Atmospheric Chemistry

- *Formation of the Atmosphere*
- *The Early Atmosphere*
- *Origin of Life and Oxygen*
- *Ozone*

Formation of the Earth

Apollo Space Program (1960's)

Otto Schmidt

Cosmic Dust → Planet (100 million years)

Ball 10 km → 12,000 km

Heat Generated during the Process

(Collisions)

Thermal Consequences

Earth's Core

Molten Fe (Density 7.86 g/cc)

Ni (Density 8.9 g/cc)

Outer Shell

Fe_2O_3 / FeO (Density 5.2/5.7 g/cc)

Si/SiO_2 (Density 2.33/2.32 g/cc)

Al/Al_2O_3 (Density 2.7/3.5 g/cc)

Formation of the Mantle

The less dense material will go toward the surface (Polar Oxides of Si, Al, Fe)

Separation will occur as Fe/Ni core is nonpolar

starts to form and cool

(Production of Iron from Iron Ore)

Isotope Distribution of the Earth

Investigation of the History of the Earth primarily relied on isotope analysis.

Decay of $^{238}U \longrightarrow {}^{206}Pb$

Decay of $^{235}U \longrightarrow {}^{207}Pb$

And the rare gases He, Ar, Xe

≈ 4.5 Billion years Old

Appearance of the Atmosphere

Did the atmosphere suddenly appear ?

Isotope Analysis gives a clue

Claude Allegre He, Ar & Xe

(Rare Gases do not react readily)

Argon has three isotopes

(^{36}Ar 0.337) (^{38}Ar 0.063) (^{40}Ar 99.60)

EC Decay $^{40}K \rightarrow {}^{40}Ar$

($t_{1/2} = 1.28 \times 10^9 y$)

Isotopes of Xe

Xenon has 9 isotopes

With the following distribution

^{124}Xe 0.1% , ^{126}Xe 0.09%, ^{128}Xe 1.91%
^{129}Xe 26.4%, ^{130}Xe 4.1%, ^{131}Xe 21.2%
^{132}Xe 26.9%, ^{134}Xe 10.4%, ^{136}Xe 8.9%

Distribution of Xe isotopes

Nucleosynthesis gives rise to ^{129}Xe

β^- Decay of $^{129}I \rightarrow {}^{129}Xe$

$(t_{1/2} = 1.6 \times 10^7 y)$

The distribution of Xe isotopes in the mantle and atmosphere can give information about the Earth's Atmosphere as the outgassed distribution will vary to that of the mantle.

Differentiation

The Atmosphere was formed due to
OUT GASSING of the mantle (Heat)
& Volcanic Activity

The Mantle does not contain any
^{40}K or ^{129}I

$\therefore$ All ^{129}Xe in mantle came from ^{129}I

Age of differentiation

From the ratio of ^{129}Xe in the Mantle to that of ^{129}Xe in the Atmosphere it possible to gain some idea of the age of differentiation as the Xe due to Nucleosynthesis would have been OUTGASSED into the atmosphere.

Ratios of Isotopes

The Argon trapped in Mantle evolved from the radioactive decay of ^{40}K

The Xenon trapped in Mantle evolved from the radioactive decay of ^{129}I

The ratio of the amount in the mantle to the atmosphere can give information about the process of differentiation..

Conclusions from Isotope Analysis

∴ If outgassing occurred at the beginning the atmosphere would not contain ^{40}Ar

But would contain ^{129}Xe

Results and Calculations indicate

80% to 85% of the Earth's Atmosphere was outgassed in the first million years

Collecting the evidence

The other 15% has arisen due to slow release over 4.4 billion years

Difficult Analytical Problem requiring

- Concentration of the samples
- Specific Choice of Sampling Sites

Early Atmosphere

Majors: CO_2, N_2, H_2O (Water Vapour)

Traces: CH_4, NH_3, SO_2, HCl

Water Vapour → Oceans

FeO/Fe_2O_3 (Grand Canyon) indicates O_2 emerged in the atmosphere about 2 billion years ago`

Origin of Life

Stanley Miller (1950) " Early Earth "

Experimental Setup

CH_4, NH_3, H_2, $H_2O_{(g)}$ (Atmosphere)

$H_2O_{(l)}$ (Oceans)

Electrode discharge (Simulate Lightning)

Analysis of Fractions

Formation of Simple Amino Acids

Glycine was found

How Glycine (NH_2CH_2COOH) Formed

$$HCOH + NH_3 + HCN \rightarrow NH_2CH_2CN + H_2O$$

Formaldehyde Cyanide Hydrogen

Aminonitrile

$$NH_2CH_2CN + 2\,H_2O \rightarrow NH_2CH_2COOH + NH_3$$

Murchison Meteor

A number of the compounds discovered in the discharge fractions are precursors to life.

