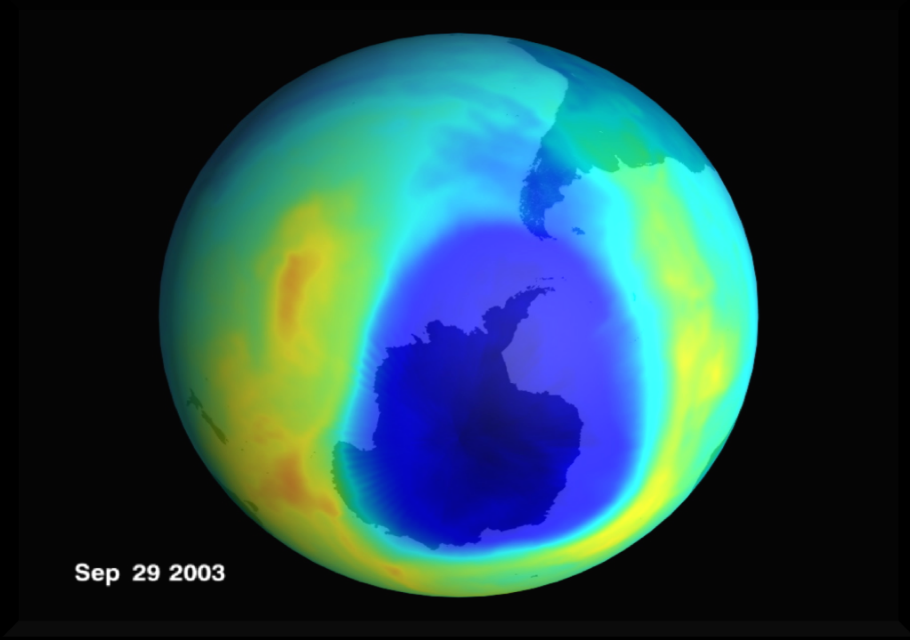
Atmospheric Ozone :
An Historical Perspective



Guy P. Brasseur

Max Planck Institute for Meteorology,
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1. The Discovery of Ozone

The Discovery of Ozone

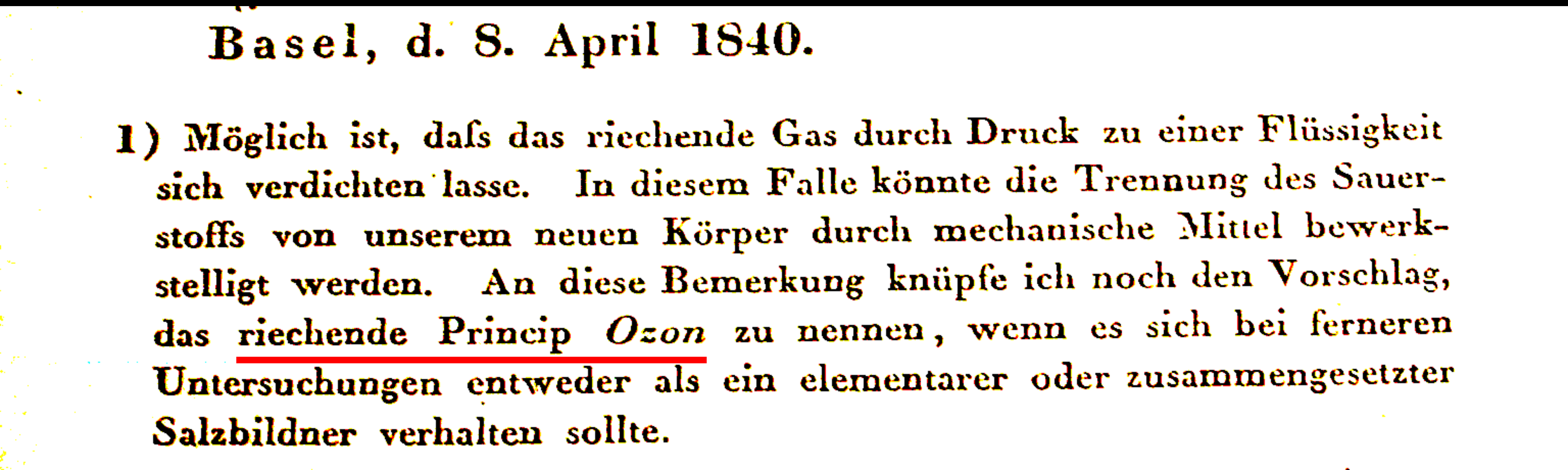
- On March 13, **1839**, **Christian Fredrich Schönbein** (1799-1868) a German Professor at the University of Basel reports to the local *Naturforschung Gesellschaft in Basel* that the electrolysis of acidulated water produces an odor at the positive electrode.

Recherches sur la Nature de l' odeur qui se manifeste dans certaines actions chimiques, *Compt. Rendus de l' Academie des Sciences, 27 April, 1840, Paris*

- Herr Prof. Schönbein macht die Gessellschaft [..] aufmerksam dass bei der Electrolyse des Wassers ein Geruch entwickelt wird […]
- *Ber. Verh. Nat. Ges. Basel,, 4*, 58, 1838-40

The Discovery of Ozone

The suggestion that this odor was due to a chemical **substance** was made by **Schönbein** in **1840** at the Bavarian Academy of Sciences. In a letter to Arago read before the French Academy of Sciences, he proposes to name this substance "**ozone**" after the Greek word όζειν (ozein, to smell). [as suggested by **W. Vischer** Professor of Greek in Basel]



Basel, d. 8. April 1840.

1) Möglich ist, dafs das riechende Gas durch Druck zu einer Flüssigkeit sich verdichten lasse. In diesem Falle könnte die Trennung des Sauerstoffs von unserem neuen Körper durch mechanische Mittel bewerkstelligt werden. An diese Bemerkung knüpfe ich noch den Vorschlag, das riechende Princip *Ozon* zu nennen, wenn es sich bei ferneren Untersuchungen entweder als ein elementarer oder zusammengesetzter Salzbildner verhalten sollte.

Confusion about the Cause of the Odor

Schönbein

- Schönbein believed that the odor must be due to some gaseous substance released by the fluid due to the decomposing power of electricity.
- Auguste Arthur de la Rive (1801-1873) suggested that the odor might be due to finely divided particles of oxidized electrode material. Schönbein responded that the odor was observed during lightning storms
- Chemical tests made by Schönbein showed that ozone reacted with potassium iodide (KI) to produce elementary iodine (I_2). This led to the starch-iodide paper to measure the ozone.

de la Rive

Two Competing Theories

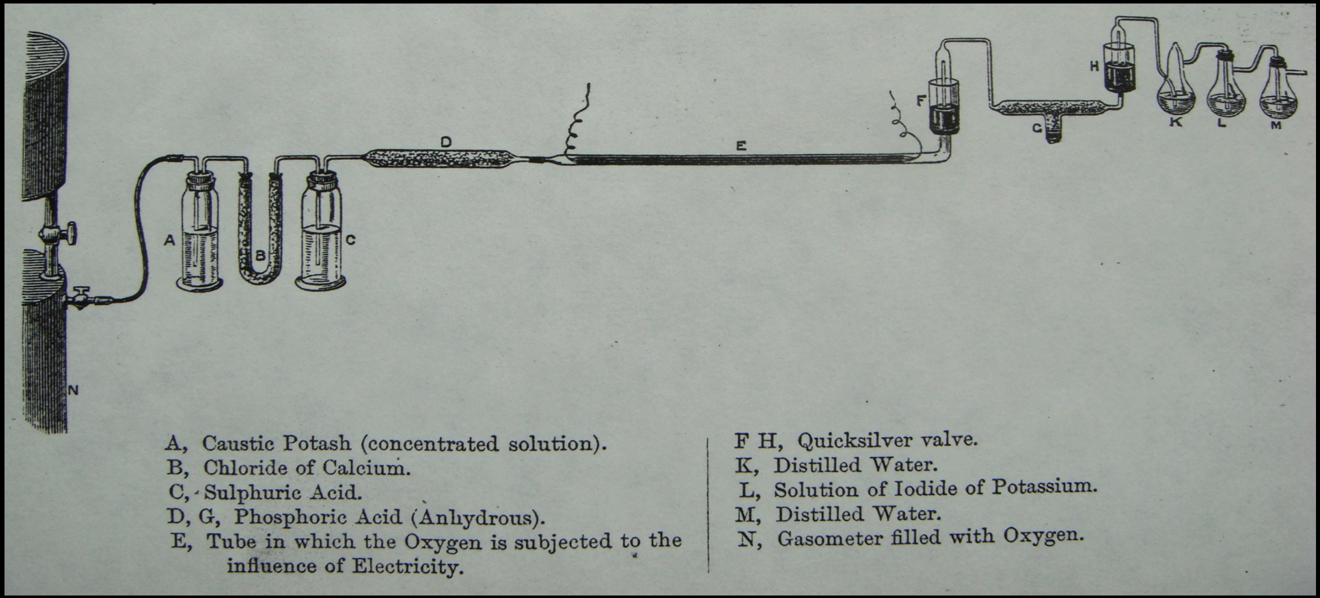
- **Christian Schönbein** (1799-1868, Basel) considers ***ozone*** to be a negatively electrified oxygen (O^-), that must be compensated by a positively electrified oxygen (O^+), which he called ***antozone***. Based on this theory, oxygen (O_2) is the association of ozone and antozone ($O_2 = O^+ + O^-$).
- **Jacques-Louis Soret** (1827 – 1890, Basel) considers that ozone is an allotropic form of oxygen: OOO or $O\text{-}O_2$ (oxygen dioxide or binoxide of oxygen).
- **Schönbein** objected to the conclusion, arguing that allotropy was reserved for solid substances. Until 1850, he maintained that ozone was a compound of hydrogen and oxygen.

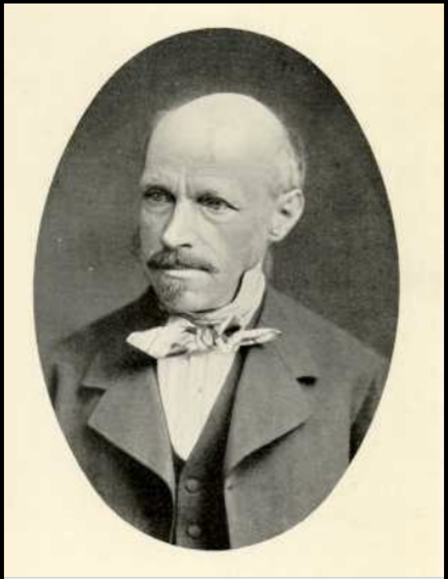
J. L. Soret.

