The Energy-Atmosphere System

Earth’s Modern Atmosphere

Earth’s Atmosphere As Seen From Space

Earth’s Primary (First) Atmosphere

Earth's primary (first) atmosphere immediately after accretion 4.57 billion years ago consisted mainly of hydrogen captured from the solar nebula by Earth’s gravity. Bombarding planetesimals contributed additional gases such as water vapor, carbon monoxide, methane, and ammonia.

Earth Struck With A Mars-sized Object ~4.5 B.Y. Ago

The moon-forming impact event ‘blew’ most of the primary atmosphere back into space

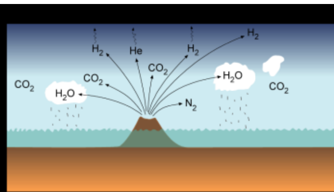
Earth’s Secondary Atmosphere

- Intense heating by the Moon-forming impact left Earth with a magma ocean
- As the early magma ocean cooled, reactions between water vapor and the magma ‘mush’ (melt + minerals) released H_2 and possibly CH_4 into the atmosphere
- Magma ocean eventually solidified to form a hard basaltic crust on Earth’s surface

Earth’s Secondary Atmosphere

- Continued cooling of Earth led to further development of a secondary atmosphere via three processes:
  - Outgassing of bombarding meteorites
  - Outgassing of Earth’s interior (major contributor)
  - Photochemical reactions involving atmospheric gases and UV radiation from the Sun

Gravity held heavier gases (H_2O, CO_2, N_2) near the surface to form Earth's secondary atmosphere while lighter H_2 and He escaped into space



Water vapor eventually condensed from the cooling atmosphere and rained down on the surface to form the early oceans by 4.4 billion years ago

Photochemical Dissociation Hypothesis

- Early atmosphere contained abundant methane, ammonia and water vapor
- This early atmosphere was exposed to ultraviolet light from the sun
- No ozone layer back then, so ultraviolet light reached the surface of the early earth

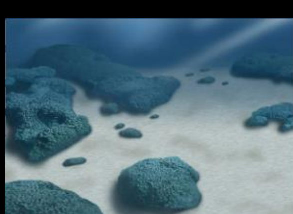
Photochemical Reactions

- **1. Dissociation of water vapor to hydrogen and oxygen with hydrogen escaping into space:**
  - $2H_2O + \text{uv light} = 2H_2 + O_2$
- **2. Newly formed oxygen reacted with methane to form carbon dioxide and water:**
  - $CH_4 + 2O_2 = CO_2 + 2H_2O$
- **3. Oxygen also reacted with ammonia to form nitrogen and water:**
  - $4NH_3 + 3O_2 = 2N_2 + 6H_2O$

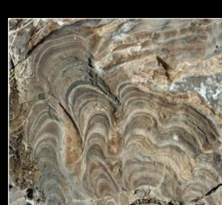
Two Sources of Free Oxygen (O_2) in Earth's Early Atmosphere

- **Photochemical dissociation:**
  - Eventually all the methane and ammonia were converted to carbon dioxide and nitrogen
  - Excess oxygen (O_2) started to accumulate as more water vapor dissociated
- **Ancient photosynthetic cyanobacteria:**
  - First appeared ~3.6 billion years ago
  - Released oxygen as a byproduct

Cyanobacterial Mats in Ancient Oceans (Source of Early Free Oxygen)