Years later a meteor struck at Murchison (Victoria) was also analyzed and its contents found to be similar to those of the discharge experiment of Stanley Miller

Early Energy System

The first living organisms gained their energy by a fermentation of the organic soup

$$C_6H_{12}O_6 \rightarrow \text{Alcohol} + CO_2 + \text{Energy}$$

However there was only a limited amount of organic nutrients in the primeval soup and to sustain life. (First Famine).

A new efficient Energy Source was required.

Role of Blue Green Algae

Blue Green Algae & Photosynthetic Bacteria developed to use water as a hydrogen donor and produced dioxygen as a by product.

Photosynthesis

$$nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2$$

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Decline of Anaerobic Bacteria

Problem for Anaerobic Organisms

Evidence of the appearance of Oxygen is indicated in the (Red Layers) of the Grand Canyon. $\mathbf{O_2}$ is believed to have entered the atmosphere about **1.8 Billion years ago**

Fe^{2+} and oxygen reactions may have delayed entry of oxygen into the atmosphere.

Oxygen Rich Planet

Oxygen Rich Planet

The build up of Oxygen in the atmosphere led to the formation of the

Ozone Layer at 15 to 60 km above the earth.

absorbs harmful UV light and this allowed organisms to colonize the Water/Land/ Atmosphere interface.

Oxygen Rich Planet

Respiration utilized the photosynthetic Compounds (Sugar) to produce Energy

$$(CH_2O)n + nO_2 \rightarrow nCO_2 + H_2O + E$$

This process was 18 times more efficient than the fermentation process .

But oxygen can damage cellular material

The trouble with oxygen

The ultilization of oxygen in producing energy resulted in emergence Eukarotic cells which contained a nucleus which protected cellular material prone to oxidation.

(DNA)

The present atmosphere

The present atmosphere has arisen from

- The distance of the earth from the sun
- Nature of the earth's composition
- The rise of life.

Distance from the Sun

The distance from the Sun determines the kinetic energy (KE) of the molecules in the atmosphere due to the Sun's heat and the molecule's velocity.

$$KE = 1/2\, mv^2 \ \& \ KE = 3/2kT$$

Where m is the mass of the molecule (M_r / N_A)

k is the Boltzmann constant (R/N_A)

(Earth ≈ !50 x 10^6km)

Transit of Venus

Capt Cook to within 2% of the value 1788

Influence of Earth's Mass

The ability of molecules to remain in the atmosphere is also related to the mass of the earth.

The escape Velocity $V_e = (2Gm/R)^{1/2}$

m = Mass, G=Universal Gravitational Constant, R = Radius

Escape Velocity

Escape Velocity (V_e)

$$V_e = (2Gm/R)^{1/2}$$

m = Mass of the Planet

G= Universal Gravitational Constant,

R = Radius of the Planet

Escape Velocities in km/s

Earth = 11.2 Venus = 10.3 Mars = 5.0

Escape Velocity

The ability of molecules to remain in an atmosphere is related to the mass.

	Density	Diameter	Distance from Sun
Mars	3.94g/ml	6794km	227.9 Mkm
Earth	5.52g/ml	12756km	149.6 Mkm

The Molecule's Escape Velocity and nature of the molecules determines the composition of the atmosphere.

No H or He in Earth's Atmosphere

At 600 K (Upper Atmosphere)

For H atoms 1 in 10^6 exceeds the escape velocity. This is High enough for rapid depletion of H from the atmosphere

As a result all the Hydrogen on earth is present in a bound state.

(Water, Organic material)

Little CO_2 in atmosphere

For Oxygen only 1 in 10^{84} atoms exceeds the escape velocity .This indicates negligible depletion of Oxygen.

Presence of Life on Earth has removed Carbon dioxide from the Atmosphere and given rise to oxygen. Shellfish/Coral.

(Calcium Carbonate and Plant Material)

Earth ,Venus & Mars

Surface Characteristics of Planets

	Temperature	Pressure (bar)*
Venus	732 K (459°C)	90
Earth	288 K (15°C)	1 (101325Pa)
Mars	223 K (-55°C)	0.006