Antozone

- According to Schönbein, **ozone** is capable of assuming 3 different conditions:
  - 2 contrary active states (ozone and antozone)
  - 1 passive state (neutral oxygen)
- **Antozone** is oxygen in the positively polar state
- In 1863, **Meissner** discovered that, if dried electrified oxygen passed through moist air, mist is formed, a substance named **Atmizone** (from the Greek ατμιζω, to smoke). It was later believed to be identical of **Antozone**.
- Antozone was believed to be the cause of cloud in tabacco-smoke, smoke of chemineys and gun-powder

Meissner's Apparatus for the Production of Antozone



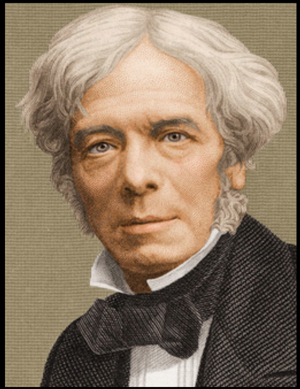


Georg C. F. Meissner, (1829-1905) Professor of Physiology, Göttingen.

G. Meissner, Untersuchungen über den Sauerstoff, Hahn, Hannover, 1863.

M. Faraday (1791-1867) and C. Schönbein (1799-1868)

M. Faraday



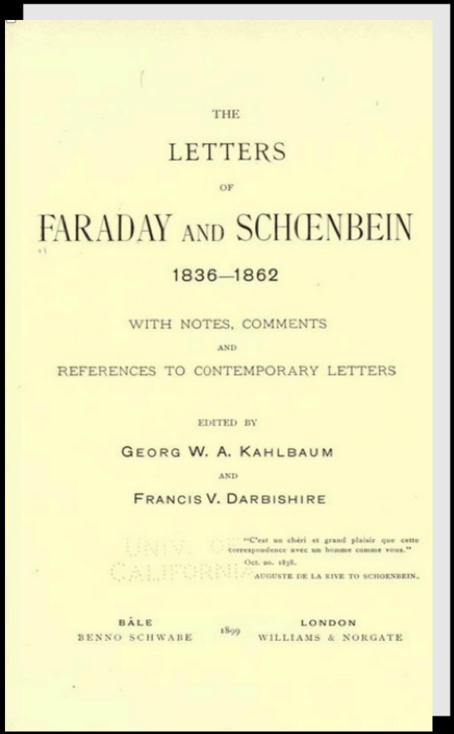
Royal Institution 13. Nov. **1858**

My Dear Schoenbein,

Daily and hourly am I thinking about you and yours, and yet with as unsatisfactory a result as it is possible for me to have. I think about Ozone, about Antozone, [..] and it all ends in a giddines and confusion of the points that ought to be remembered.

I want to tell our audience what your last results are upon this most beautiful investigation, and yet am terrified at the thoughts of trying to do so, from the difficulty of remembering from the reading of one letter to that of another, what the facts in the former were. I have never before felt so seriously the evil of loss of memory and of clearness in the head; and though I expect to fail some day at the lecture table, as I get older, I should not like to fail in ozone, or in any thing about you.

M. Faraday



THE

LETTERS

OF

FARADAY AND SCHŒNBEIN

1836—1862

WITH NOTES, COMMENTS

AND

REFERENCES TO CONTEMPORARY LETTERS

EDITED BY

GEORG W. A. KAHLBAUM

AND

FRANCIS V. DARBISHIRE

"C'est un chéri et grand plaisir que cette correspondence avec un homme comme vous."

Oct. 20. 1858.

AUGUSTE DE LA RIVE TO SCHOENBEIN.

BÂLE — BENNO SCHWABE — 1899 — LONDON — WILLIAMS & NORGATE

The Ozone Chemical Formula

- In **1845**, **Auguste de la Rive** and **Jean-Charles de Marignac** (Geneva) announce that ozone is a form of oxygen.
- In **1852**, **Becquerel and Frémy** (France) demonstrated that pure oxygen may be converted to ozone by prolonged action of electrcity.
- In **1856**, **Andrews** (England) demonstrates that ozone is oxygen in an altered or allotropic form, and is therefore denser than oxygen.
- In **1868**, **Jacques-Louis Soret** (Basel) determines 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-O_2 (oxygen dioxide or bi-oxide of oxygen). [Just before the death of Schoenbein]

Soret`s Determination of the Density of OZONE

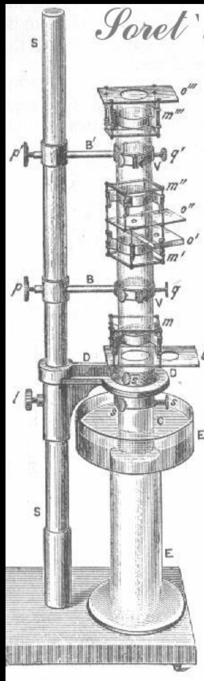


FIG. 155.—Density of ozone by diffusion (Soret).

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

CHIMIE. — *Sur les relations volumétriques de l'ozone.* Note de **M. J.-L. Soret**, présentée par M. Regnault.

On pourrait, par exemple, concevoir que 1 molécule d'ozone fût composée de 3 atomes OOO, et constituât un bioxyde d'oxygène.

COMPTES RENDUS DES SÉANCES DE L'ACADÉMIE DES SCIENCES. 1863

The End of Antozone

- A. R. Leeds (**1879**), summarizing the purported chemistry of antozone wrote, "By far the most important fact in the long and perplexing history of antozone, is the recent discovery that there is no antozone."

- A. R. Leeds, "The History of Antozone and Peroxide of Hydrogen," *Ann. N.Y. Acad. Sci.*, **1879**, *1*, 405-417.

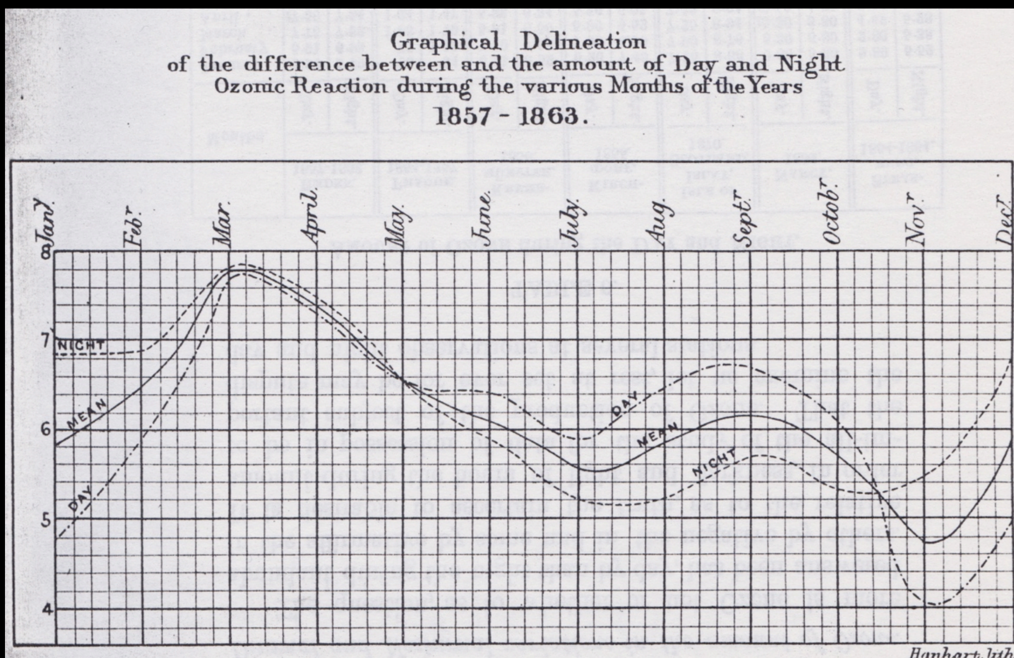
Chemical Measurements in the Atmosphere

- In **1858**, **Jean Auguste Houzeau** (1829-1911), Agronomist and professor of Chemistry at *École Supérieure des Sciences et des Lettres* in Rouen and at *École d'agriculture du Dept. de la Seine-inférieure*.) used a mixture of iodine and arsenic to measure ozone, and discovers that ozone is a permanent chemical constituent of the atmosphere.

A. Houzeau, "Nouvelle méthode pour reconnaitre et doser l'ozone (**oxygène odorant, oxygène naissant**)," Ann. Chim. Phys. [3], 1863, 67, 466-84.

First Systematic Ozone Observations

Emden, Germany 1857-1863



Paris 1866-1867

Stations.		Mean of Daily Observations during the years 1866 and 1867.
Passy	(a)	6·39
Monceau		4·04
Montmartre		4·48
La Villette	(b)	·96
Charonne		4·34
Ménilmontant	(c)	1·16
Boulevard de Picpus		4·49
La Boule-Rouge		2·45
Fontaine-Molière	(d)	·38
École de Médicine	(e)	·80
Rue Racine	(f)	1·69
Panthéon		2·83
Saint-Victor		4·98
Boulevard d'Italie		3·08
Vaugirard		·89
Réservoir de Vaugirard	(g)	8·37
La Chapelle	(h)	3·08
Butte-aux-Cailles	(h)	4·79
		1866.
Batignolles		4·75

(a) Near resinous trees.
(b) Close to a quay on the Seine.
(c) Near a tallow manufactory.
(d) A public urinal is situated almost directly underneath the test.

[1] *Bulletin de Statisque Municipale*, February 1868.

Systematic Observations

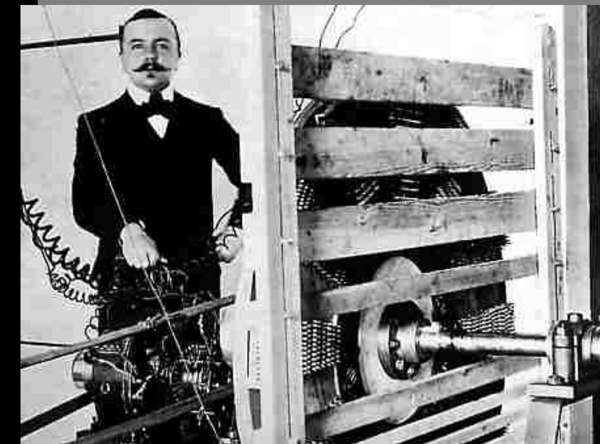
Between **1850** and **1900**, ozone became routinely measured in 300 sites in Europe and the United States, because ozone was believed to reduce epidemics (cholera).

Municipal Observatory of Paris at Parc Montsouris where Albert Levy measures ozone from 1877 to **1907**

(iodine-catalyzed oxidation of arsenate)

Ozone for Water Disinfection

- The first ozone generator was manufactured in Berlin by **von Siemens.** This caused a number of pilot projects to take place, during which the disinfection mechanism of ozone was researched.
- The French chemist **Marius Paul Otto after his** doctorate (**1907**) was the first person to start a specialized company for the manufacture of ozone installations: 'Compagnie des Eaux et de l' Ozone'.
- The first technical-scale application of ozone took place in Oudshoorn, Netherlands, in **1893**, and another unit was installed in Nice in **1906**.



