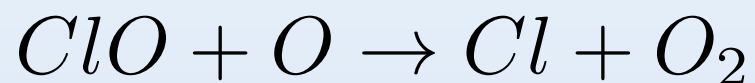
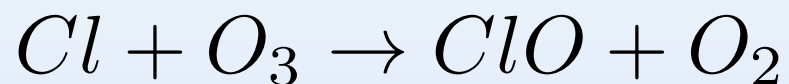


# Atmospheric Chemistry

## Lecture 9

# Stratospheric Chlorine and the Chlorofluorocarbon-Ozone Problem

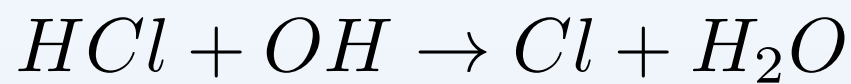
## *Chlorine Catalytic Cycle for Ozone Loss*



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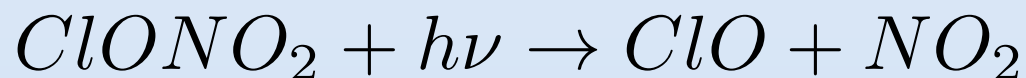
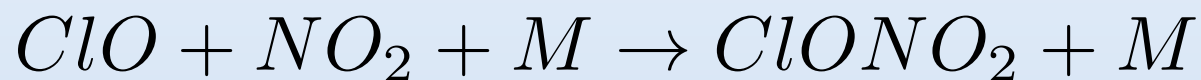
## HCl as a temporary reservoir for catalytically-active chlorine