*1 bar = 100,000Pa
= 10m in depth of the Ocean

Distribution of Gases on Earth Venus & Mars

Composition of Planet's Atmospheres in %

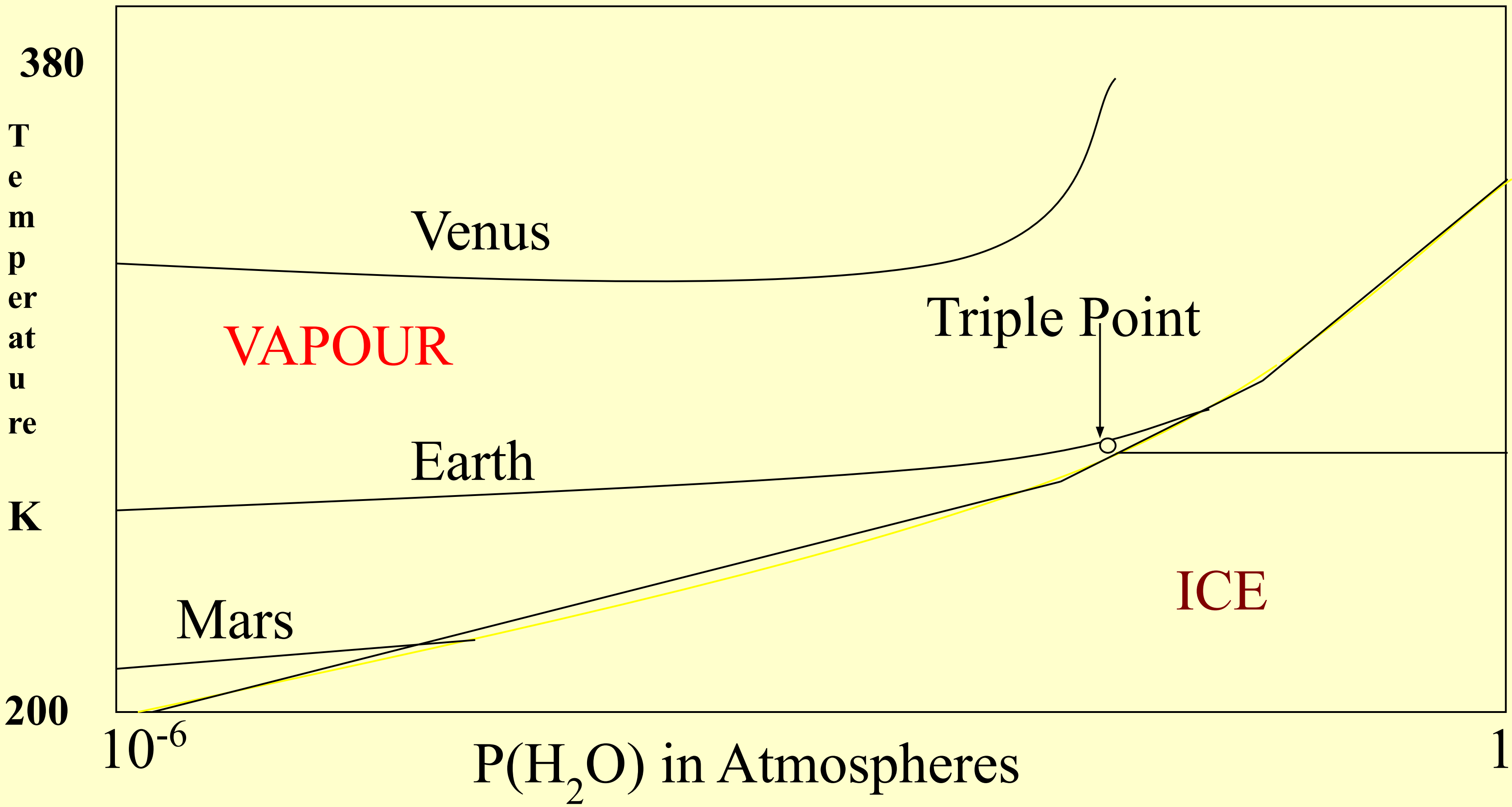
	CO_2	N_2	O_2	SO_2	H_2O
Venus	96.5	3.5		0.015	
Earth	0.03	78.1	20.9		(varies)
Mars	95.3	2.7	< 0.1		0.03

Role of Shellfish

Presence of Life on Earth has removed Carbon dioxide from the Atmosphere and given rise to oxygen.

Shellfish/Coral. in the Sea,Air,Land Interface has immobilized Carbon dioxide as Calcium Carbonate while Photosynthesis has given rise to oxygen and Plant Material

Triple point of H_2O



Water (Solid,Liquid, Gas)

The Surface temperature of the Earth at 1 atmosphere Pressure is close to the Triple Point for water. Water is the only compound that can exits in the environment as a Solid, Liquid and Gas simultaneously.

The thermodynamic properties of Water have been essential in determining our present climate and support of life.

Super Greenhouse & Acid Rain

On Venus ,the high level of CO_2 and its distance from the Sun have lead to a super greenhouse effect and Sulphuric Acid Rain. Where the surface pressure in 90 times that of Earth's (≈ 900 m in the Ocean)

and surface temperature is about 460°C

(Melting point of Zn = 419°C)

Current Atmosphere

Composition of Current Atmosphere %Vol

	N_2,	O_2,	Ar,	CO_2,	H_2O
	78.08	20.95	0.93	0.03	(Variable)
ppm	Ne	He	K	CH_4	
	18	5.2	1.1	1.25	

Early Atmosphere Rich in CO_2, CH_4

Present Level of Oxygen

The present level of Oxygen in the atmosphere is balanced at a such a level that less would impede survival of a number of organisms while more would lead to a greater probability of fires.