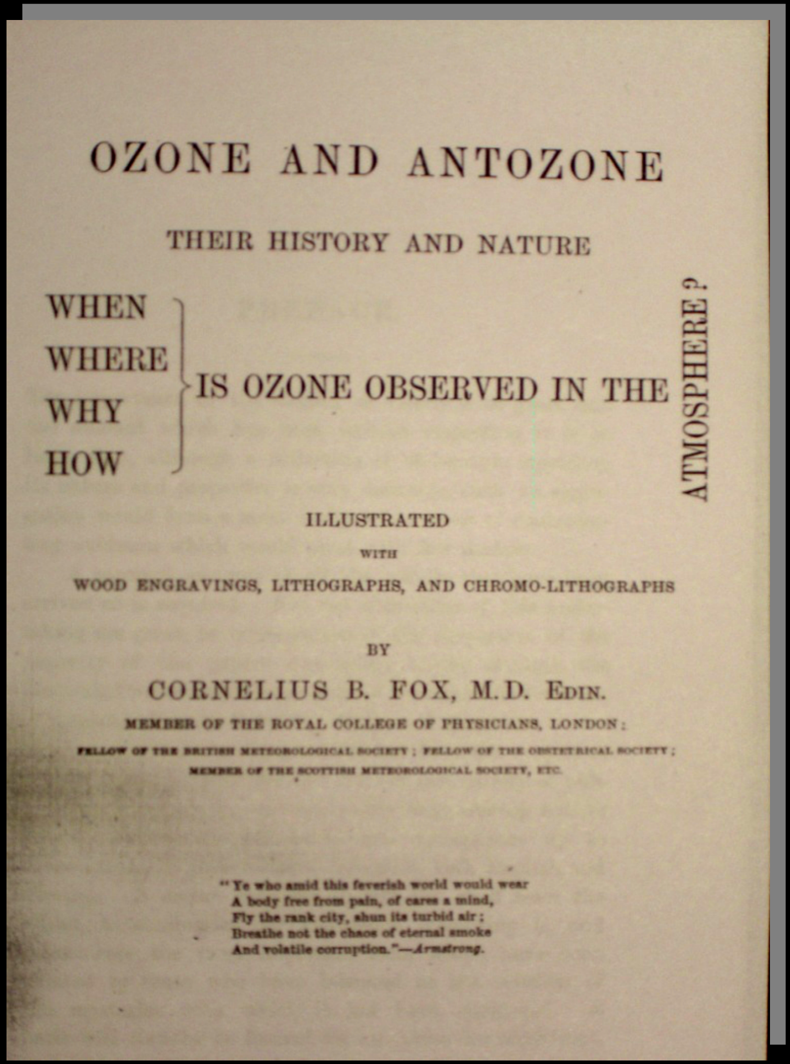
Otto

2. Ozone and Human Health

Ozone and Health

Starting in the **1870**'s ozone is believed to be provide a powerful therapy against diphtheria, cholera, and later to treat tuberculosis, anemia, pneumonia, diabetes and even cancer and now AIDS.

A book entitled: ***Ozone and Antozone*** *published by B. Cornelius Fox, MD. in* ***1873.***


OZONE AND ANTOZONE

THEIR HISTORY AND NATURE

WHEN / WHERE / WHY / HOW — IS OZONE OBSERVED IN THE ATMOSPHERE?

ILLUSTRATED

WITH

WOOD ENGRAVINGS, LITHOGRAPHS, AND CHROMO-LITHOGRAPHS

BY

CORNELIUS B. FOX, M.D. EDIN.

MEMBER OF THE ROYAL COLLEGE OF PHYSICIANS, LONDON;

FELLOW OF THE BRITISH METEOROLOGICAL SOCIETY; FELLOW OF THE OBSTETRICAL SOCIETY;

MEMBER OF THE SCOTTISH METEOROLOGICAL SOCIETY, ETC.

"Ye who amid this feverish world would wear
A body free from pain, of cares a mind,
Fly the rank city, shun its turbid air;
Breathe not the chaos of eternal smoke
And volatile corruption."—*Armstrong.*

Ozone and Health: Many Hypotheses in the 19th Century

- **Cholera** is coincident with an absence or diminution of ozone (Glaisher, Moffat, Hunt).
- In Lyon (France), the "**city without ozone**", cholera is more frequent and more severe than elsewhere (M. Fournet)
- **Malarial fever** only reigns when the ozononmeter indicates zero (Dr. T. Boeckel).
- **Ozone minima** coincide with periods when **fever** is most severe (M. Pouriau).
- Presence of ozone in the air corresponds to the appearance of **bilious remittent fevers** (Dr. E.S. Gaillard).
- No connection between the proportion of atmospheric ozone and the number of cases of **pulmonary affections** (Dr. Prosper de Pietra Santa)

Ozone Therapy

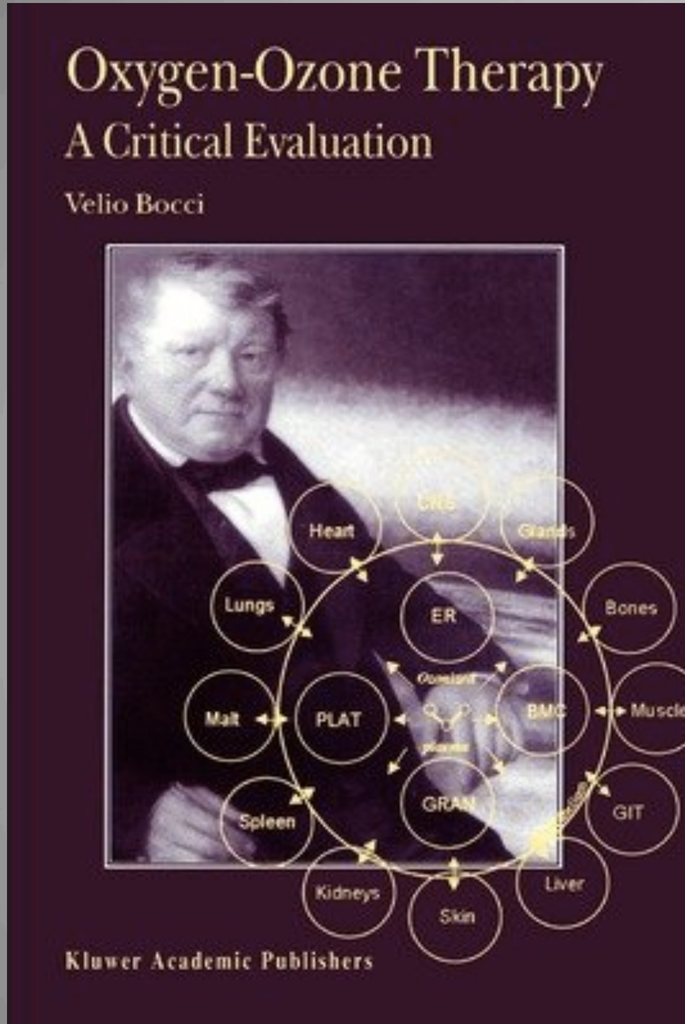
- From **1880**, the first American **therapeutic use** of ozone against **diphtheria** is provided by John Kellogg in ozone steam saunas at a sanitarium in Battle Creek, Michigan.
- In **1898**, the **Institute for Oxygen Therapy Healing** is started in Berlin by Thauerkauf and Luth.

In **1926**, **Otto H. Warburg** (Kaiser Wilhelm Institute in Berlin) suggests that the cause of **cancer** is a **lack of oxygen** at the cellular level. For this discovery, he was awarded the Nobel Prize of Medicine in **1931** (and again in **1944**)

Otto Heinrich Warburg

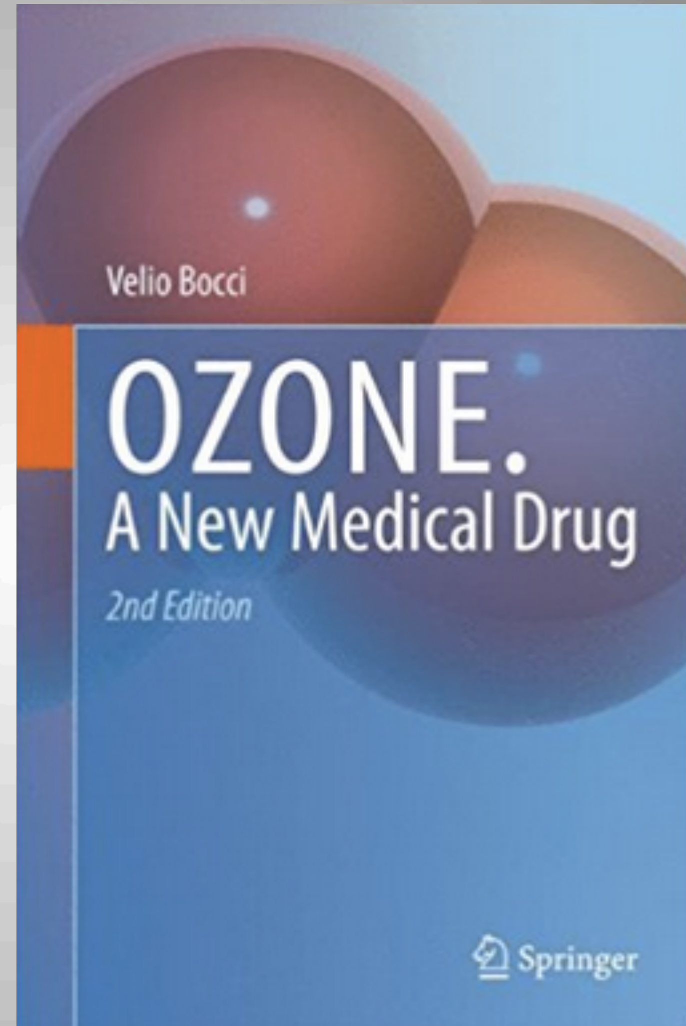
WARNING: CONTROVERSIAL CONTENT

the Warburg Method is the life-saving CANCER TREATMENT we've been seeking.



Oxygen-Ozone Therapy
A Critical Evaluation
Velio Bocci
Heart
CNS
Glands
Lungs
ER
Bones
Malt
PLAT
BMC
Muscle
Spleen
GRAN
GIT
Kidneys
Skin
Liver
Kluwer Academic Publishers

2002



Velio Bocci
OZONE.
A New Medical Drug
2nd Edition
Springer

2010

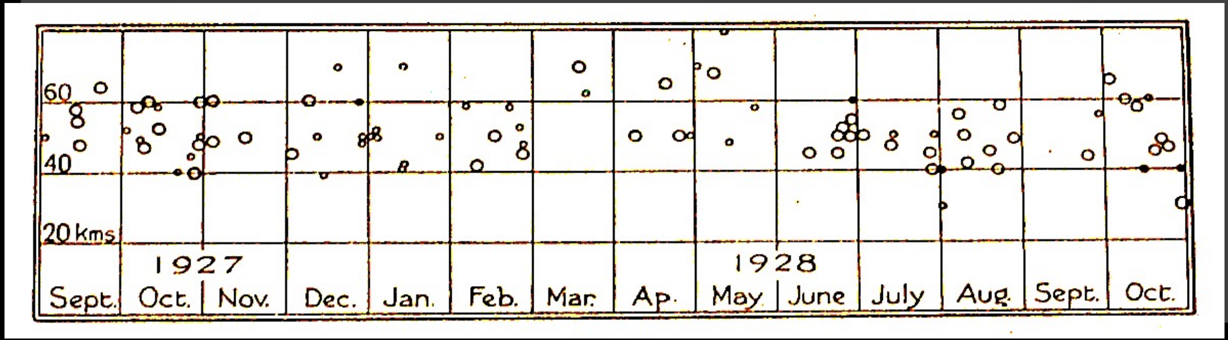
3. Determination of the Vertical Distribution of Ozone

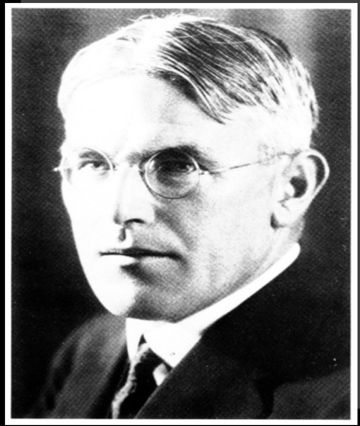
Determination of the Height of the Ozone Layer

In **1928, Jean Cabannes** and **Jean Dufay** in France note that the 300 DU of ozone observed by **Dobson** can only be explained if there is an ozone layer in the upper atmosphere. From the measurement of ozone absorption at 3 different wavelengths, they locate this layer near **50 km** altitude.

