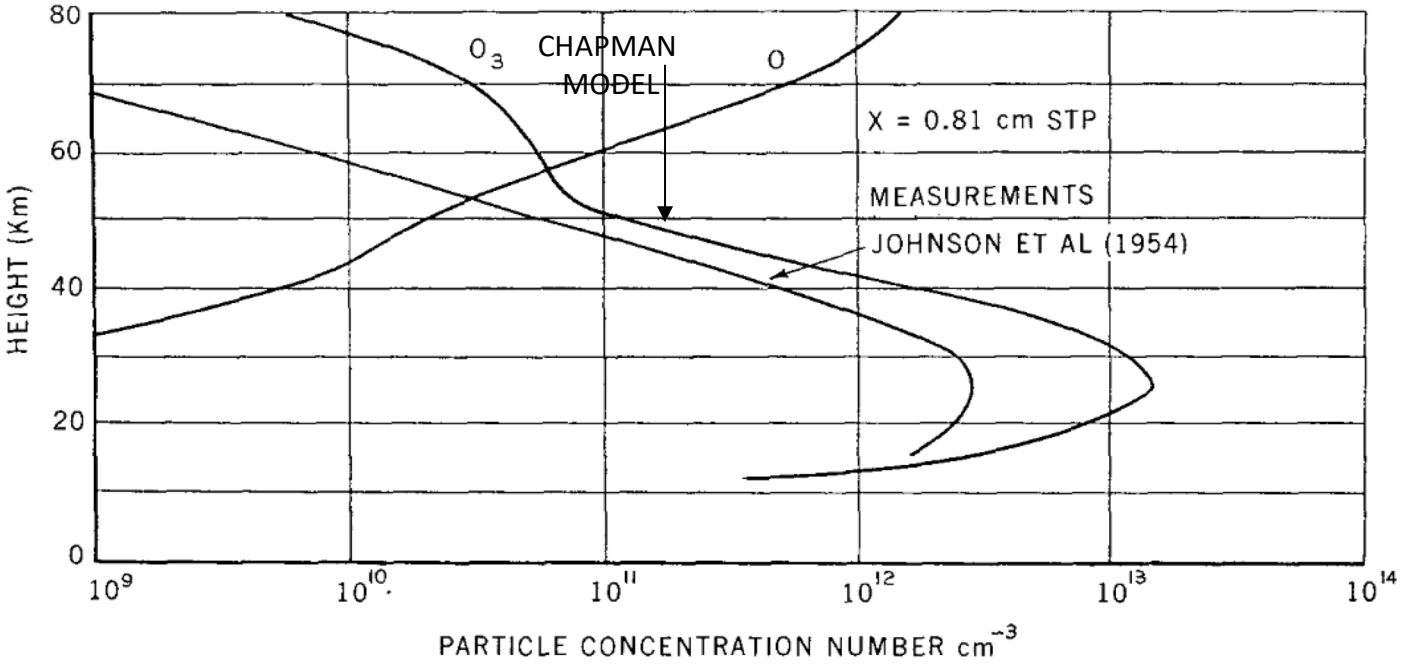
B. G. HUNT[1]

Weapons Research Establishment, South Australia

(Manuscript received 11 March 1965, in revised form 30 August 1965)

ABSTRACT

It is shown that when rate constants confirmed by recent laboratory studies are used in photochemical O_3 calculations unacceptably high O_3 concentrations and total O_3 amounts are obtained. In order to account for this disagreement, an investigation has been made to see whether reactions between O_3 and excited forms of molecular and atomic oxygen are of importance in the atmosphere, following recent laboratory work in this field. It was found that excited molecular oxygen may be neglected in the O_3 reaction scheme but that reactions between O_3 and $O(^1D)$ could be of importance in the stratosphere. The importance of this reaction depends very markedly on the rate of deactivation of $O(^1D)$ in the atmosphere, and a conflict of requirements exists between the O_3 and 6300 Å airglow values for this rate. Hence, in view of this conflict, the photochemical O_3 problem has been left unresolved.



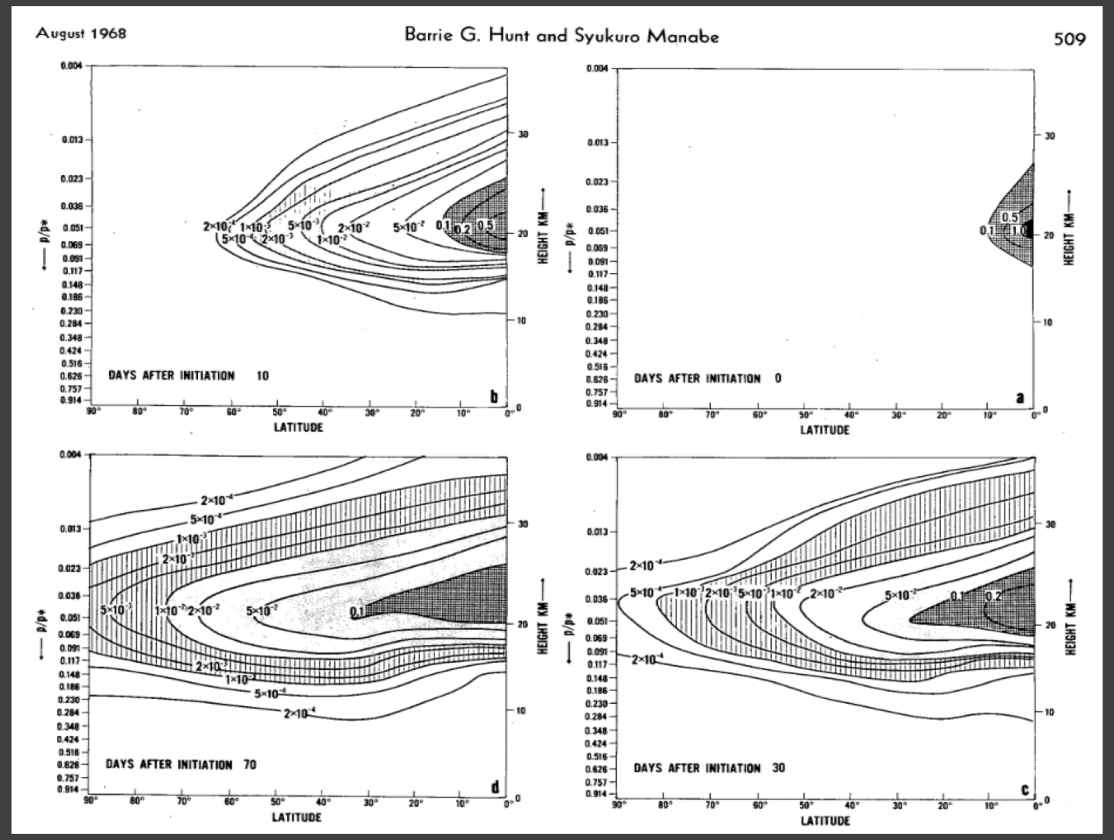
1969: First simulations of ozone in a General Circulation Model (oxygen-hydrogen atmosphere)