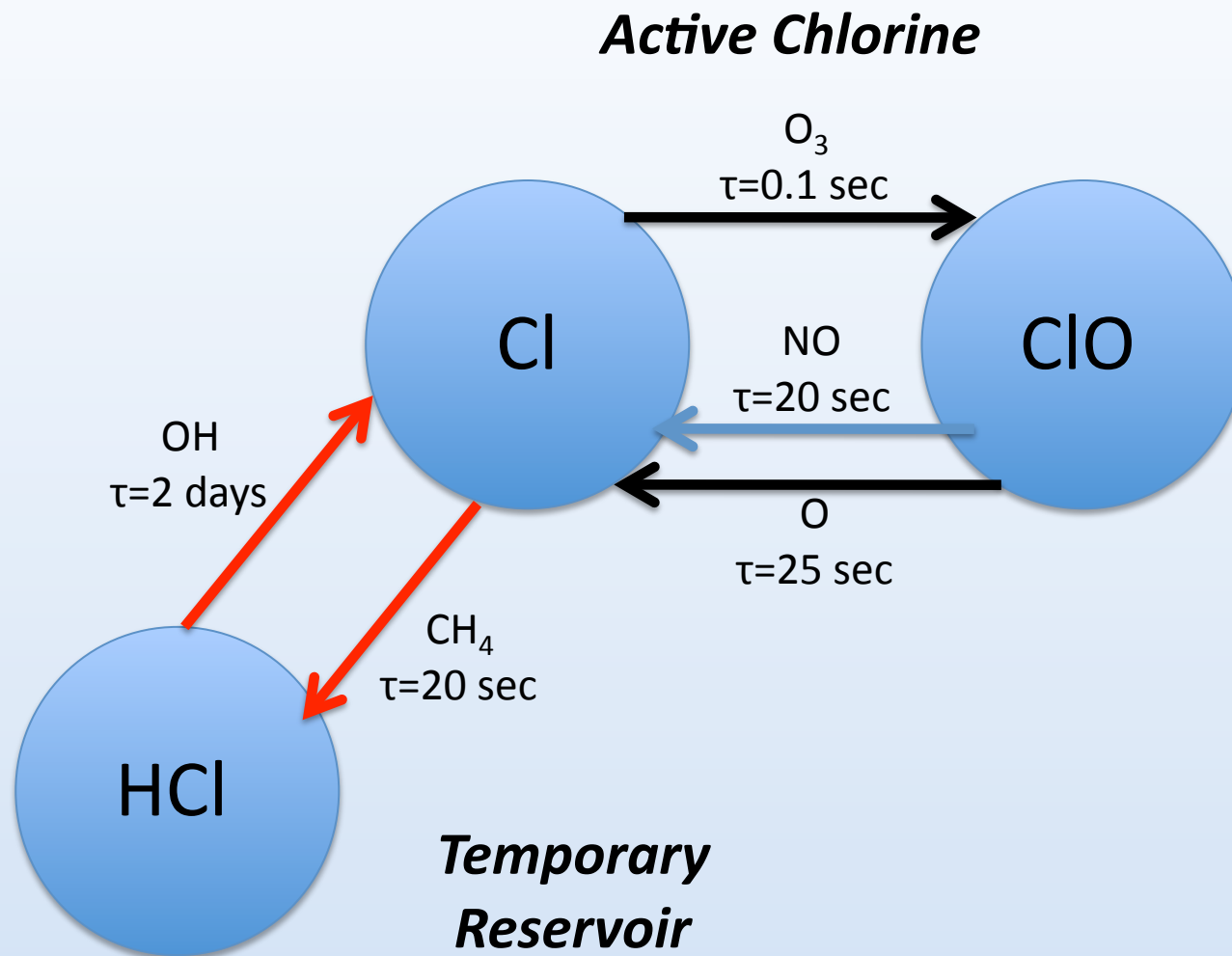
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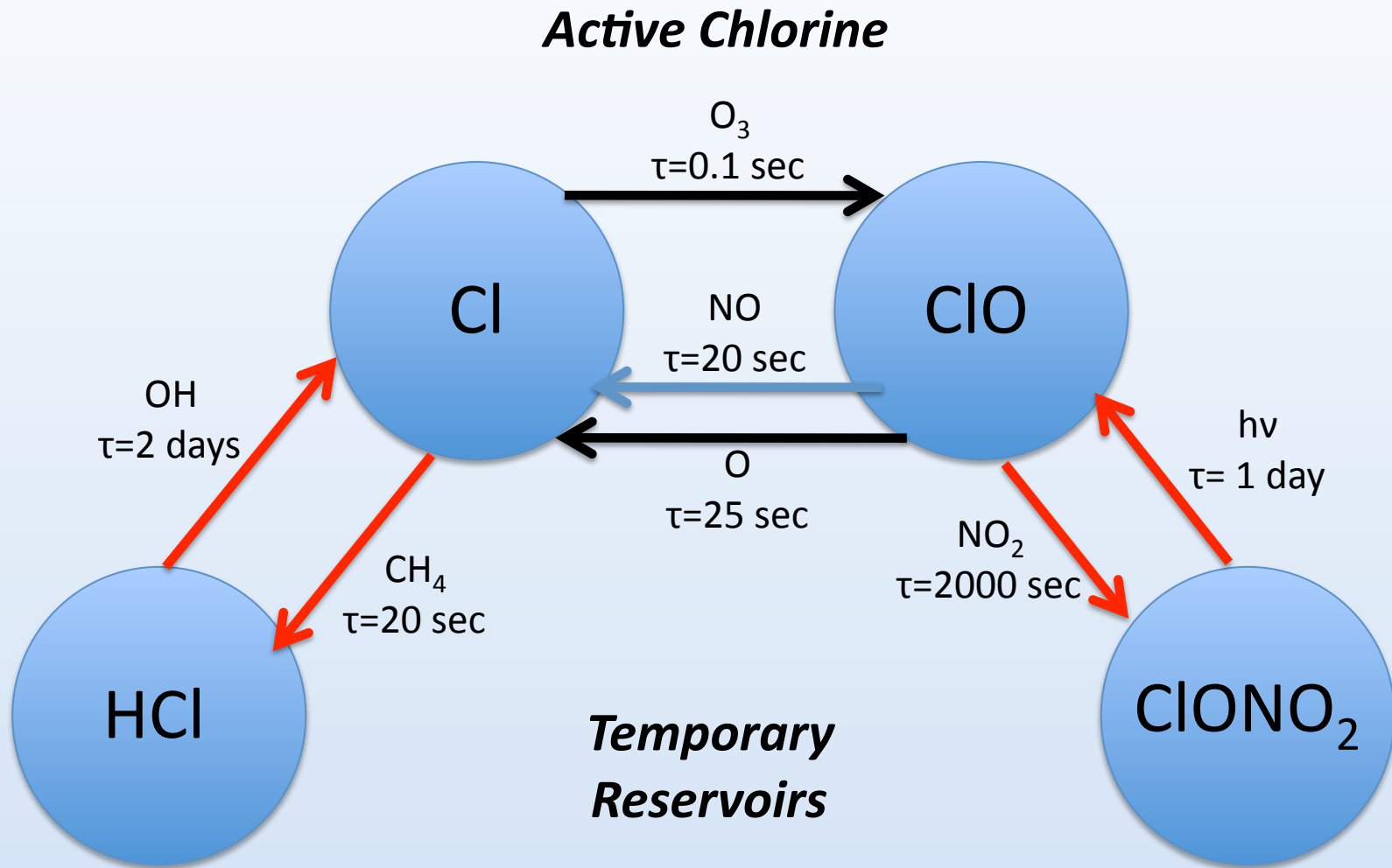
## Chlorine nitrate as a temporary reservoir