Cabannes and his family

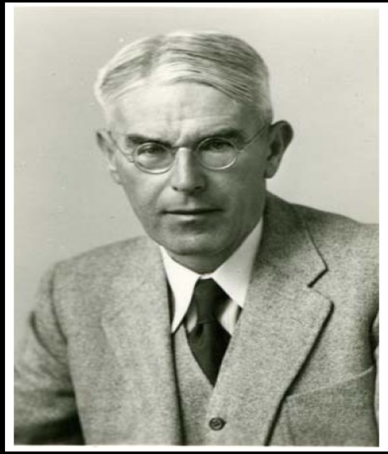
In **1928-1929, Paul Götz** and **Dobson** first confirm from measurements made in **Arosa** that this layer is located near **40-50 km**.





Götz

Determination of the height of the ozone layer: The Umkehr Effect



- During a Spitzbergen expedition in **1929**, **Paul Götz** (by inverting Dobson spectrophotometer measurements at high solar zenith angles) shows that the maximum ozone concentration is located near **25 km** altitude.

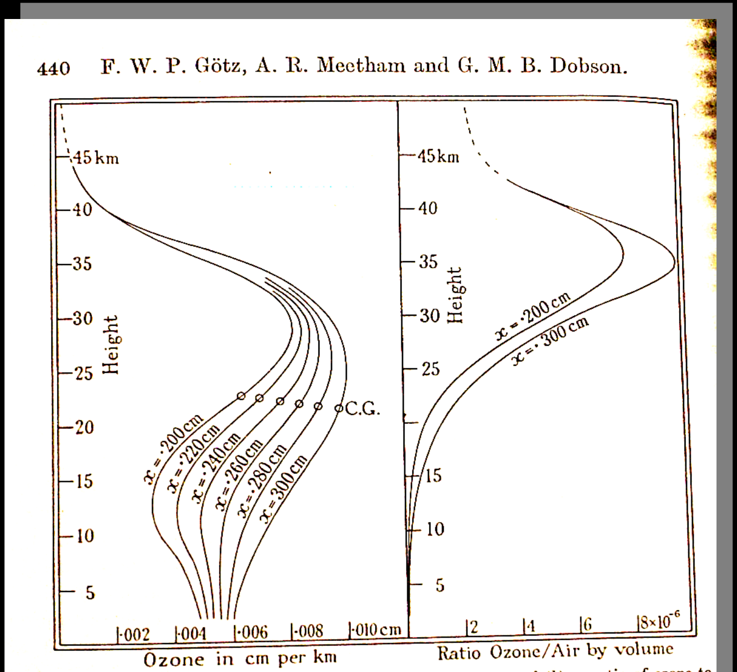


Fig. 8.—Distribution of ozone, (a) in cm. per km. of height, and (b) as ratio of ozone to air. (Method B.)

Height of the Ozone Layer

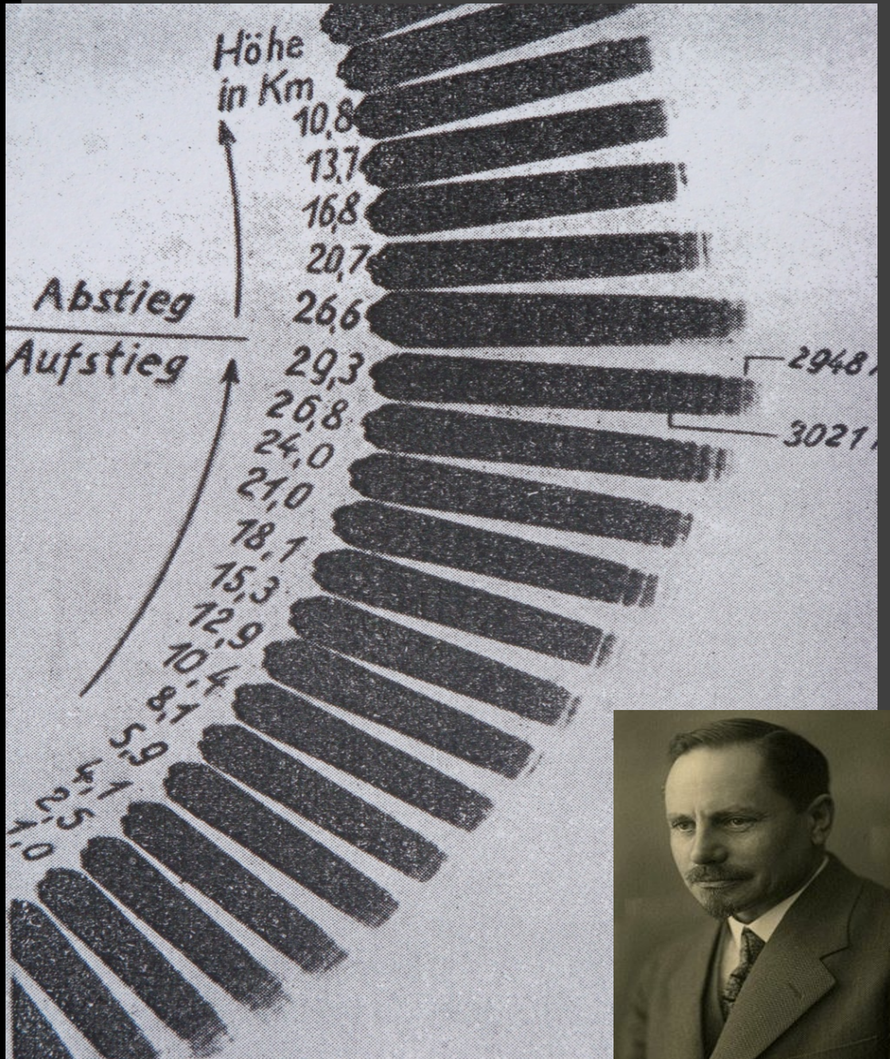
Stuttgart, Germany 1934

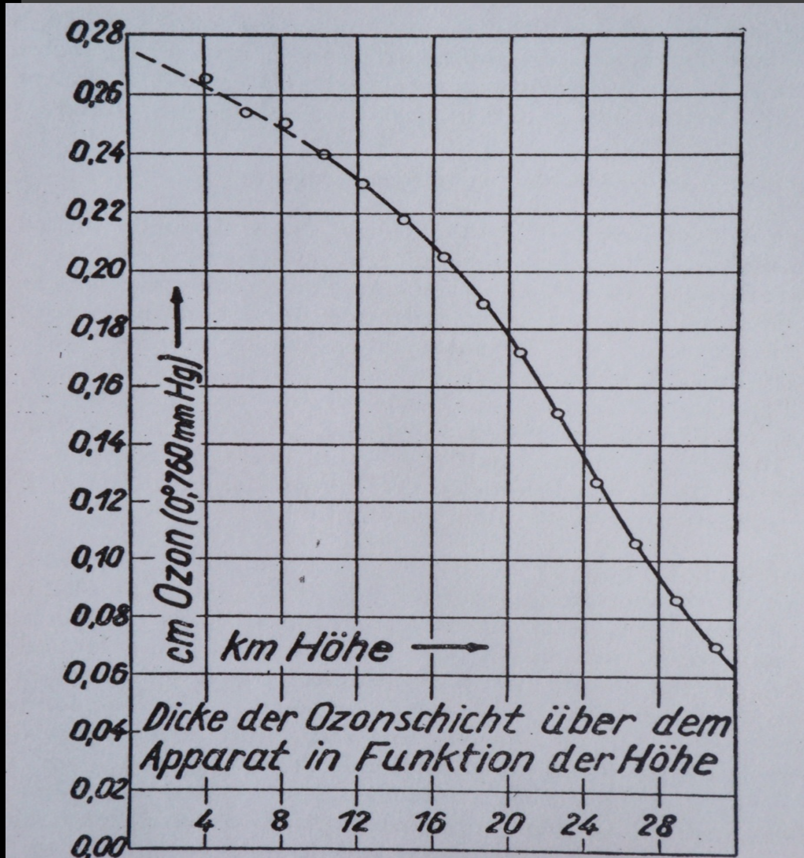
Erich Regener
1881-1955

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.

Regener's Data





Explorer I (1934)

- With funding from the National Geographic Society, **Explorer I** was launched on July, 28, **1934** from Rapid City, Iowa to explore the stratosphere, and to measure the penetration of cosmic rays and ultraviolet solar radiation. This provided an opportunity to derive the **vertical ozone profile**.

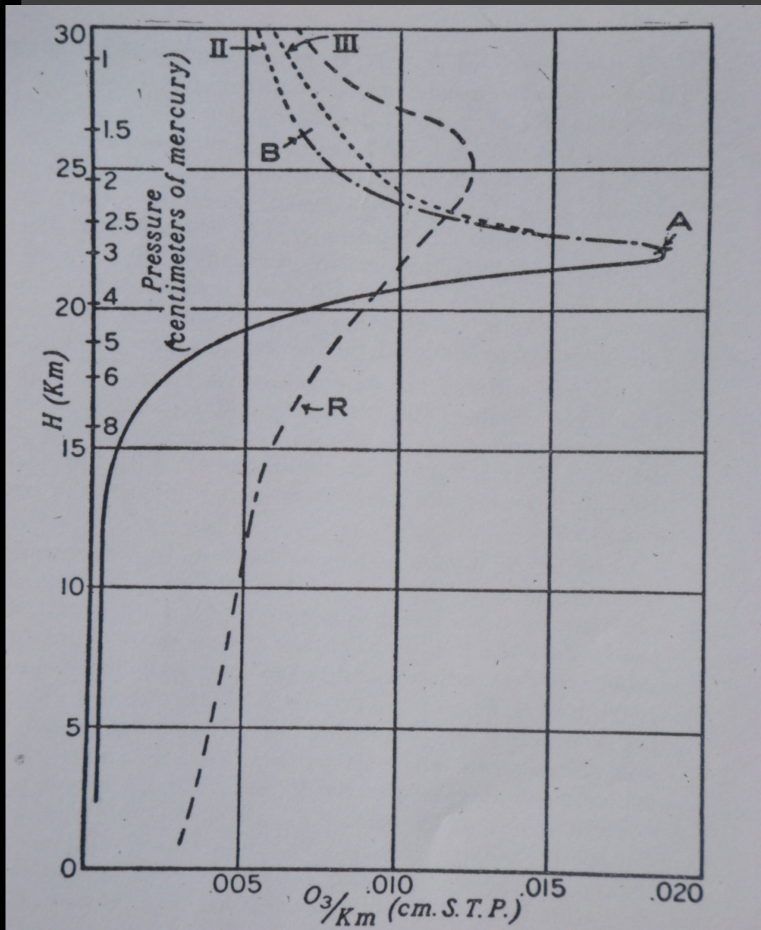
Explorer I (1934)

- The Explorer I flight ended in **disaster** when the balloon ripped and its hydrogen mixed with air **exploded**. After a harrowing few moments while Stevens had trouble escaping through the manhole, he and his two fellow aeronauts **parachuted to safety.**

Explorer II (1935)

- Launched on November 11, 1935, from the Stratobowl near Rapid City, South Dakota, Explorer II carried Captain **Albert Stevens**, Captain **Orvil Anderson**, and an assortment of instruments to a world record altitude of **22,066 kilometers** (72,395 feet).