The "Ozone problem" is not solved

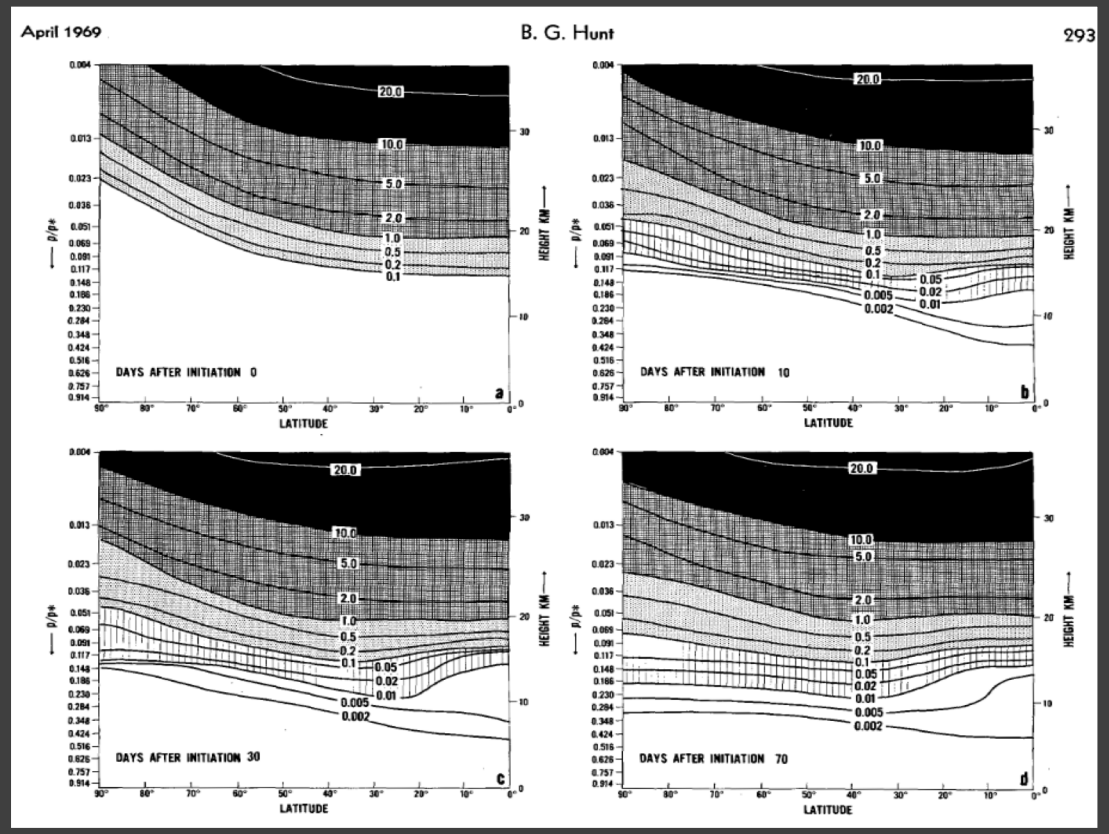
GFDL Model

G. E. Hunt

Inert Tracer mixing ratio



Ozone mixing ratio



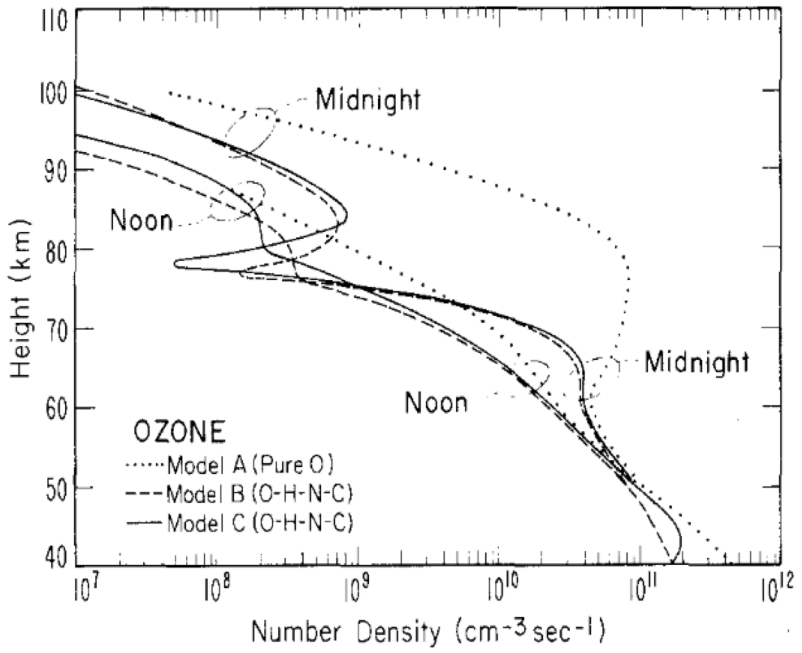
The 1970’s and 1980’s

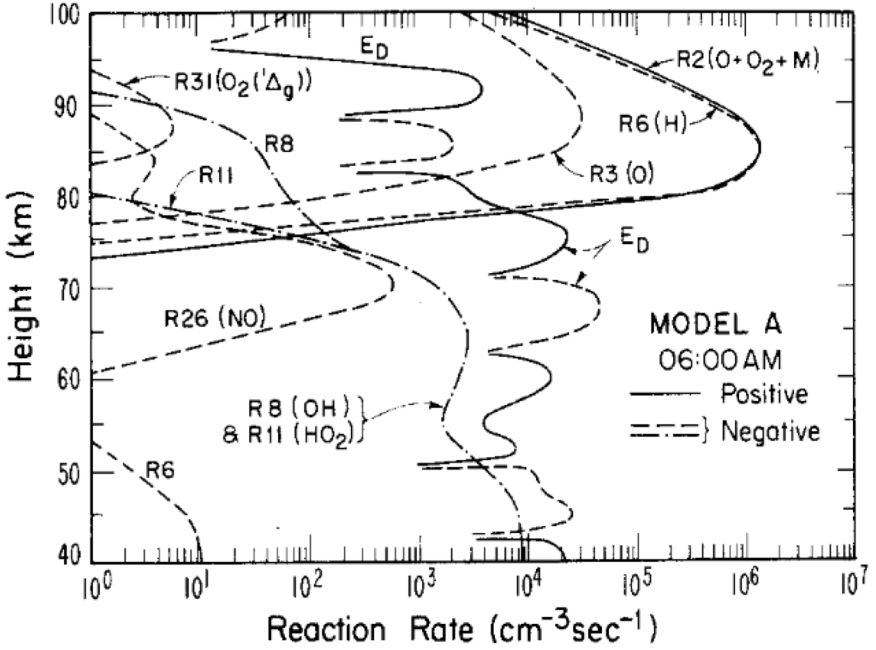
The focus moves to the upper atmosphere

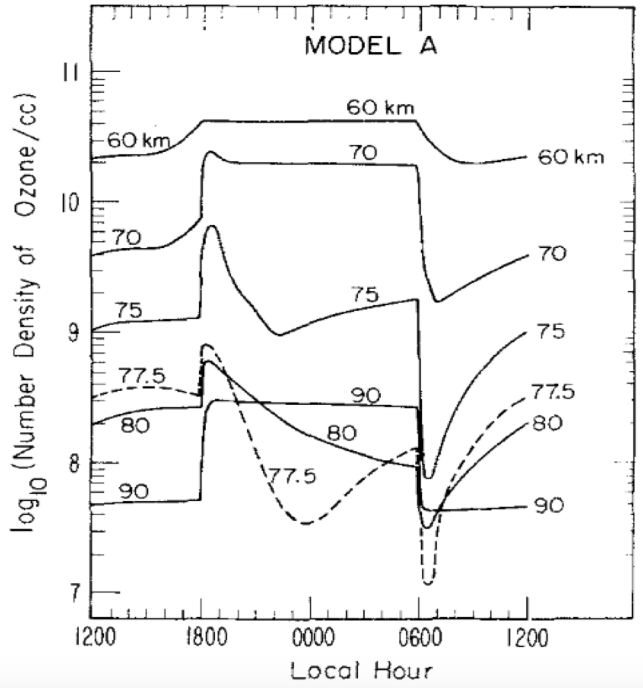