At 25 % oxygen damp twigs and grass of a rain forest would ignite.

Structure of Atmosphere

Earth's Atmosphere

Altitude	Temperature	REGION	Species
500 km	(1200ºC)	Thermosphere	O_2^+, O^+, NO^+
85 km	(-92ºC)	Mesosphere	O_2^+, NO^+
50 km	(-2ºC)	Stratosphere	O_3
10-16 km	(-56ºC)	Troposphere	N_2,O_2,CO_2,H_2O
	15ºC	Earth's Surface	

Ozone Layer

Ozone in the Stratosphere

≈ 16 - 50km above the Earth's Surface

acts as a blanket preventing harmful radiation that can marked affect living material from reaching the surface of the Earth.

Ozone and Radiation

Oxygen that lies above the stratosphere filters out UV light 120nm - 220nm

Ozone O_3. In the Stratosphere filters out UV light 220nm - 320nm

Regions UV C 200nm - 280nm

UV B 280nm - 320nm

UV A 320nm - 400nm (less harm)

Effects of Reduction in Ozone

(Effects of Reduction)

1% Reduction In O_3 → 2% increase in UV-B

Skin sunburns, tans, Skin cancer

Absorbed by DNA → DNA damage

Possible eye cataracts

Interferes with photosynthesis

Organisms in 1st 5metre of the Oceans at risk

(phytoplankton in particular)

Chlorofluorocarbons & Ozone

Destruction of the Ozone Layer discovered in 1970's by CFC's (Chlorofluorocarbons)

First synthesized Swartz (1892)

Used as refrigerants 1928 (Midgely & Henne)

$$CCl_4 + xHF \longrightarrow CCl_{(4-x)}F_x + HCl$$

(Aerosol Propellants & Air conditioners)

Ozone Protection

Protection

$$O_2 + h\nu \rightarrow 2O^{\bullet}$$

$$O^{\bullet} + O_2 \rightarrow O_3$$

$$O_3 + h\nu \qquad O^{\bullet} + O_2$$

(UV-B)

Ozone Destruction

Destruction $CFCl_3 \xrightarrow[\text{(UV-C, UV-B)}]{} Cl^{\bullet}$ Chlorine Radical

$$Cl^{\bullet} + O_3 \rightarrow O_2 + ClO^{\bullet}$$

$$ClO^{\bullet} + O^{\bullet} \rightarrow Cl^{\bullet} + O_2$$

$ClO^{\bullet} + ClO^{\bullet}$ $\rightarrow$ ClOOCl (relatively stable)

Control of CFC's

CFC's are now under strict control and their use has been curtailed.

Australia signed the international treaty.

"The Montreal Protocol" in June 1988 which has a program controlling the use and reduction of CFC's.

Uses of CFC's

Compound		Use
CFC- 11	$CFCl_3$	Refrigeration, aerosol, foam
CFC-12	CF_2Cl_2	sterilization, cosmetics food freezing, pressurized blowers.
CFC-113	CCl_3CF_3	solvent, cosmetics
Halon 1301	$CBrF_3$	fire fighting (discontinued)

Lifetime of CFC's

Compound	Ozone Depleting Potential	Lifetime(yrs)
CFC- 11	1.0	65 -75
CFC-12	1.0	100 - 140
CFC-113	0.8	100 - 134
CFC-115	0.6	500
CCl4	1.2	50 - 69
Halon 1301	10	110

Naming of CFC's

(90 Rule)

CFC's name is related to its Formula.

CFC 123 $\quad$ 123 + 90 = 213

The remaining bonds are allocated to Cl or Br

C $\quad$ H $\quad$ F

C = 2 , H =1 , F = 3 , Cl = (8 - 6) = 2

CFC 123 is CF_3CHCl_2

Letters with the number indicate an isomer.