Cyanobacterial mats in Precambrian oceans

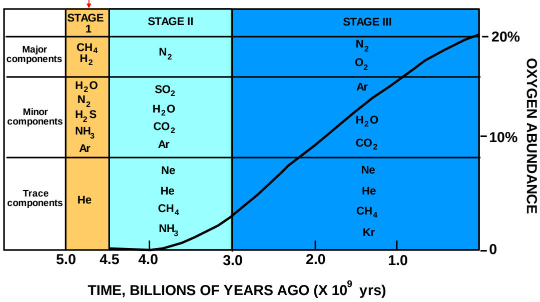


Fossilized mats preserved as stromatolites

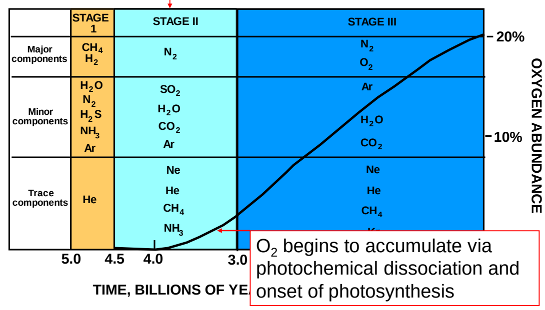
Atmospheric Oxygen Accumulates

- Photosynthetic cyanobacteria released oxygen (O_2) into the oceans and atmosphere
- Over time, oxygen in atmosphere continued to increase:
  - Aerobic bacteria appeared by ~2.0 billion years ago as anaerobic forms sought oxygen-poor environments
  - Stratospheric ozone layer gradually began to develop and was likely in place by 400 million years ago

Stage 1:Early meteorite bombardment, outgassing of Earth's interior, and atmospheric reactions with magma ocean

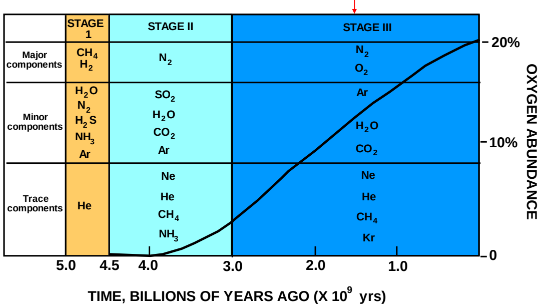


Stage 2: Continued outgassing of Earth's interior and photochemical dissociation reactions



O_2 begins to accumulate via photochemical dissociation and onset of photosynthesis

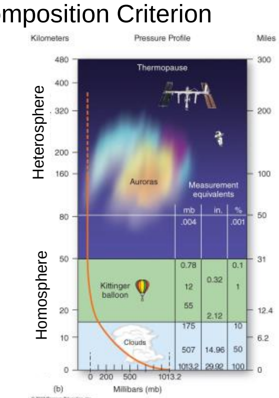
Stage 3:Continued outgassing of interior and increased photosynthesis eventually leads to modern atmosphere



Atmospheric Composition Criterion

Using chemical composition, the modern atmosphere is divided into:

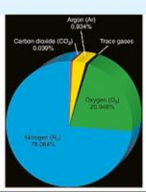
- Heterosphere:
  - Outer atmosphere beginning 80 km above surface
  - Less than 0.001% of atmosphere's mass
  - Gases not evenly mixed
- Homosphere:
  - Extends from Earth's surface to altitude of 80 km
  - Atmospheric pressure decreases with height
  - Uniform blend of gases
  - Mostly nitrogen and oxygen



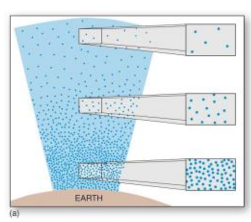
Stable Components of Homosphere

Table 3.2 Stable Components of the Modern Homosphere

Gas (Symbol)	Percentage by Volume	Parts per Million (ppm)
Nitrogen (N_2)	78.084	780,840
Oxygen (O_2)	20.946	209,460
Argon (Ar)	0.934	9,340
Carbon dioxide (CO_2)*	0.039	386.50
Neon (Ne)	0.001818	18
Helium (He)	0.000525	5
Methane (CH_4)	0.00014	1.4
Krypton (Kr)	0.00010	1.0
Ozone (O_3)	Variable	
Nitrous oxide (N_2O)	Trace	
Hydrogen (H)	Trace	
Xenon (Xe)	Trace	

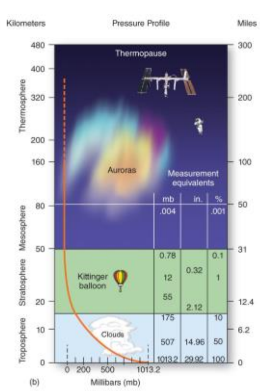


*May 2007 average measured at Mauna Loa, Hawai'i (see: http://cdiac.esd.ornl.gov/ftp/maunaloa-co2/maunaloa.co2 and http://www.esrl.noaa.gov/gmd/ccgg/trends/co2_data_mlo.html.