# Stratospheric Chlorine Chemistry



# Stratospheric Chlorine Chemistry

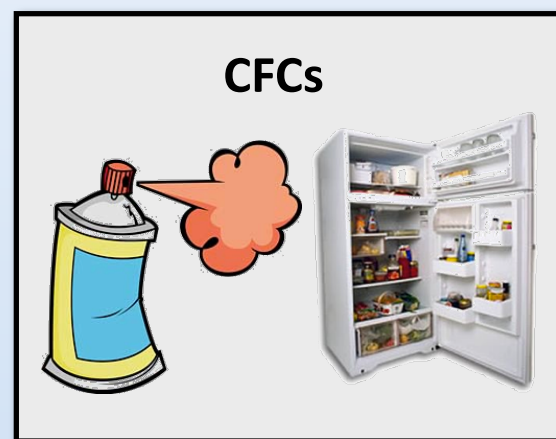
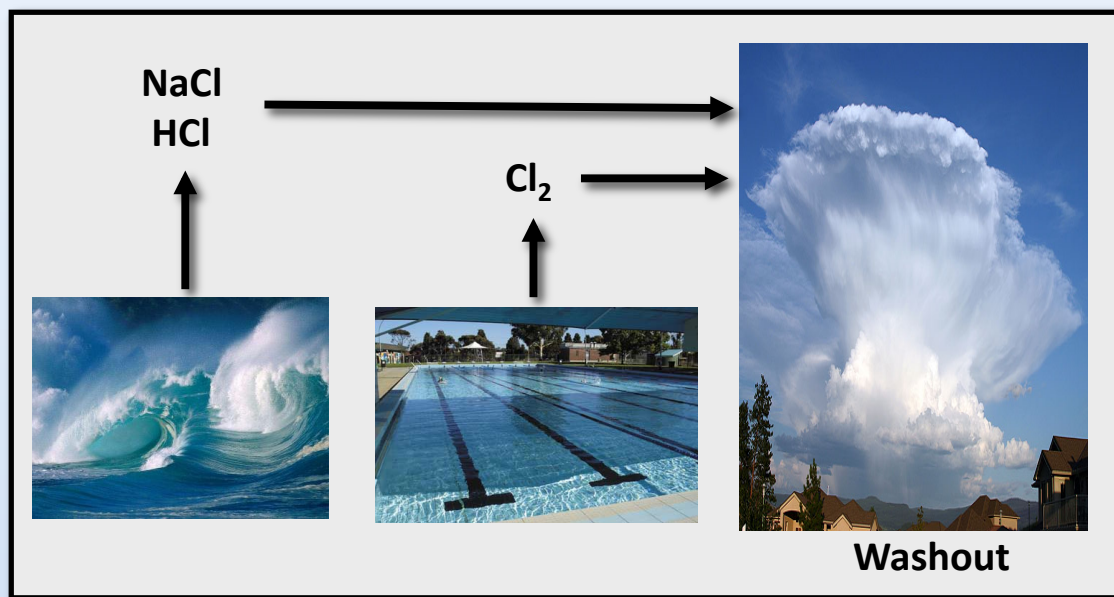