Chloromonoxide

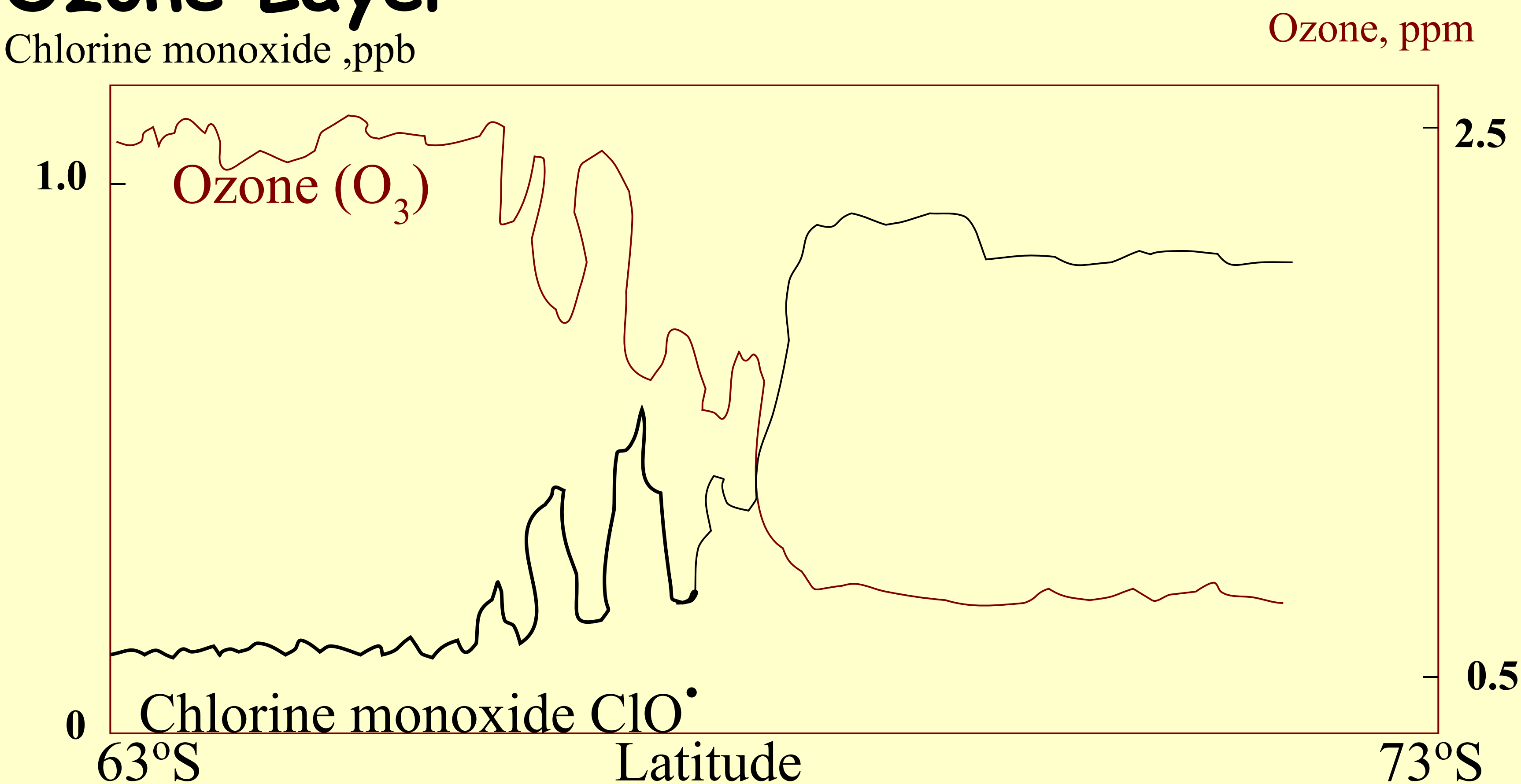
Evidence for the destruction has been linked to the catalytically active Chloro monoxide

$ClO^{\bullet}$ & Ozone profiles as one goes South.

It is interesting to note how little Chloro monoxide effects the amounts of Ozone.

Relationship between ClO. & O_3

Ozone Layer



Thickness of Ozone Layer

The thickness of the Ozone Layer is expressed in Dobson units (DU) and is equivalent to 0.001 mm thickness of pure O_3 at the density it would possess at ground level (1 atm)

Equator	= 250 DU
Temperate Latitudes	= 350 DU
Subpolar regions	= 450DU

Other Ozone Depleters

But has the reduction and removal of CFC's solved the problem of the Ozone Hole ?

Or could there be other causes that are producing the Ozone Hole. ?

Could our pollution arising from NO_2 and CO_2 contributing factors ?

Interactive Catalytic Forms

Destruction: Halide Radicals destroy Ozone.

The majority of Chlorine does not exit as

$Cl^{\bullet}$ or $ClO^{\bullet}$. The two major nonradical inactive as catalysts species in the Stratosphere are:

HCl	Hydrogen chloride
$ClONO_2$	Chlorine nitrate gas

Interactive Catalytic Forms

Formation of nonradical chlorine species.

$$ClO^{\bullet} + NO_2^{\bullet} \rightarrow ClONO_2$$

$$Cl^{\bullet} + CH_4 \rightarrow HCl + CH_3^{\bullet}$$

But HCl react with Hydroxyl Radical

$$HCl + OH^{\bullet} \rightarrow H_2O + Cl^{\bullet}$$

Origin of Ozone Hole

The major destruction of the hole in the lower atmosphere occurs as a result of special winter weather conditions when the chlorine stored as the catalytically inactive forms (HCl & $ClONO_2$) are converted to

the catalytically active forms ($ClO^{\bullet}$ & $Cl^{\bullet}$)

(This occurs in Polar Stratospheric Clouds)

Ice crystal formation

Nitric acid in the atmosphere forms from

the reaction between $OH^{\bullet}$ & $NO_2^{\bullet}$

Catalytically inactive to active chlorine occurs on the surface of ice crystals formed from water and nitric acid in the lower stratosphere in winter when the temperature drops to

≈ -80°C over the South Pole.