The atmosphere rapidly decreases in density at higher altitudes

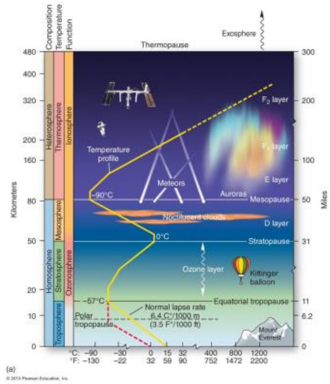
Fig. 2.17



Atmospheric Layers Based On Temperatures

Layers/Boundaries:

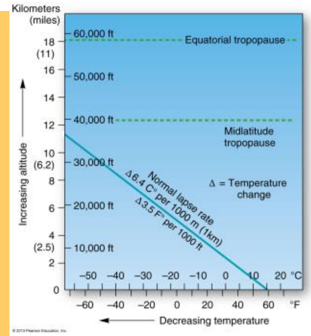
- Thermosphere
  - Mesopause
- Mesosphere
  - Stratopause
- Stratosphere
  - Tropopause
- Troposphere



(a)

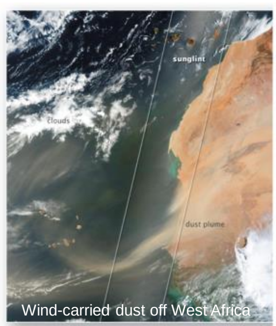
The Troposphere

- Extends from Earth's surface up to the tropopause
- Expands in thickness from 8 km at the poles to 18 km at the equator
- Temperature decreases at higher altitudes
- Contains 80 to 90 % of the mass of the atmosphere
  - Heated at the bottom
  - Rising air cools
  - It rains or snows and blows
- These features of the troposphere cause our weather



Variable Atmospheric Components

- The troposphere contains variable natural and human-generated gases, dust particles, and chemicals
- Aerosols like soot have produced a dimming of sunlight reaching Earth's surface by 4-8%
- World Health Organization estimates that air pollution kills ~4.3 million people worldwide



Wind-carried dust off West Africa

(b)

TABLE 2.5 Sources of Natural Variable Gases and Materials

Source	Contribution
Volcanoes	Sulfur oxides, particulates
Forest fires	Carbon monoxide and dioxide, nitrogen oxides, particulates
Plants	Hydrocarbons, pollens
Decaying plants	Methane, hydrogen sulfides
Soil	Dust and viruses
Ocean	Salt spray and particulates

Anthropogenic Pollution

- **Human-caused air pollution most prevalent in urbanized regions:**
  - **Particulates and aerosols: small particles of dust, soot and suspended pollution**
  - **Combustion of fossil fuels**
  - **Power and industrial plants**
  - **Photochemical smog resulting from interaction between sunlight and combustion products**
  - **Industrial Smog**