# Sources of Chlorine

STRATOSPHERE



TROPOSPHERE



# Why are CFCs Important?

They are carriers for chlorine to get to the stratosphere

Ozone  
Loss

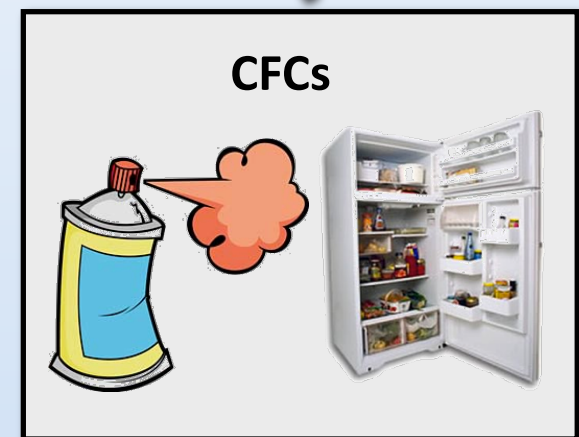
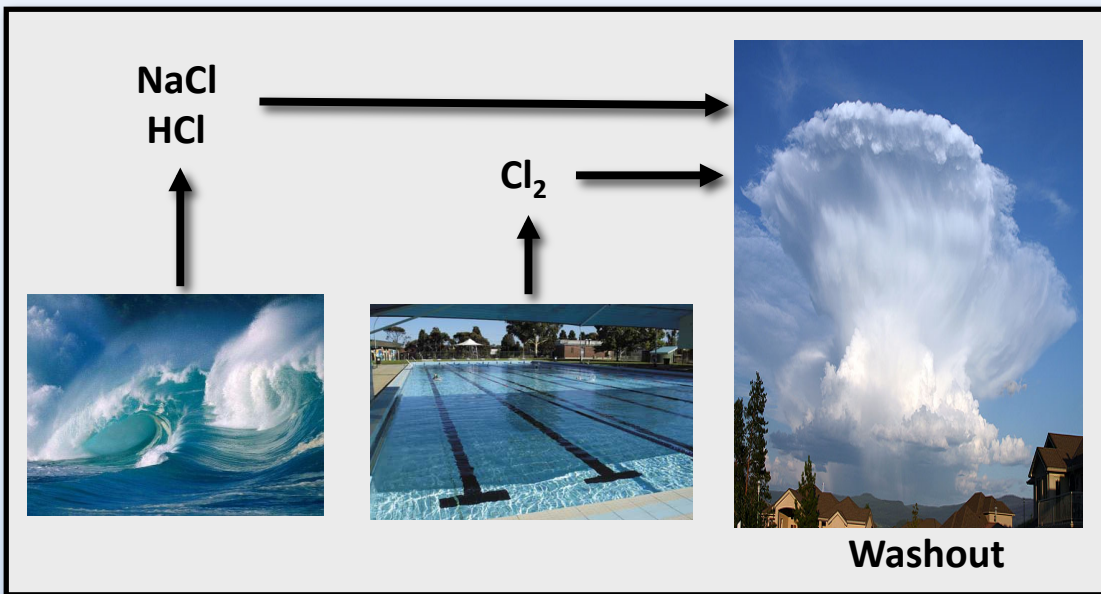
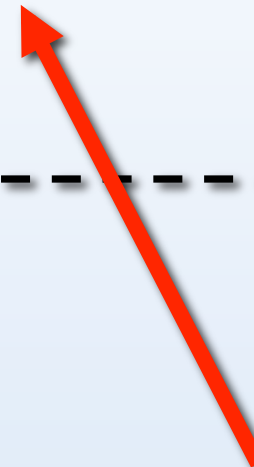