Possible Role of CO_2

" CO_2 acts as a blanket in the lower atmosphere," says Salawitch. " To balance the books the Stratosphere has to cool"

Thus CO_2 could be contributing to helping PSC formation due to reduced temperatures in the stratosphere.

New Scientist, 1 May 1999 p28

Impenetrable Vortex formation

The usual warming mechanism from of

$$O + O_2 \longrightarrow O_3 + \text{Heat}$$

is absent due to total darkness and the stratosphere becomes very cold. As a result the air pressure drops ($PV=nRT$) and due to the rotation of the earth an impenetrable vortex forms with winds up to 300km/hr

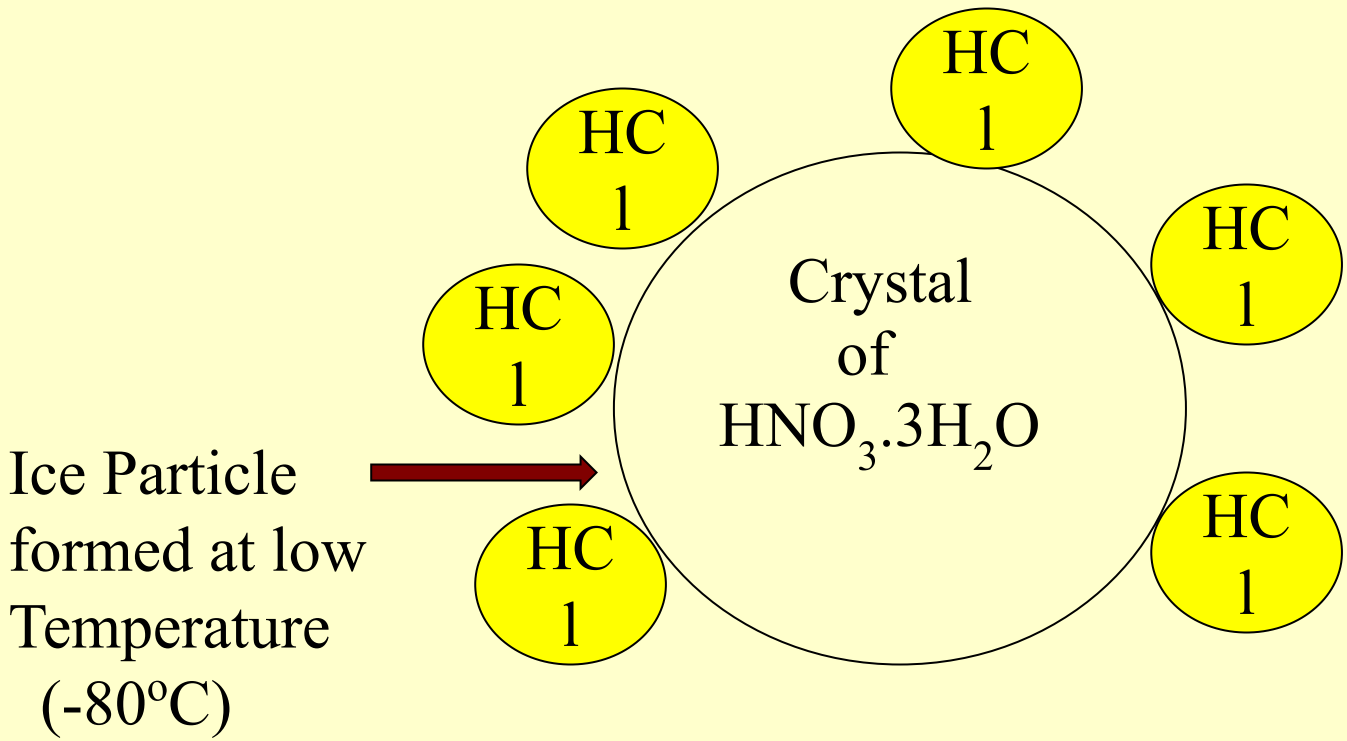
PSC's

Matter cannot readily enter this vortex and the air inside is isolated and remains cold for many months. (Mid October)

The crystals formed by the condensation of the gases within the vortex form Polar Stratospheric Clouds which consist of crystals of trihydrate of Nitric Acid.