Vertical Ozone Profile



- The vertical ozone profiles deduced from the measurements of solar ultraviolet radiation during the Explorer experiment (A and B) showed a maximum in the ozone concentration near **22 km**, and were different from the profile (R) retrieved by Regener in Germany (maximum at **26 km**).

4. The Theory

The First Photochemical Theory (1929, Paris)

S. Chapman

- **Sydney Chapman** introduces the first scheme that describes the photochemistry of ozone by considering only 5 reactions:

$$O_2 + UV \rightarrow O + O$$
$$O + O + M \rightarrow O_2 + M$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$O_3 + UV \rightarrow O + O_2$$
$$O + O_3 \rightarrow 2\ O_2$$

The view of Charles Fabry in 1945

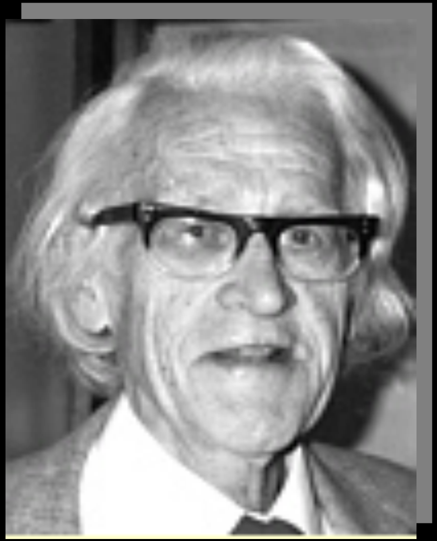
- Il est un peu décevant de constater qu'après 30 ans de recherches, on ne soit pas arrivé à construire une théorie cohérente […] de l'ozone atmosphérique

- On a fait une théorie en admettant que l'ultraviolet solaire est seul en jeu comme agent producteur, avec l'ultraviolet moyen comme agent destructeur, et l'on s'efforce de croire à l'exactitude de cette théorie; mais en fait, on y réussit mal et l'on pousse la théorie jusqu'au bout presque sans croire à son exactitude.

Maurice Paul Auguste Charles Fabry

Ozone and Hydrogen (1950)

Bates



- In 1950, during a **sabbatical at CalTech in Pasadena, Sir David Bates** (Belfast) and Baron **Marcel Nicolet** (Brussels) 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*.**

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O \rightarrow OH + O_2$$

Net: $O + O_3 \rightarrow 2O_2$

Nicolet

Ozone and Nitrogen (1970)

Crutzen

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$O + O_3 \rightarrow 2O_2$$

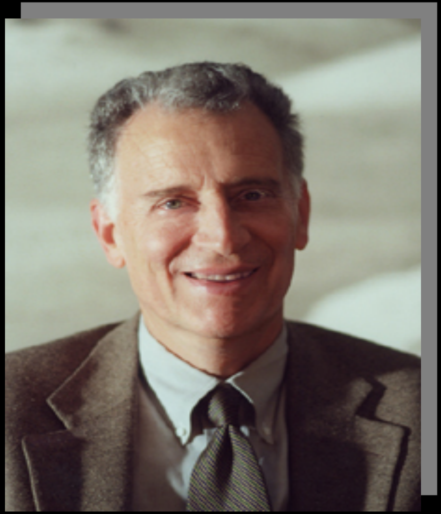
- **Paul Crutzen** shows that the major ozone loss in the stratosphere is provided by a catalytic cycle involving the presence of nitric oxide (NO).
- The solar proton event of 1972 confirms that ozone is depleted by NOx
- Nitric oxide is produced in the stratosphere by oxidation of nitrous oxide (N_2O). This gas is produced by bacteria in soils.

Ozone and Chlorine (1974)

- 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 had been studying for NASA the possible impacts of the **Space Shuttle**. They also identified **volcanoes** as a natural source of atmospheric chlorine

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$O + O_3 \rightarrow 2O_2$$

Stolarski



Cicerone

5. Ozone: A Vulnerable Layer in the Stratosphere

Purposeful Damage to Stratospheric Ozone

- In **1934** S. Chapman proposed making a temporary "***hole in the ozone layer***" for the benefit of astronomers.

- In the **1960**'s. there is a ***military interest*** in ***attacking the ozone layer*** over a rival nation.

The Cold War

540-5-01-A

"MODIFICATION OF THE EARTH'S UPPER ATMOSPHERE BY MISSILES"

10 September 1961

GEOPHYSICS CORPORATION OF AMERICA
Bedford, Massachusetts

1

"The subject of weather and climate control is now becoming respectable to talk about."

"Modification Of The Earth's Upper Atmosphere by Missiles"
Geophysics Corporation of America - 9/10/1961

Bumper V-2 and WAC Corporal, 24 July 1950

Harry Wexler

Father of weather satellites and proponent of climate control

Modification of the Earth's Atmosphere by Missiles

HW 12/61 – 2/62

SUMMARY OF SOME ARTIFICIAL INFLUENCES ON RADIATION BALANCE

Material added	Particle Radius	~~Wt.~~ Required (Millions of Tons)	Geographical Distribution	Region or Ht. of Dispersion	Effect on Radiation or Albedo	Effect on Temperature
Powder	0.2μ (optimum)	~~10~~ 2	Equatorial orbit, 10°N to 10°S	1200 km (belt 60 km thick)	10% decr. in insolation 10°N-10°S or 1.2% pt.-incr. in Earth albedo	World Temperature decrease by 1.2°C
~~Chlorine or~~ Bromine	-	~~50~~ 0.1 ~~200~~ 0.4	65° - 90°N 10°N - 10°S	Ozonosphere	Ozone hole and decreased ultra-violet absorption	Raises tropopause Strat. temp. decreases 10°C at 12 km, 45°C at 20 km, 80°C at 32 km (Spring 35°N)

From James Fleming, Colby College

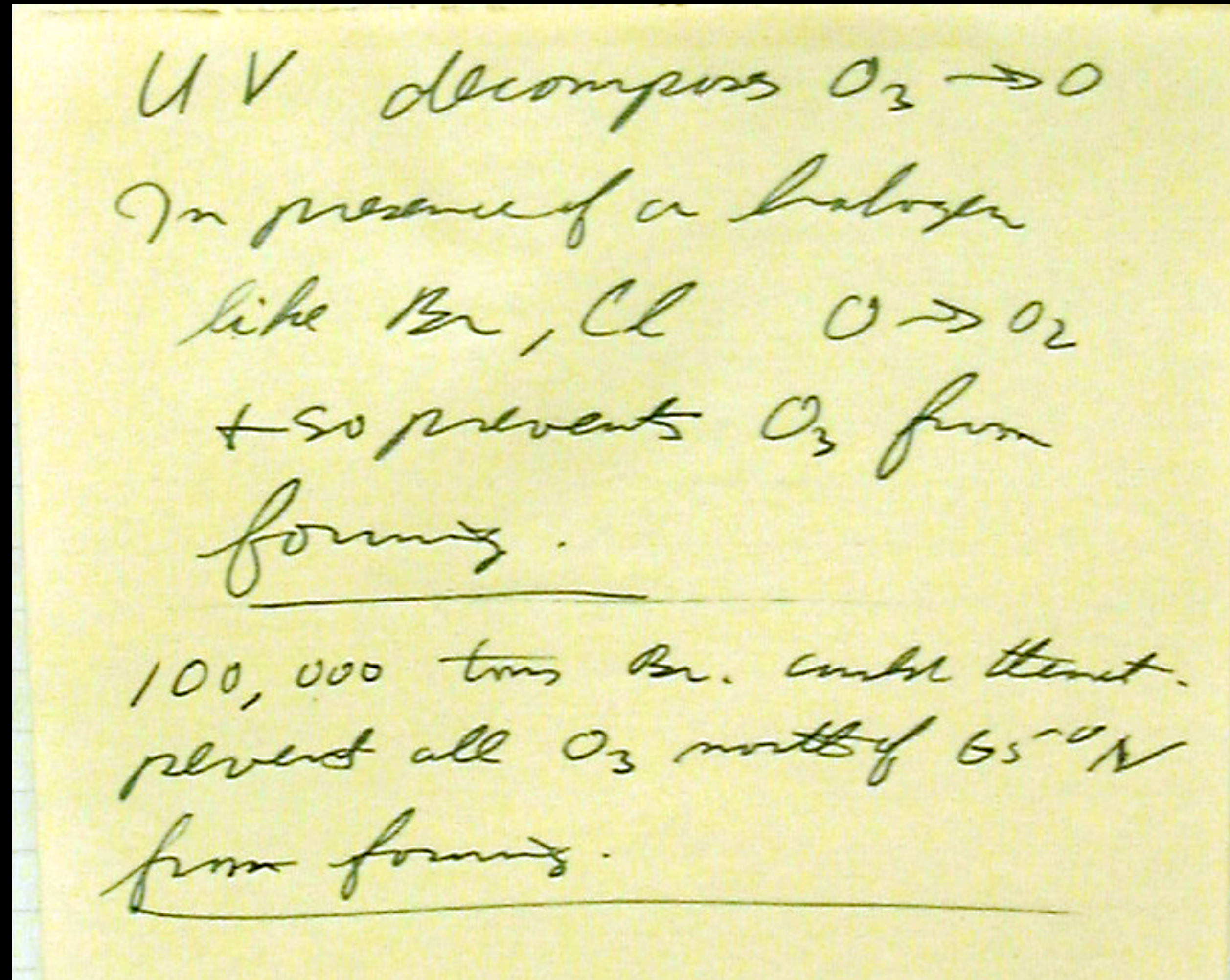
Wulf

On the possibilities of climate control, 1962

Between December 1961 and April 1962, **Wexler** got advises from Calth Professor **Oliver R. Wulf** (1897-1987) on how to cut a "hole" in the ozone layer. The conclusion was that bromine and chlorine might act as a catalyst to destroy ozone.

Meteorologist Wexler 1962:

Prevent all O_3 from forming



UV decomposes $O_3 \rightarrow O$
In presence of a halogen
like Br, Cl $O \rightarrow O_2$
+ so prevents O_3 from
forming.