Reactive  
Chlorine

STRATOSPHERE

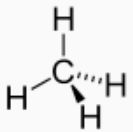




TROPOSPHERE



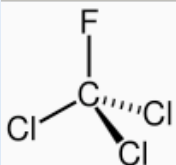
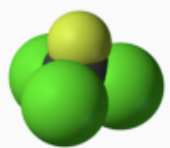
# What are CFCs? (Chlorofluorocarbons)



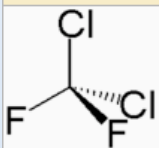
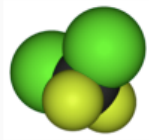
Methane	
	
	
Other names	Marsh gas, <a href="#">firedamp</a>

Simplest CFCs are just methane (CH<sub>4</sub>) with hydrogen replaced by halogen (chlorine or fluorine): e.g. CFC-11 (CFCl<sub>3</sub>) or CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>)

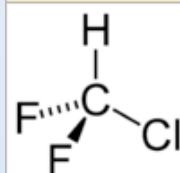
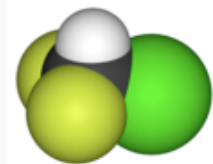


Trichlorofluoromethane	
	
IUPAC name	Trichlorofluoromethane
Other names	Trichloro(fluoro)methane, Fluorotrichloromethane, Fluorochloroform, Freon 11, CFC 11, R 11, Arcton 9, Freon 11A, Freon 11B, Freon HE, Freon MF



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



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



# Fluorine is a small atom and can replace a hydrogen with little change in the shape of a complex molecule

- Carbon-fluorine bonds seldom occur in nature.
- Replacing hydrogen with fluorine can significantly change chemical properties of a molecule.