One-dimensional Models

On the Theoretical Model for Vertical Ozone Density Distributions in the Mesosphere and Upper Stratosphere

By T. SHIMAZAKI and D. J. WUEBBLES[1])







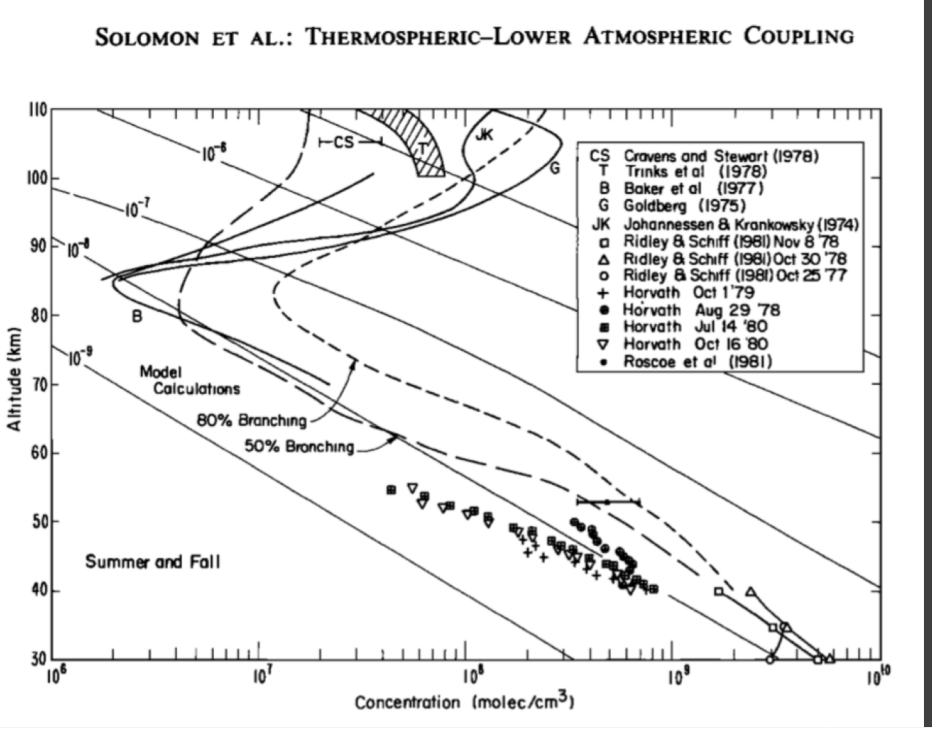
1970: Catalytic Ozone Destruction by Nitrogen Oxides

- **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)