100,000 tons Br. could thereby
prevent all O_3 north of 65°N
from forming.

James Fleming, Colby College

Ozone Destruction by Supersonic Aircraft

The Impact of Stratospheric Transport (Water vapor emissions)

•Already in **1963**, chemist and meteorologist **Jerry Pressman** suggests that supersonic aircraft may have an effect on the global stratosphere, especially **water vapor** from exhaust.

• In **1970**, **Halsted Harrison** (Boeing's Scientific Research Laboratories) calculates a 3.8% ozone reduction from water vapor injected by a proposed fleet of **500 American SSTs**. Published in *Science* in November 1970

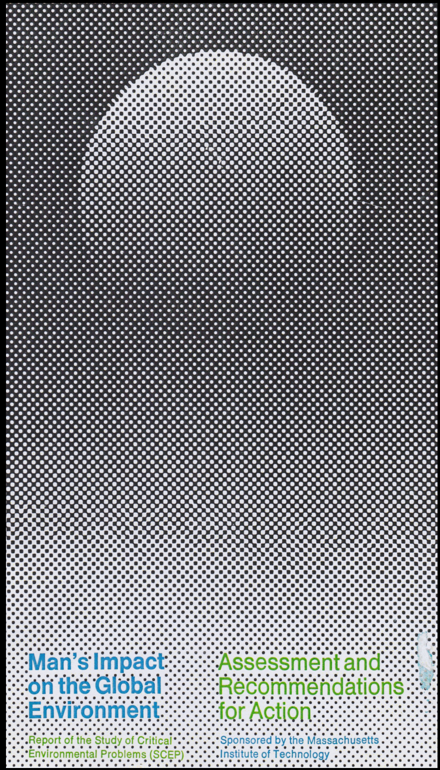
•During the early 1970's there was intense **political debate** in the US whether the SST program should continue.

•In Europe, 16 **Concorde** were operating, and the Russians had developed the **Tupolev 144.**

Concorde

The SCEP Report on Man's Impact on the Global Environment (1970) examines the potential impact of supersonic aviation

- "We have concluded that no problem should arise from the introduction of carbon dioxide and that the reduction of ozone due to the interaction by water vapor or other exhaust gases should be insignificant."
- "Both carbon monoxide and nitrogen oxides can also play a role in stratospheric photochemistry, but these contaminants would be much less significant than the added water, and may be neglected."
- "A feeling of genuine concern has emerged from these conclusions. The projected SSTs can have a clearly measurable effect in a large region of the world and quite possibly on a global scale."



The Tense SST debate

- Environmental opposition to the planned SST became prominent in the late **1960**'s and early **1970**'s. One major issue was the effects on the ozone layer of **water vapor** injected by the aircraft at 20 km altitude.
- **Congressional hearings** were organized in **1971**.
  - **James McDonald** (U. of Arizona), a proponent of the extra-terrestrial hypothesis to explain the presence of **UFO**, told the House Appropriation Committee that 800 SST would cause 10,000 new cases of skin cancers in the United States.
  - **Will Kellogg** (NCAR) stated to the Senate Appropriation Committee that natural climate variations were historically of grater magnitude than any change that might result from SST operations

The Role of James McDonald

- In **1970**, **James McDonald**, who was convinced that the SST could potentially harm the Earth's ozone layer, suffered a public humiliation when testifying in front of a committee of the US Congress.
- During his testimony Congressman **Silvio O' Conte** tried to discredit McDonald's SST testimony by switching the hearing to a discussion of McDonald's UFO research.
- Conte bluntly stated that anyone who "believes in little green men" was, in his opinion, not a credible witness.
- McDonald was deeply humiliated by Conte's mocking attitude, and by the open laughter of some committee members.
- He committed suicide on 13 June **1971** in the Arizona Desert.

James E. McDonald professor of Meteorology University of Arizona, Tucson.

Republican Congressman from Massachusetts Silvio Ottavio Conte

The 18-19 March 1971 Meeting in Boulder

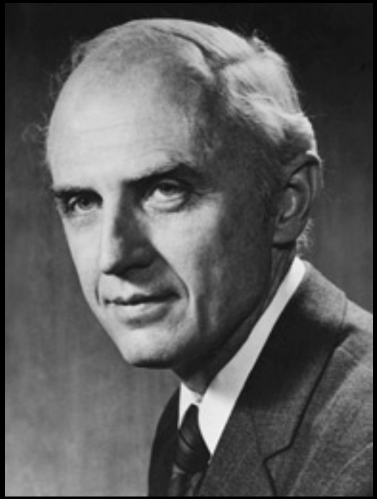
- In September **1970**, the Department of Commerce Technical Advisory Board established a "SST Panel" to address environmental concerns about the operations of a fleet of supersonic aircraft.
- In **1971**,the Panel called a meeting in Boulder that included prominent scientists such as Will Kellogg (NCAR), James McDonald (University of Arizona), Harold Johnston (Berkeley), Julius London (University of Colorado), Fred Kaufmann (Penn State) and representatives from Boeing (e.g., Arnold Goldburg , Chief Scientist at Boeing's SST Division)

Water Vapor or Nitrogen Oxides?

- At the NCAR meeting (18-19 March, 1971), **Julius London** (U. of Colorado) presented model estimates of the impact of a fleet of 500 SSTs: **1.2%** of ozone reduction from SST water and **1.8%** from SST nitrogen oxides (with an increase in the lower stratosphere).
- **Fred Kaufman** (Pennsylvania) insisted that many rate constants used by London were very poorly known.
- **Harold Johnston** (Berkeley) showed in one of the 4 NOx reactions used by London, the rate constant had been overestimated by a factor of 13,000.

- Johnston, H. Atmospheric Ozone, *Annu. Rev. Phys. Chem.* 1992, 43, 1-32

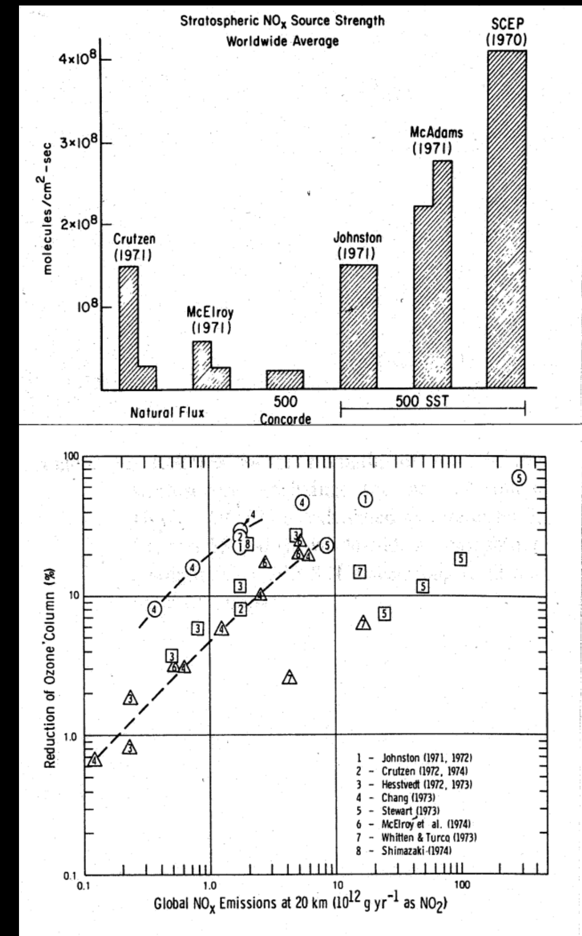
London



Johnston

Assessment of the Impacts of Supersonic Transport (1972-1974)

- The US establishes a 4 year DOT **Climatic Assessment Program** (CIAP) led by **Alan J. Grobecker** to assess the impact of climatic changes resulting from the perturbation of the upper atmosphere by the propulsion effluents of a world high-altitude fleet as projected to 1990.
- France establishes the **COVOS** chaired by **E. Brun** (Académie des Sciences) and the UK establishes **COMESA** chaired by **R. Murgatroyd** (Met Office).



Is Concorde allowed to land in the US? (1976)

U.S. DEPARTMENT OF TRANSPORTATION
FEDERAL AVIATION ADMINISTRATION

DEPARTMENT OF TRANSPORTATION • UNITED STATES OF AMERICA

CONCORDE SUPERSONIC TRANSPORT AIRCRAFT

FINAL
ENVIRONMENTAL IMPACT STATEMENT
VOLUME I

ADDENDUM

FEBRUARY 1976

SOURCE	OZONE REDUCTION	SKIN CANCER INCREASE (cases/year)	COMMENTS
"Normal Rate"	"Normal Level"	250,000 cases	Today's level with no ozone reduction
Present Subsonic Fleet	0.1%	500	DOT/CIAP estimate
Concorde SST			
12 transatlantic ops/day	0.04%	200	EIS:requested action
40 aircraft, 7.5 hrs/day in	0.29%	1500	EIS:worst-case forecast
Formerly proposed U.S. SST (500 aircraft)	15%	75,000	1971 "SST debate"
Present USAF Fleet	0.0033%	17	Assumes FY76-FY80 ops remain constant
Present World Military Ops	0.01%	50	Assume 3 times USAF
"Freons"			
Today's impact	0.5 to 2%	2,500 to 10,000	Builds up very slowly to maximum ozone reduction in 100 years
Continue release at present rate	~8%	~40,000	Effect felt in 100-150 years and persists many decades
60 Space Shuttles/yr	< 0.5%	< 2,500	Estimate being revised by NASA
Fertilizer Use	Possibly very large		Needs much additional study

Note: Figures for "Freons" represent a global average; all others are Northern Hemisphere averages, assuming all releases take place in the Northern Hemisphere and are not dispersed across the Equator.

BEST CURRENT ESTIMATES OF ANTICIPATED OZONE REDUCTION FROM CURRENT HUMAN ACTIVITIES ACCORDING TO CIAP CALCULATION METHODS

TABLE 1

Ozone Destruction by Chlorofluorocarbons

The First Synthesis of CFCs

- The first synthesis of chlorofluorocarbons was performed in 1892 by Belgian chemist **Frédéric Swarts** (Sept. 2, 1866 - Sept. 6, 1940). He prepared $CFCl_3$ (CFC-11) by
$SbF_3Br_2 + CCl_4 \rightarrow CFCl_3 + SbF_2Br_2Cl$

Swarts

The Invention of Chlorofluorocarbons

Midgley

The pioneering work of **Frederic Swarts** prompted American scientists **Thomas J. Midgley Jr.** (1889-1944) and his assistants **Albert L.Henne** (1901-1967) and **Robert R. McNary** (1903-1988) at the Thomas and Hochwalt Laboratory in Dayton, Ohio to develop in **1928** chlorofluorocarbons as referigerants.