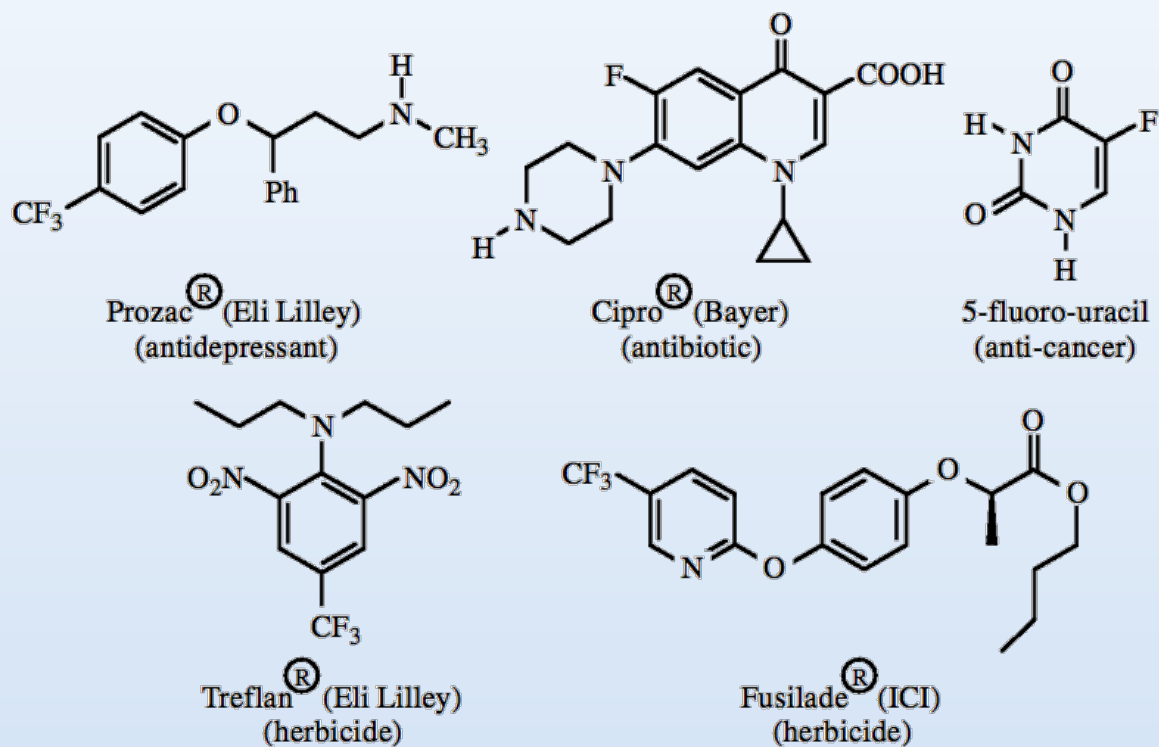
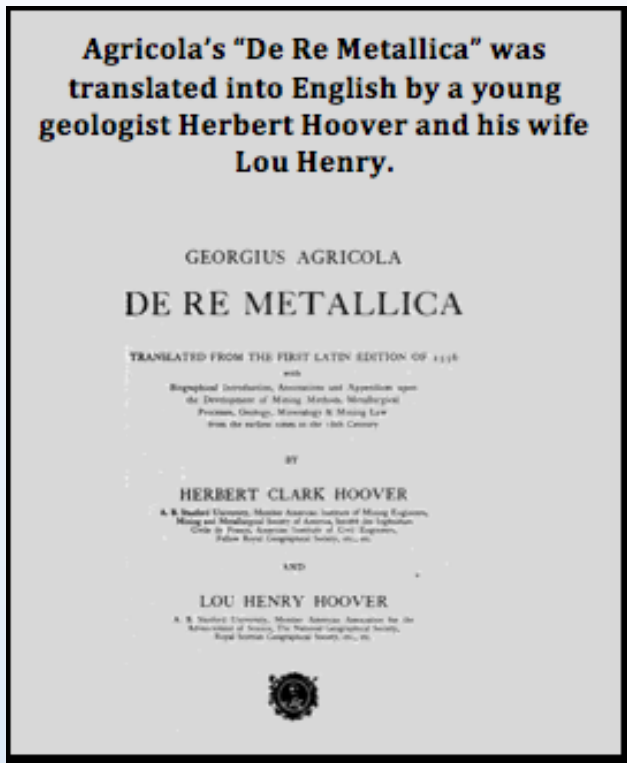


Figure 11. Pharmaceuticals and agrochemicals that have fluorine atoms in their structure.

# Georgius Agricola (Georg Bauer)



Fluorite



Wrote the first comprehensive book on mining and ores "De Re Metallica" (published posthumously in 1556). Described the natural mineral fluorite (fluorspar or calcium fluoride,  $\text{CaF}_2$ ).