$$NO + O_3 \rightarrow NO_2 + O_2$$

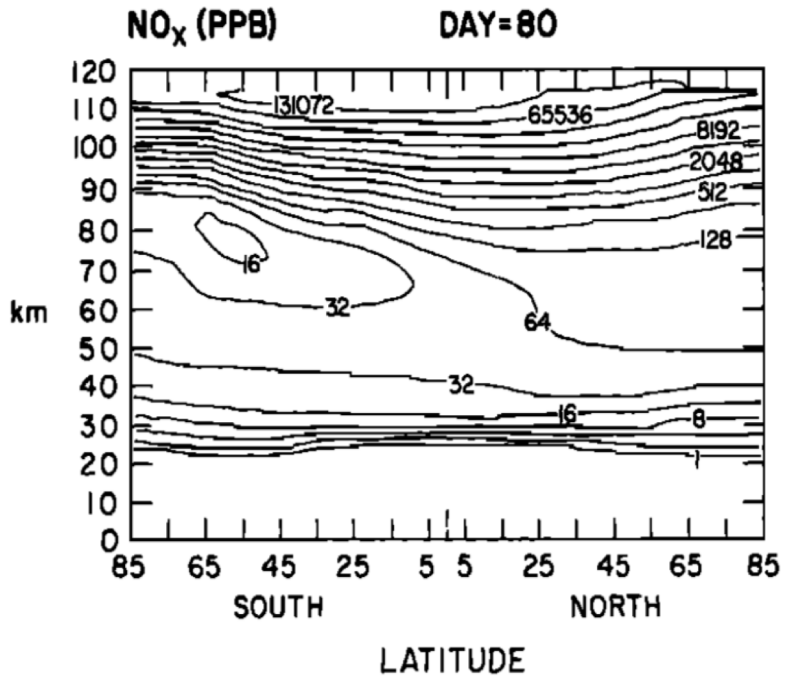
$$NO_2 + O \rightarrow NO + O_2$$

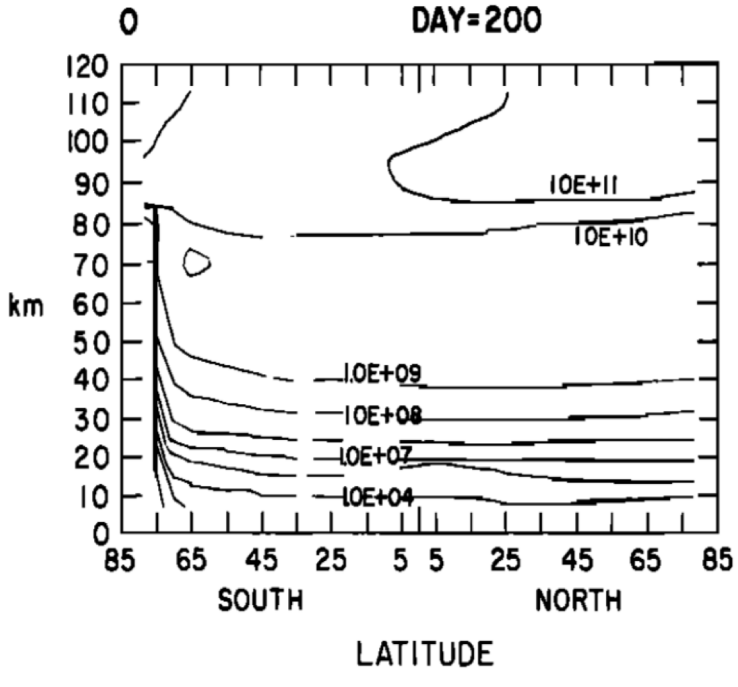
$$O_3 + O \rightarrow O_2 + O_2.$$ (net effect)

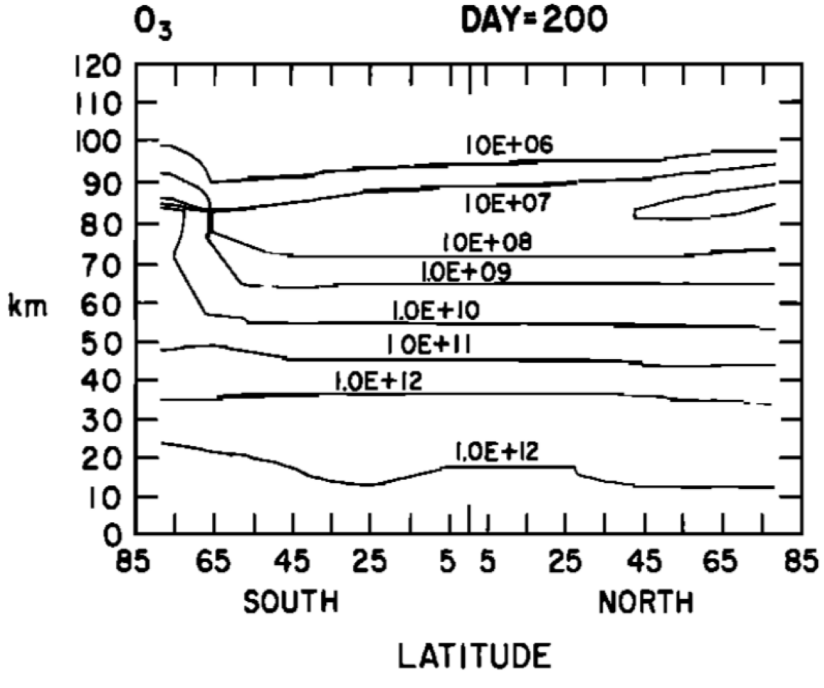


The importance of nitrogen oxides in the middle atmosphere

Two-dimensional Model
S. Solomon, P. Crutzen, R. Garcia

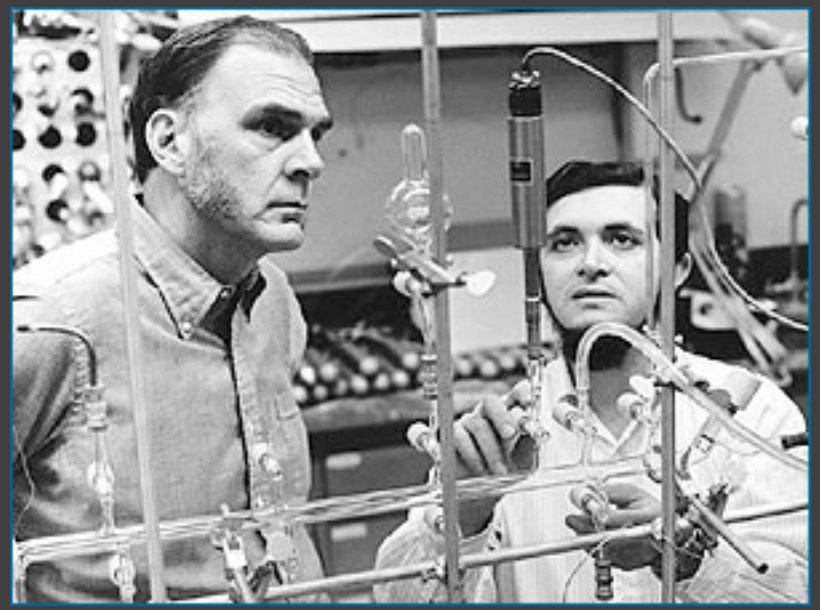




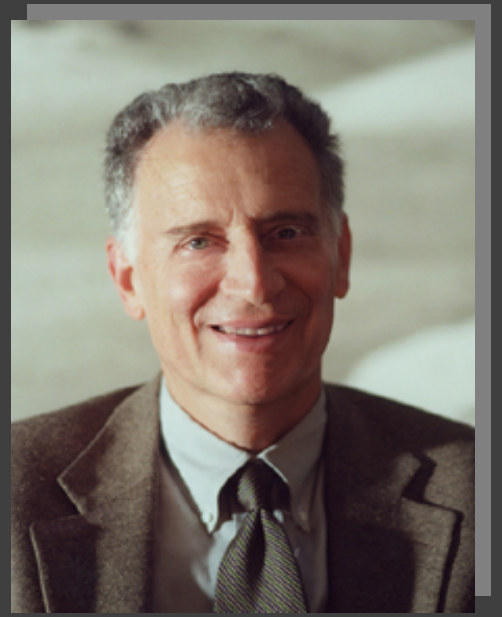


1974: Catalytic Destruction of Ozone by Chlorine

- In 1974, **Richard Stolarski** and **Ralph Cicerone**, then at the University of Michigan, suggested that chlorine could also catalytically destroy ozone in the stratosphere.