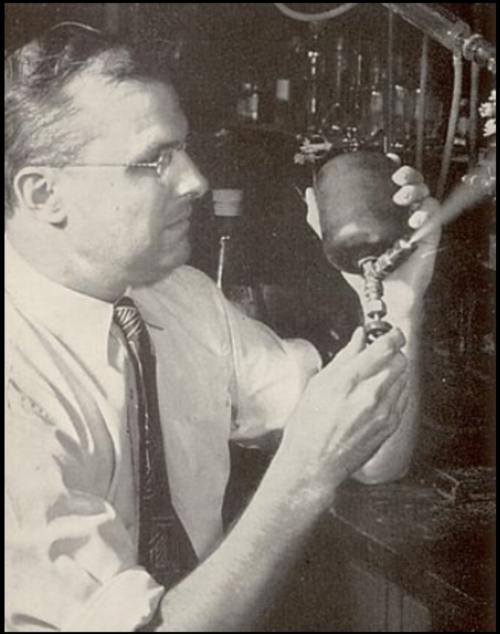
- Midgley demonstrated the **nontoxic** and **nonflammable** properties of the CFCs at a meeting of the American Chemical Society in April **1930** by inhaling CFC-12, then blowing it over a candle flame, extinguishing the flame.
- "*It is demonstrated that even under the worst possible circumstances life is not endangered*."
- Midgley also invented the **leaded gasoline**.

The Invention of Chlorofluorocarbons

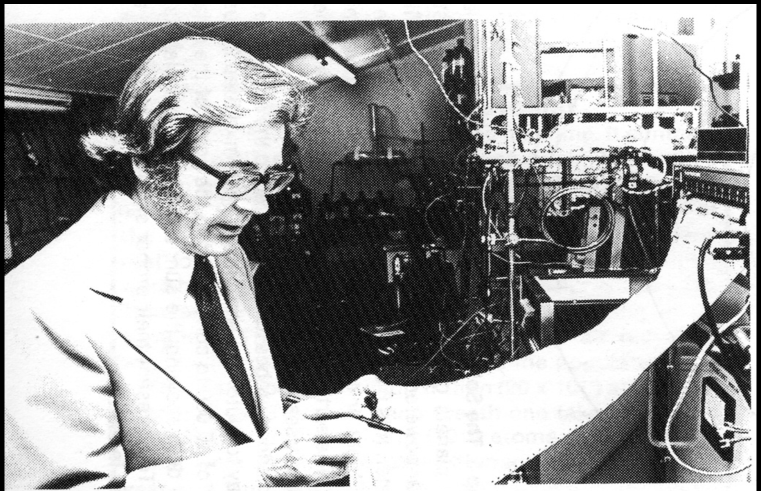
- In **1931**, CFC-12 was produced by the DuPont chemical manufacturer under the trade name of **Freon.**
- The first use of CFC-12 was in small ice cabinets.
- CFC-11 was first produced in 1932 and adopted in **air conditioning** units.
- In **1934**, the Frigidaire Department of General Motors used in its **refrigerators**.
- In **1943**, CFC-11 and -12 were introduced as propellants in **spray cans** by **Goodhue** and **Sullivan** (D. of Agriculture).

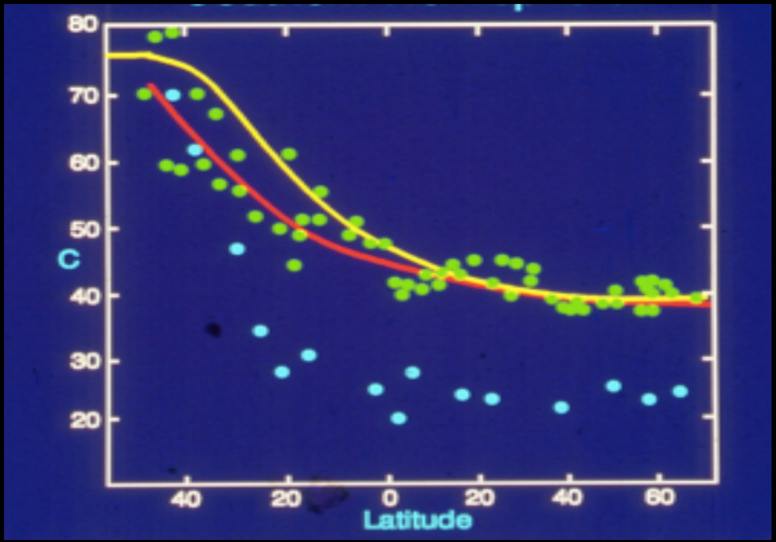
Midgley

Goodhue



In 1971, James Lovelock detects the presence of Chlorofluorocarbons in the Northern and Southern Hemisphere


Lovelock in his laboratory.



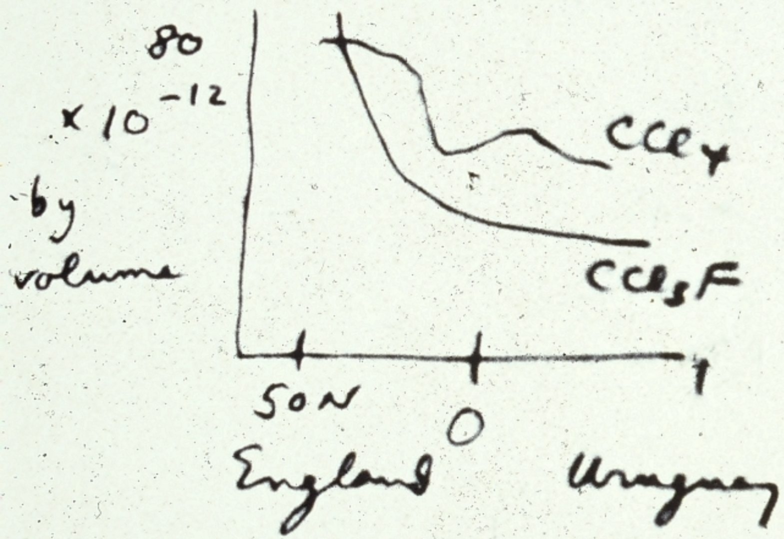
- Distribution of CFC-11 mixing ratio (pptv) in the air over the Atlantic Ocean (Measurements using an electron capture detector during a cruise on the RRS Shackelton in November 1971).

Lovelock's data

Lester Machta reports on Lovelock's measurements

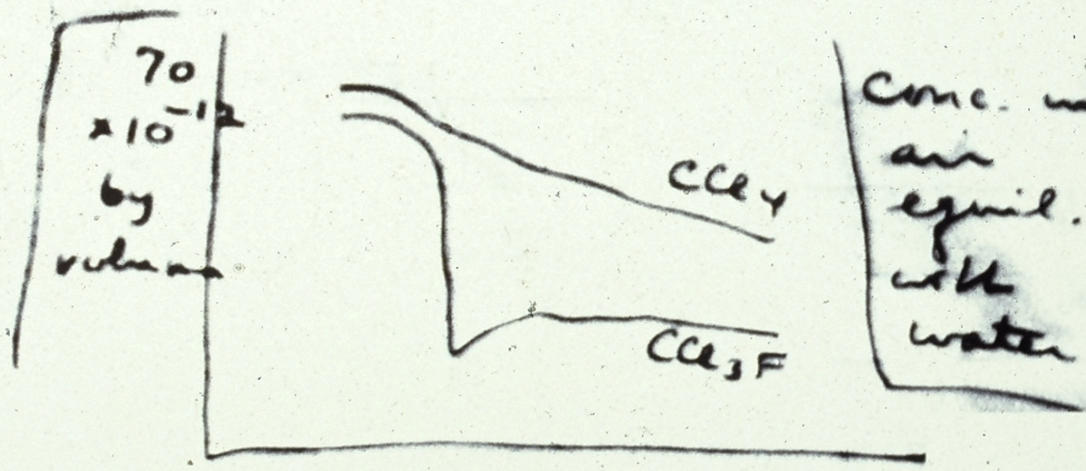
Lecture notes, F. S. Rowland, Fort Lauderdale, Florida, Feb. 1972

CCl_3F – Freon-11 inert gas in spray cans.



Dr. J. Lovelock

CCl_4 – appreciably different



Cruise of R. R. Shackelton
Nov. 1971

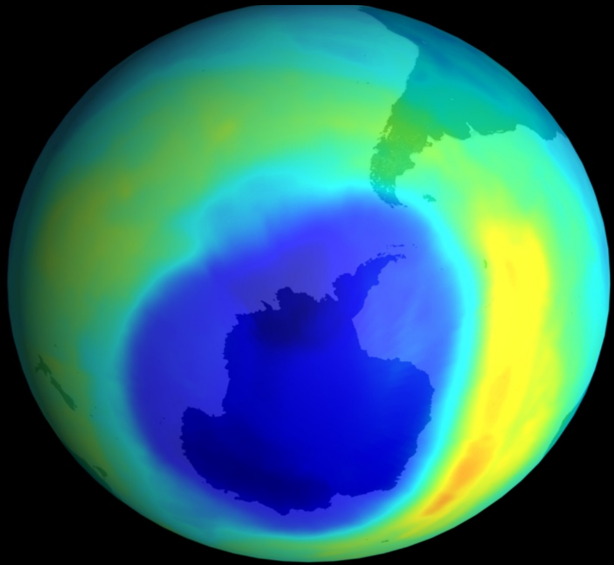
DuPont's estimates
most put out since 1960

Chlorofluorocarbons and Ozone

Mario Molina and F. Sherwood Rowland

- In **1974**, **Mario Molina** and **Sherry Rowland** at the University of California, Irvine, show that industrially manufactured **chloro-fluorocarbons** provide the major source of stratospheric chlorine and therefore are a major threat to the ozone layer.