# Fluorspar or Fluorite ( $\text{CaF}_2$ )

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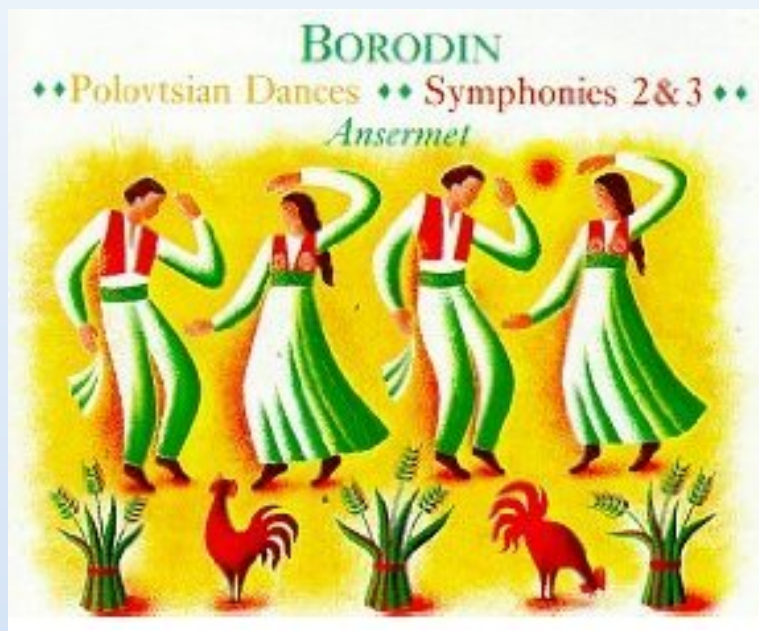
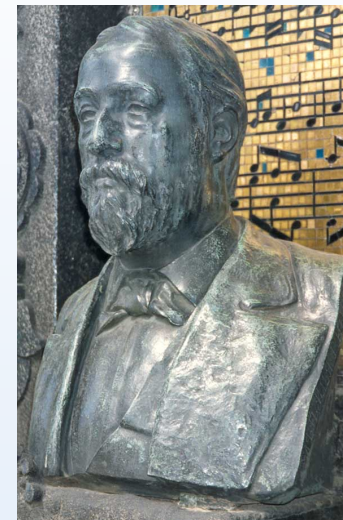
- **Used as a feedstock in metallurgical and chemical industries**
  - > 50% for HF production
  - 24% for iron and steel making
  - 17% for aluminum processing ( $\text{AlF}_3$ )
- **Global Consumption**
  - 5 Million tons/year
  - 60% comes from China
  - China has recently become net importer