- **Mario Molina** and **Sherry Rowland** show that the major source of stratospheric chlorine is provided by the decomposition of chlorofluorocarbons.



1970’s: Tropospheric Chemistry

1973: Paul Crutzen and William Chameides introduce a photochemical theory for tropospheric ozone

Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air

By PAUL J. CRUTZEN,[1] *National Center for Atmospheric Research,*[2] *and University of Colorado, Boulder, Colorado 80302*

Observational and theoretical evidence in support of a significant in-situ photochemical source of tropospheric ozone

By JACK FISHMAN, *Department of Atmospheric Science, Colorado State University, Ft. Collins, Colorado 80523, U.S.A.*, SUSAN SOLOMON, *National Centre for Atmospheric Research,*[1] *P.O. Box 3000, Boulder, Colorado 80307, U.S.A.* and *Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, U.S.A.*, and PAUL J. CRUTZEN, *National Centre for Atmospheric Research,*[1] *P.O. Box 3000, Boulder, Colorado 80307, U.S.A.*

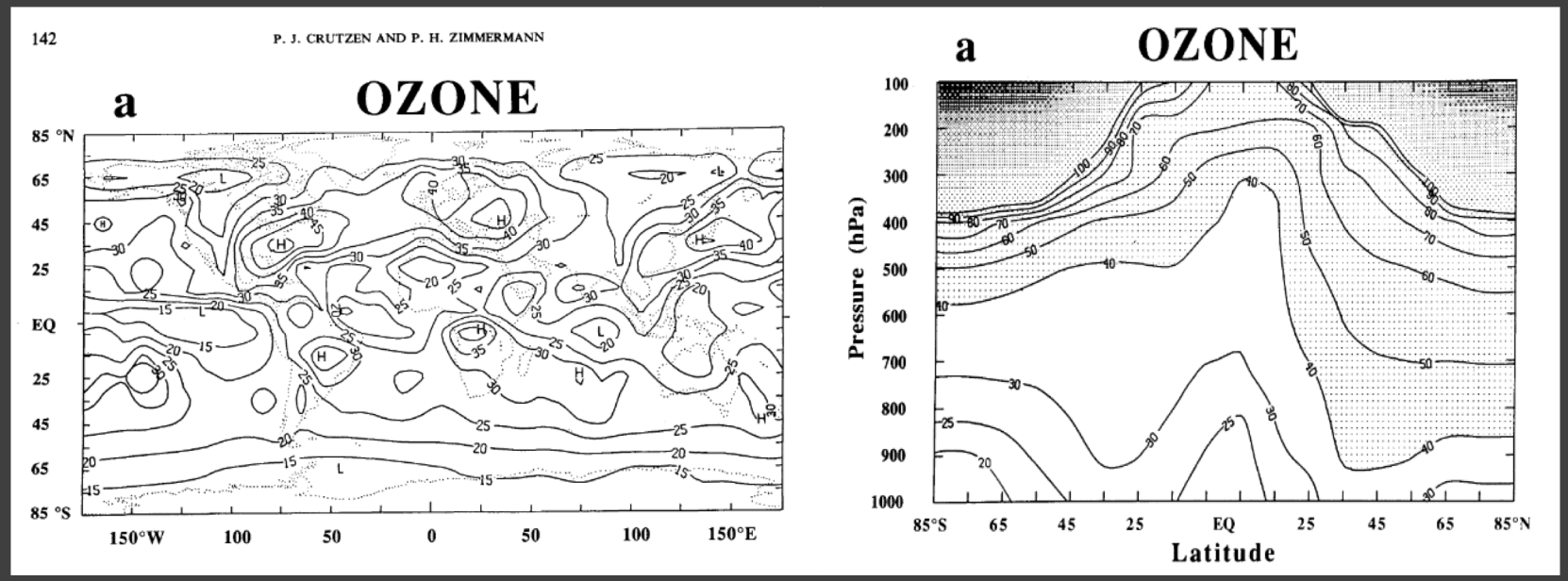
A Photochemical Theory of Tropospheric Ozone

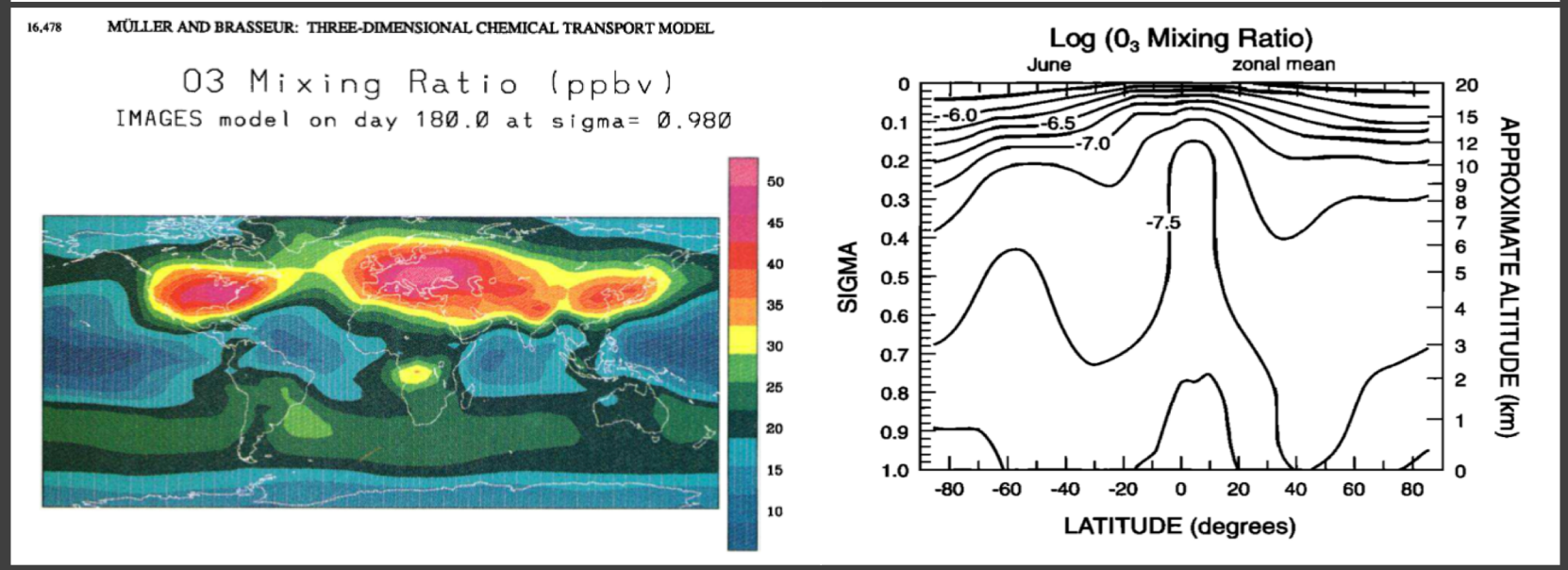
WILLIAM CHAMEIDES AND JAMES C. G. WALKER

Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520

$$n(O_3) = \frac{\{n(NO)[n(HO_2)k_{22} + n(CH_3O_2)k_6 + 2n(NO_3)k_{32}] + n(HNO_3)k_{25a}\}F}{f_2[n(H_2O)k_{16a} + n(H_2)k_{16b}] + n(NO)k_{29}(1 - F) + n(NO_2)k_{28}}$$

1990's: Simple 3-D global models of Tropospheric Chemistry





MONGUNTIA Model
MPI-Chemistry, Mainz
Peter Zimmermann

The first low resolution 3-D models use simple meteorology with mean winds and turbulent eddy diffusion, simple chemical schemes. Physical processes are highly parameterized.

IMAGES Model
Belgian Aeronomy Institute, Brussels
J.-F. Müller

Eulerian or Lagrangian chemical transport models account for

--emissions and deposition

--chemical transformations

--advection

--sub-scale transport

Daniel Jacob, Harvard

Chemical transport model (CTM):

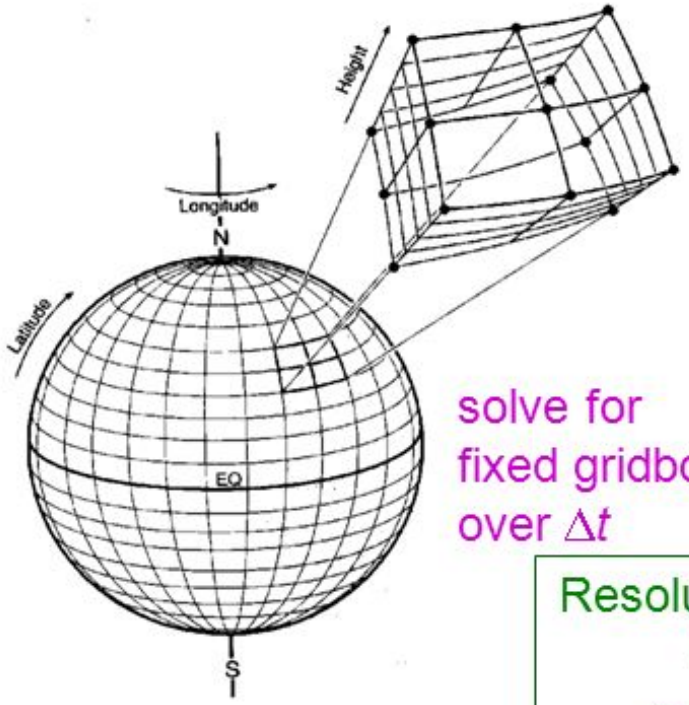
forward model for inverting emissions from atmospheric observations

Solve 3-D continuity equation for chemical concentrations in the atmosphere:

$$\partial C / \partial t = -\mathbf{u}\nabla C + \nabla K \nabla C + P - L + E - D$$

change in concentration with time	grid-resolved transport (advection)	subgrid transport (turbulence)	chemical production and loss	emission, deposition

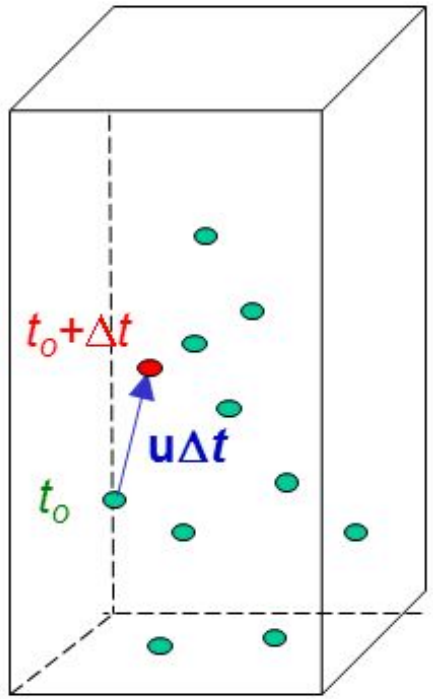
Eulerian framework



solve for fixed gridboxes over Δt

Lagrangian framework

solve for point masses moving with the flow



Resolution of current models:
~100 km (global)
~ 10 km (continental)
~ 1 km (regional)

Around 2000: complex chemical transport models

Complex chemical-transport model (off line) include detailed chemistry, accurate advection schemes, a full representation of the hydrological cycle and a refined formulation of physical (sub-grid) processes. Increasing spatial resolution.
Models can be “off-line” (dynamics is specified) or ”on-line” (coupled with a dynamical model)

MOZART (NCAR)

MOZART, a global chemical transport model for ozone and related chemical tracers 1. Model description

G. P. Brasseur,[1] D. A. Hauglustaine,[1,2] S. Walters,[1] P. J. Rasch,[1] J.-F. Müller,[3] C. Granier,[2,4,5] and X. X. Tie [1]

Table 3. Annual Budget of Ozone in the Troposphere (Below 250 mbar) Calculated by MOZART, Tg-O_3/yr

	NH	SH	Global
Photochemical production	2023	995	3018
Stratospheric influx	170	221	391
Total source	2193	1216	3409
Photochemical destruction	-1540	-971	-2511
Dry deposition	-625	-273	-898
Total sink	-2165	-1244	-3409
Burden (Tg)	114	79	193
Lifetime (days)	19	23	21

GEOS-CHEM (Harvard)