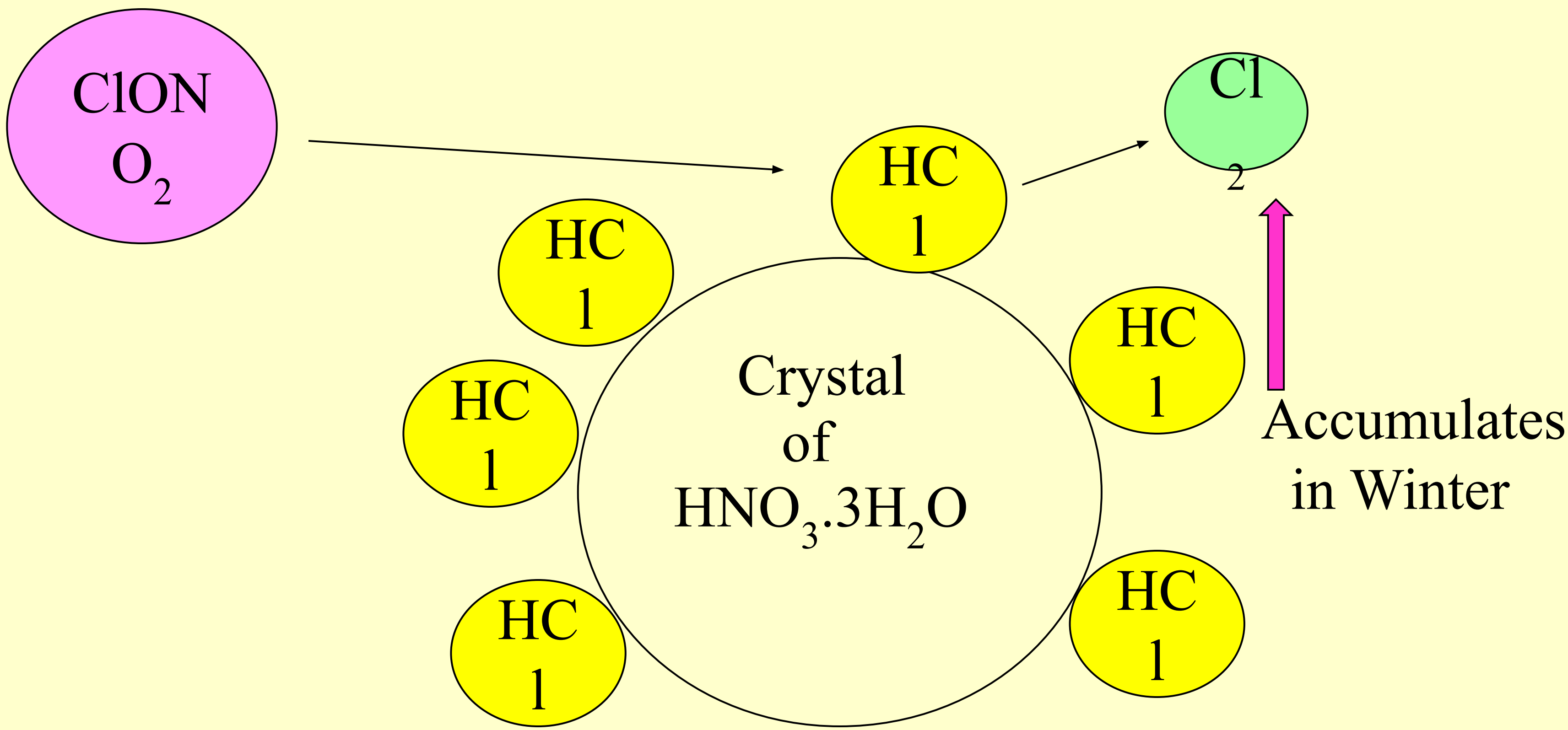
HCL attachment

Gas phase HCl attaches to the ice particle



Role of $ClONO_2$

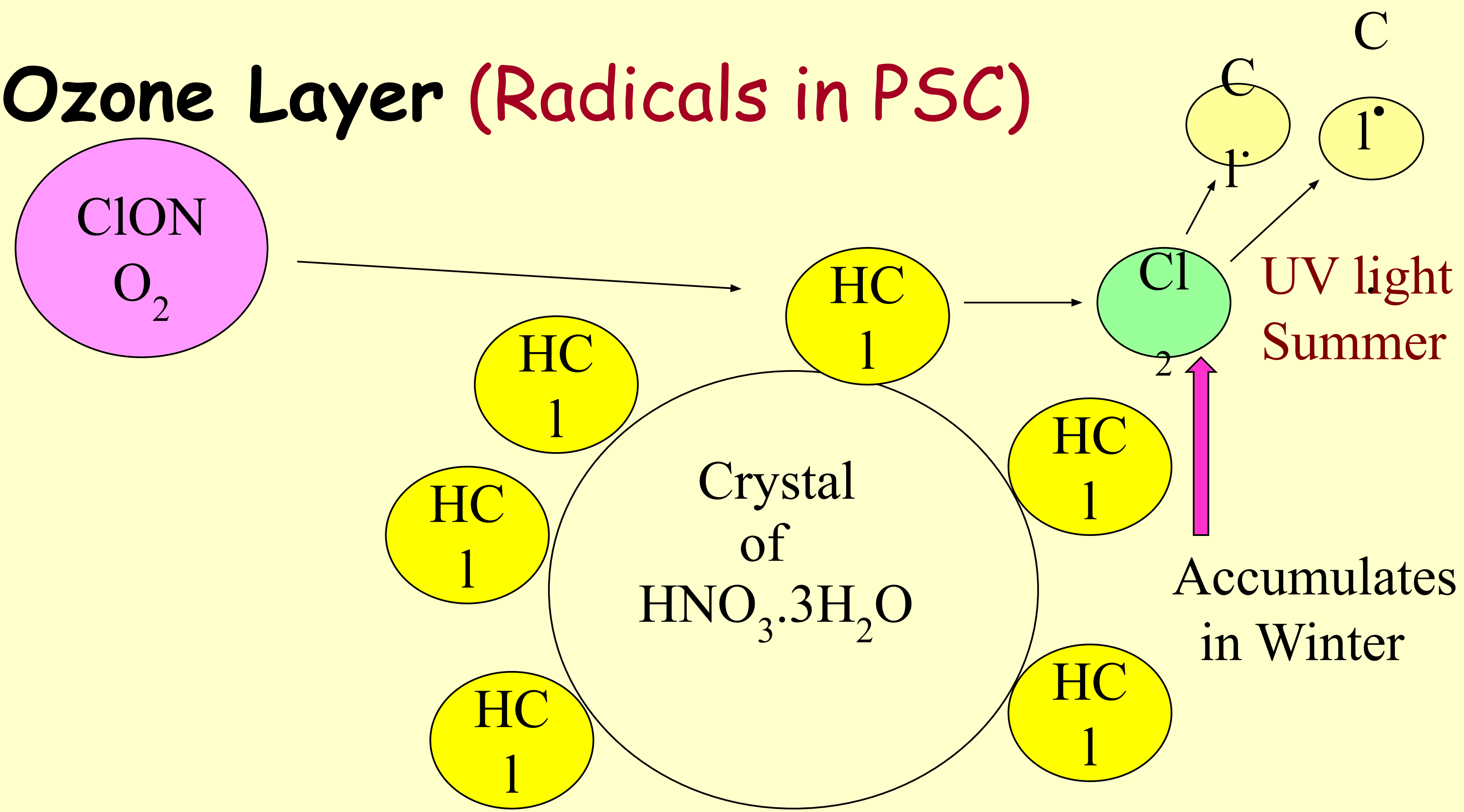
Ozone Layer (Radicals in PSC)



$ClONO_2$ collides with HCl to form Molecular Chlorine

Formation of Cl· Radicals

Ozone Layer (Radicals in PSC)



When the Light in Summer appears Cl_2 is converted to $Cl^{\bullet}$

Hole Closure

$ClONO_{2(g)}$ also reacts with water

$$H_2O(s) + ClONO_{2(g)} \rightarrow HOCl_{(g)} + HNO_{3(s)}$$

$$HOCl + \text{UV light} \rightarrow OH^{\bullet} + Cl^{\bullet}$$

It is only when the vortex has vanished does chlorine predominate in its inactive forms and the hole closes.

Dimer ClOOCl

$ClO^{\bullet}$ also builds up in the dark and this dimerizes to for a relatively stable species.

$$ClO^{\bullet} + ClO^{\bullet} \rightarrow ClOOCl$$

When the Sun Appears

$$ClOOCl \rightarrow 2\,Cl^{\bullet} + 2O^{\bullet}$$

Which contributes to Ozone destruction

Antarctic and Arctic Vortexes

Ozone Layer (PSC's)

The Antarctic vortex is more intense than the Arctic which is more sensitive to temperature.

The Arctic vortex is broken down more readily by rise of planetary waves created when air flows over mountains.

Current research is using a U2 type aeroplanes to probe PSC's

Possible Link

Ozone Layer

"But PSC's were here long before any one had the bright Idea of putting CFC's into refrigerators. It's our pollution that's reacting with clouds and causing the problem. And our CO_2 that will make the clouds more prevalent."

"Possible link : Greenhouse & Ozone Hole ?"

Further Reading

Ozone Layer

"The Hole Story" by G.Walker

New Scientist, p24 , March 2000

Websites

www.nilu.no/projects/theseo2000/

www.ozone-sec.ch.cam.ac.uk

SOLVE, http :/cloud1.arc.nasa.gov/solve/