# Aleksandr Borodin (1833-1887)

**Chemist and Composer**

**First to substitute fluorine  
in a hydrocarbon**



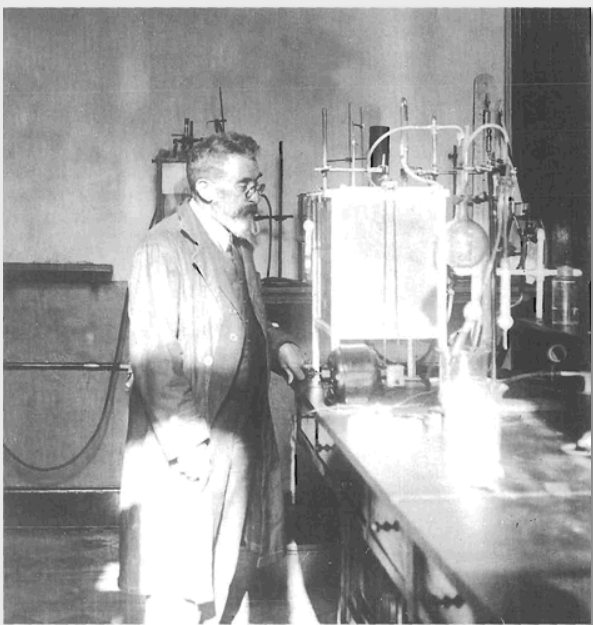
**Могучая кучка**

**Moguchaya Kuchka, "The Mighty Handful"**



**M. Balakirev, N. Rimsky-Korsakov, C. Cui,  
Modest Mussorgsky, Aleksandr Borodin**

# 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 !**



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

## Article

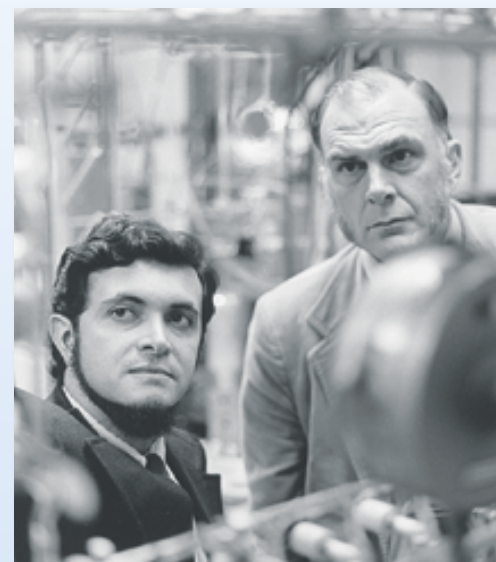
*Nature* **249**, 810-812 (28 June 1974) | doi:10.1038/249810a0

## Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone

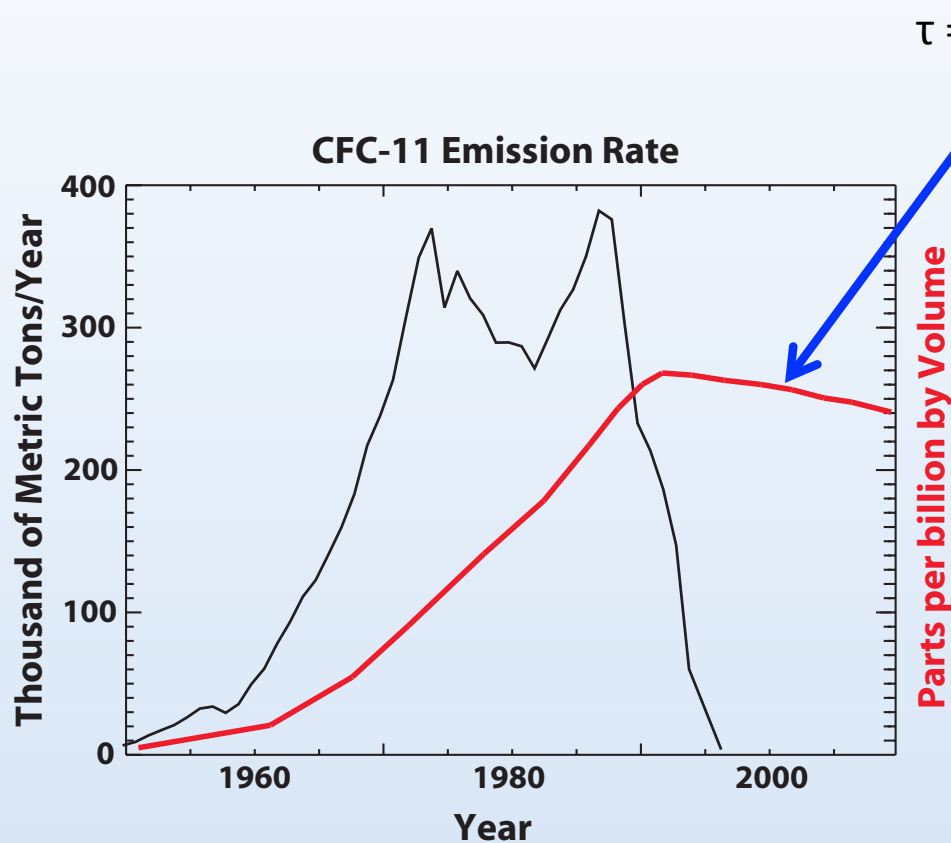
Mario J. Molina & F. S. Rowland

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.**



# Example: CFC11 = $\text{CFCl}_3$



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



# The Atmosphere as a Simple Box Model