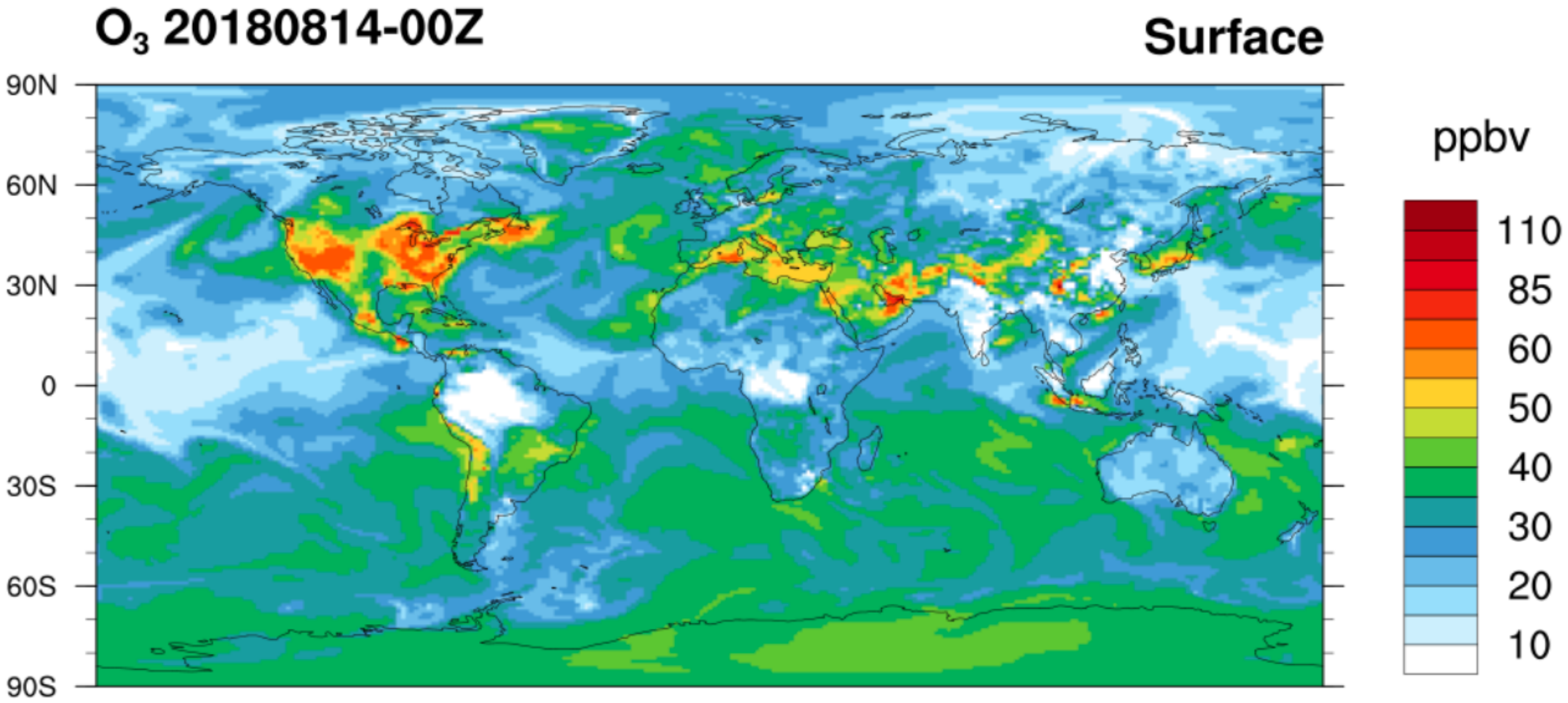
Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation

Isabelle Bey,[1] Daniel J. Jacob, Robert M. Yantosca, Jennifer A. Logan, Brendan D. Field, Arlene M. Fiore, Qinbin Li, Honguy Y. Liu, Loretta J. Mickley, and Martin G. Schultz[2]

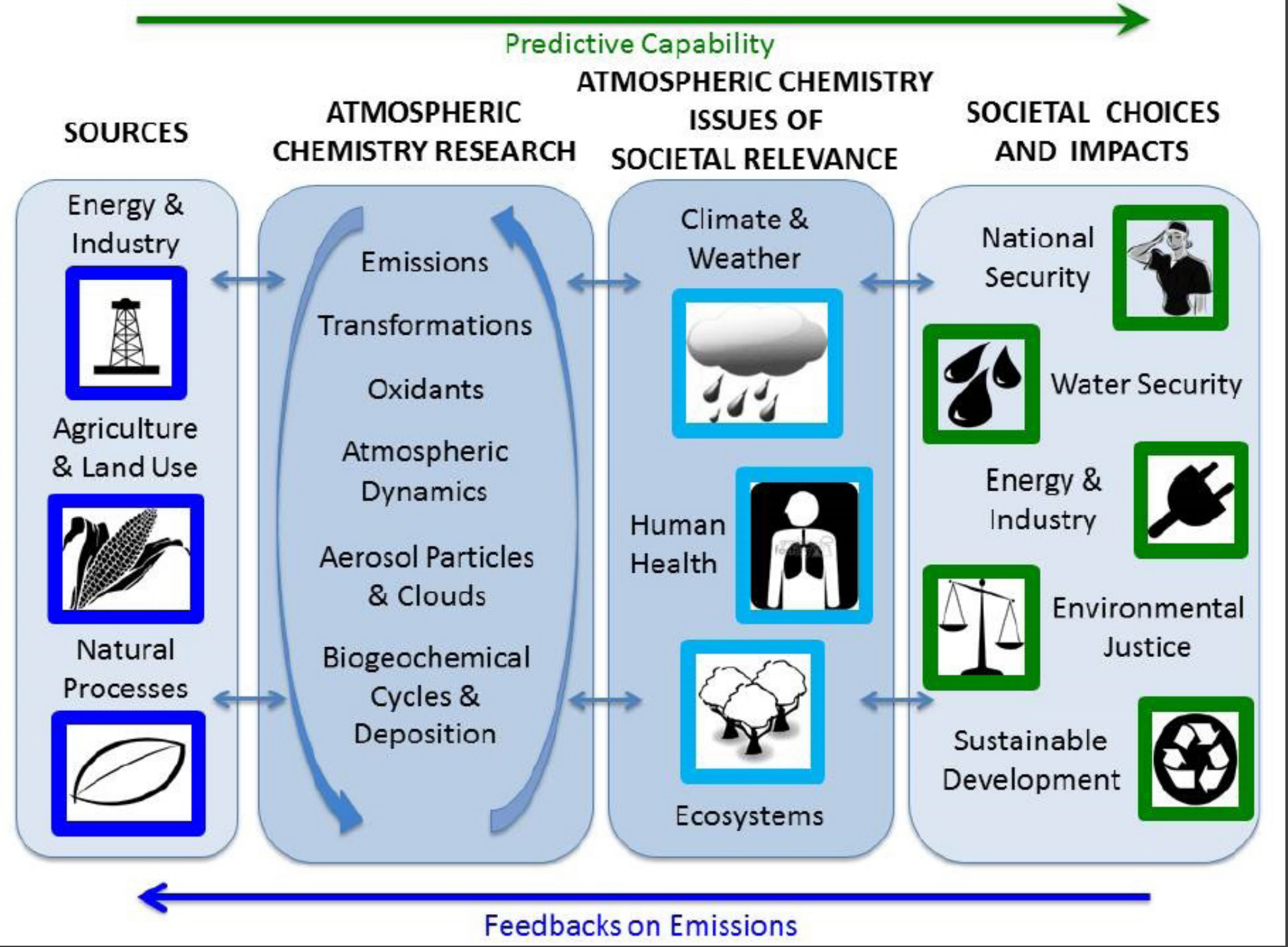
Table 5. Global Budget for Tropospheric Ozone in the GEOS-CHEM Model