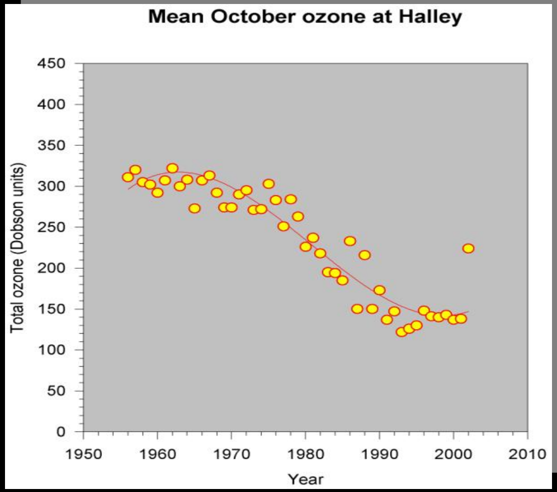
The Ozone Hole



The Ozone Hole: A challenge for the scientific community

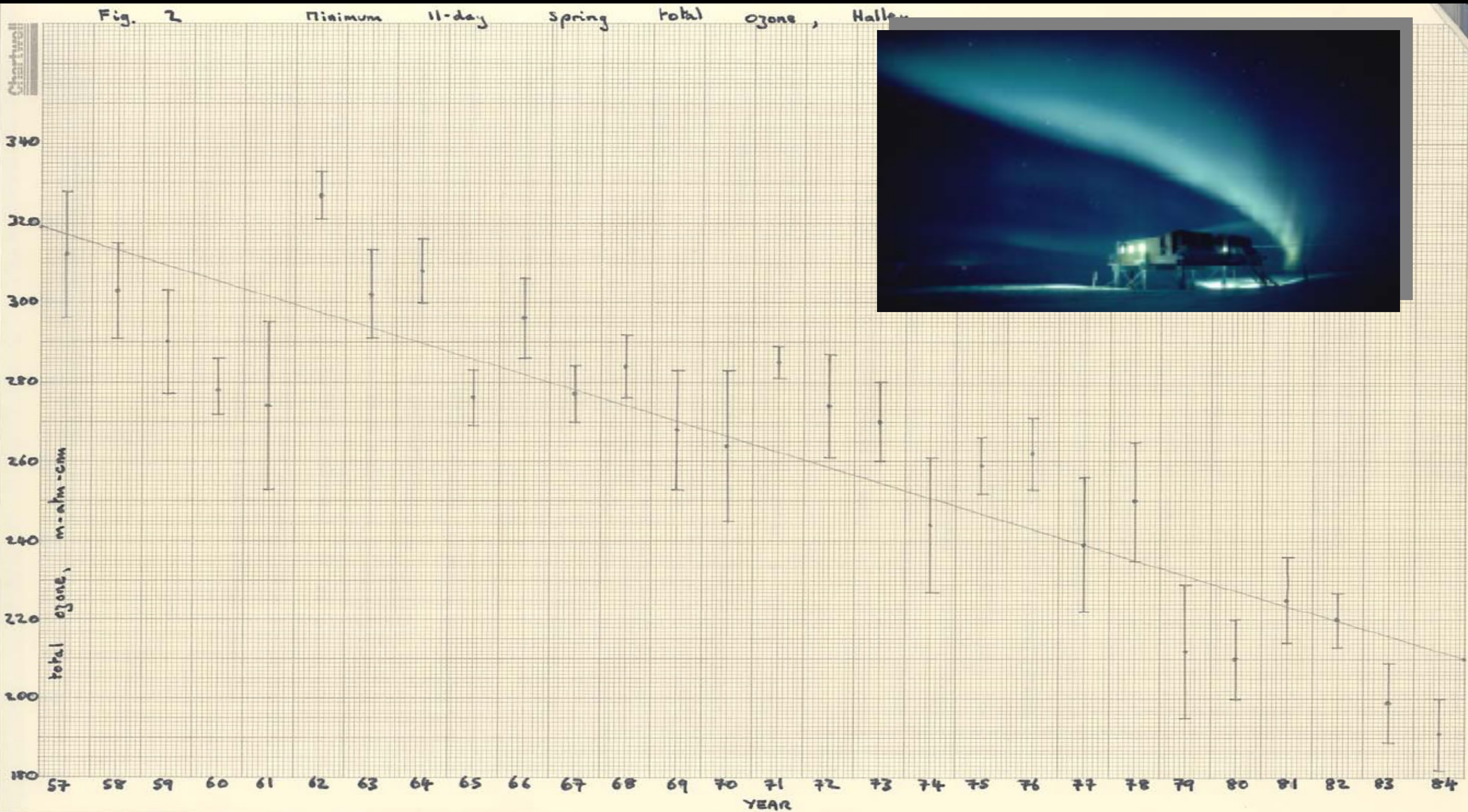
Chubachi

Observations by **Farman** and coworkers at the British Antarctic station of Halley Bay show a dramatic decrease in the ozone column during the 1970's that is ***not simulated*** by atmospheric models. **Chubachi also observed a large ozone decrease** at the Japanese station Syowa.



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

Minimum Ozone at Halley Bay



A letter from the British Antarctic Survey and the response of NASA (1983)

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,

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

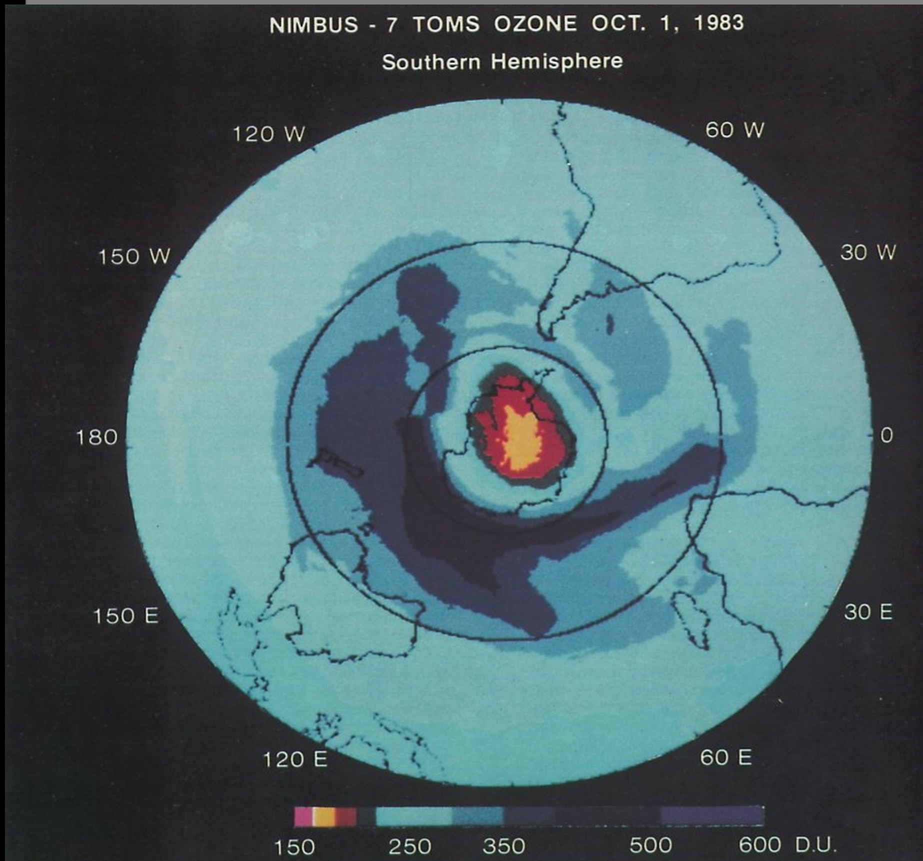
Subject: Request for Ozone Data

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

The First Satellite View of the Ozone Hole (1985)



- Total Ozone observed on October 1, 1983 by Nimbus-7 TOMS

- P. K. Bhartia et al., 1985.

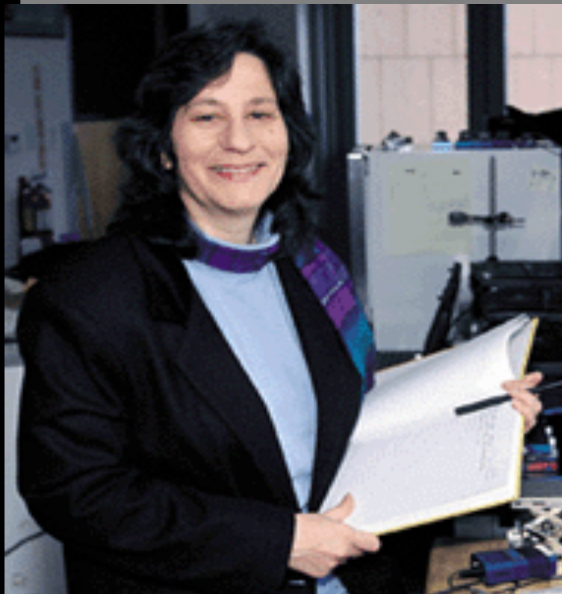
What causes the ozone hole?

Theories

- **Dynamical theory (Tung et al., 86)** vertical lifting of low ozone from lowest stratosphere and troposphere. Invalid N_2O from ER_2 during AAOE show low values associated with O_3 loss.

- **Solar theory (Callis and Natarajan, 86)** production of reactive nitrogen (NO_x). Invalid ER_2NO_x measurements, ozone hole should have disappeared in late 80s.

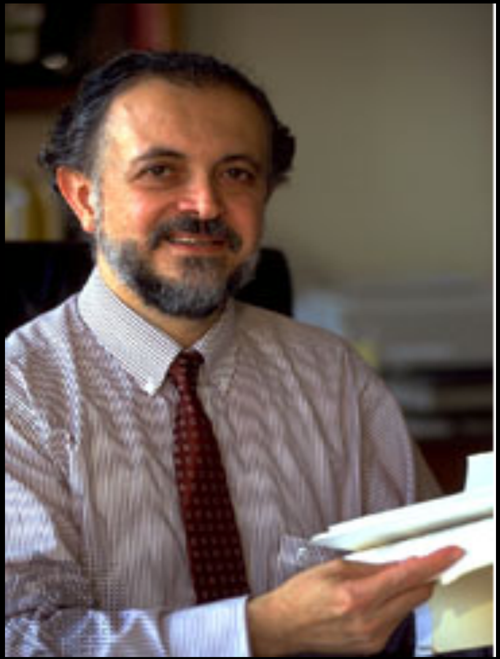
- **Heterogeneous Chemistry (Solomon et al., 86; McElroy et al., 86a; Toon et al., 86; Crutzen and Arnold, 86; McElroy et al., 86b)** heterogeneous chemical processes free Cl from reservoir species via reactions on surfaces of PSCs.



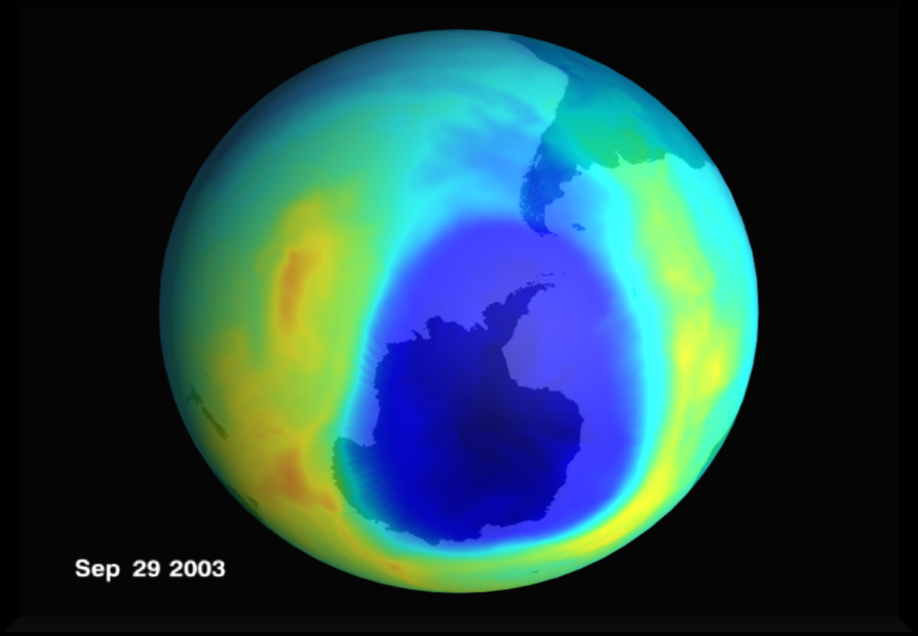
The Explanation

- **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 and **field campaigns** take place in Antarctica. They confirm the role of ***anthropogenic chlorine***.

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



Thank You


Sep 29 2003


30
MONTREAL
PROTOCOL
caring for all life under the sun
Home
19 - 20
September
2017
Fondation
Del Duca
Paris, France