	Global	Northern Hemisphere	Southern Hemisphere
Sources, Tg O_3 yr^{-1}			
Chemical production	4900	3100	1800
Stratospheric influx	470	280	190
Total	5370	3380	1990
Sinks, Tg O_3 yr^{-1}			
Chemical loss	4300	2600	1700
Deposition	1070	740	330
Total	5370	3340	2030
Burden, Tg O_3	315	175	140

Prediction of surface ozone for 14 August 2018



The Future



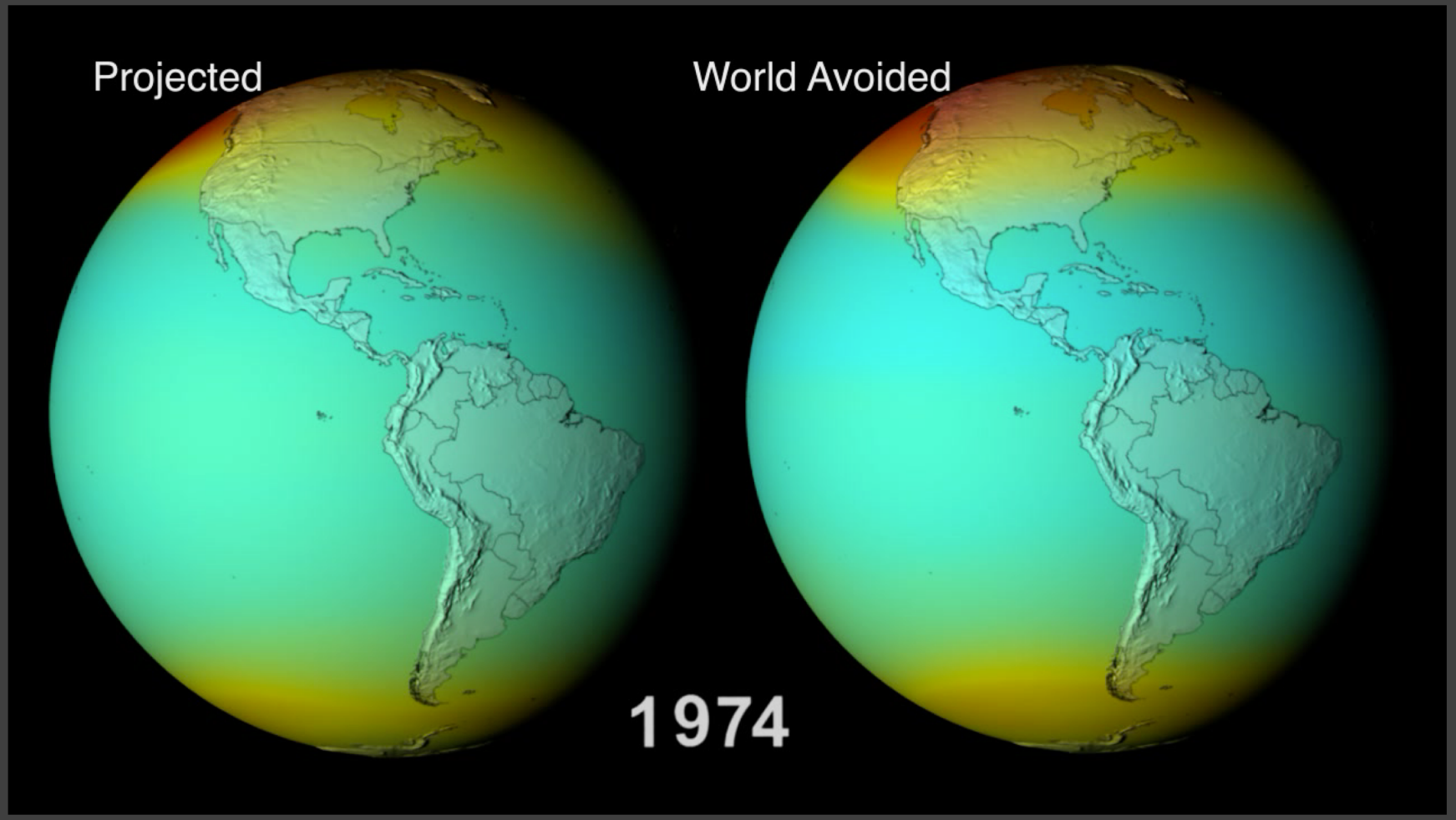
Chemical models are increasingly embedded in more comprehensive Earth System Models to address complex interactions between the natural and the social system.

Important questions are
--Predictive capability
--Feedbacks on forcing

Future Evolution of Chemical Models

Towards a diversity of approaches

- Advanced chemical transport models will be **inserted in complex Earth System models**. More **modular architecture** to accommodate for different formulations of the physics and the chemistry. Downscaling in regions. Unstructured grids to address specific problems. Coupling with LES models
- Increasing needs for flexible and portable models to provide **operational** global to regional to local air quality predictions
- Stronger **fusions with observations**: adjoint models, data assimilation, bias corrections
- **New approaches**: hyper-explicit models with focus on chemical processes, neural networks, machine learning.



Thank you

Paul Newman, NASA/GFSC

In the early 1980's, after decades of intense research, everyone believes that the ozone problem is fully understood.

Models represent very well the observed distribution of ozone.

But, in 1984, the community is faced by an embarrassing surprise…….

An abrupt ozone decline that has not been predicted even by the best models……

"The history of science is the history of failed models"

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