TABLE 2.6 Anthropogenic Gases and Materials in the Lower Atmosphere

Name	Symbol	Sources	Description and Effects of Criteria Pollutants
Carbon monoxide	CO	Incomplete combustion of fuels, mainly vehicle emissions	Odorless, colorless, tasteless gas Toxicity; affinity for hemoglobin Displaces O_2 in bloodstream; 50 to 100 ppm causes headaches and vision and judgment losses
Nitrogen oxides	NO_x (NO, NO_2)	Agricultural activities, fertilizers, and high temperature/pressure combustion, mainly from vehicle emissions	Reddish-brown choking gas Inflames respiratory system, destroys lung tissue Leads to acid deposition
Volatile organic compounds	VOC	Incomplete combustion of fossil fuels such as gasoline; cleaning and paint solvents	Prime agents of surface ozone formation
Ozone	O_3	Photochemical reactions	Highly reactive, unstable gas Irritates human eyes, nose, and throat Damages plants
Peroxyacetyl nitrates	PAN	Photochemical reactions	No human health effects Major damage to plants, forests, crops
Sulfur oxides	SO_x (SO_2, SO_3)	Combustion of sulfur-containing fuels	Colorless, but with irritating smell, Impairs breathing, taste threshold Causes human asthma, bronchitis, emphysema Leads to acid deposition
Particulate matter	PM	Industrial activities, fuel combustion, vehicle emissions, agriculture	Complex mixture of solids and aerosols, including dust, soot, salt, metals, and organics Dust, smoke, and haze affect visibility Various health effects: bronchitis, pulmonary function
Carbon dioxide	CO_2	Complete combustion of fossil fuels	Principal greenhouse gas (see Chapter 7)
Methane	CH_4	Organic processes	Secondary greenhouse gas (see Chapter 7)
Water vapor	H_2O vapor	Combustion processes, steam	See Chapter 5

Natural Factors Affecting Air Pollution

- **Winds:**
  - **Gather and move pollutants**
  - **Movement of pollutants from one country to another can affect international relations**
- **Local and Regional Landscapes:**
  - **Surrounding mountains and hills can form barriers to air movement**
  - **Volcanoes eruptions can erupt particulates into the atmosphere and lead to acid rain**
- **Temperature inversion**

Temperature Inversion Traps Pollution Near The Surface

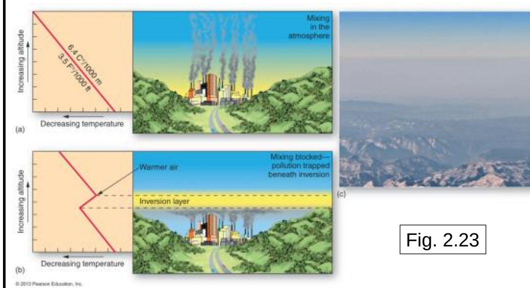


Fig. 2.23

Photochemical Smog

- Photochemical smog developed with the advent of the automobile
- Smog results from interaction of sunlight with combustion products in automobile exhaust (mainly nitrogen oxides and VOCs)
- Major air pollutants:
  - Peroxyacetyl nitrate (PAN) damages plants
  - Ground-level ozone
  - Nitrogen dioxide (interacts with water vapor to produce nitric acid)

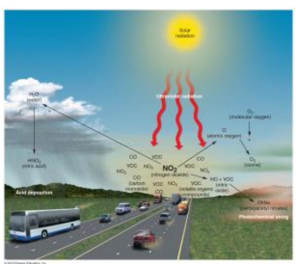
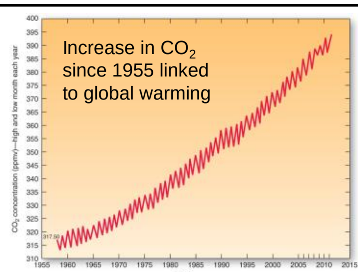


Fig. 2.24

Particulate Matter

- Particulate matter is a diverse mixture of fine particles:
  - Haze
  - Smoke
  - Dust
- WHO established links between PM pollution and poor health:
  - Asthma prevalence in U.S. doubled since 1980

Sources of Carbon Dioxide



- The sources of carbon dioxide in the troposphere include:
  - Volcanism
  - Weathering and erosion of carbonate rocks like limestone
  - Respiration
  - Burning of fossil fuels (the only source we can control)

Clean Air Act

- **Clean Air Act legislation (1970, 1977, 1990) resulted in significant reductions of many pollutants:**
  - **Carbon monoxide (-45%)**
  - **Nitrogen oxides (-22%)**
  - **Volatile organic compounds (-48%)**
  - **Particulate matter (-75%)**
  - **Lead (-98%)**
- **However, benefits must be weighed against economic considerations:**
  - **Political debate continues**

Annual Sulfate Wet Deposition (Acid Rain)

1990 - 1994 | 2000 - 2004

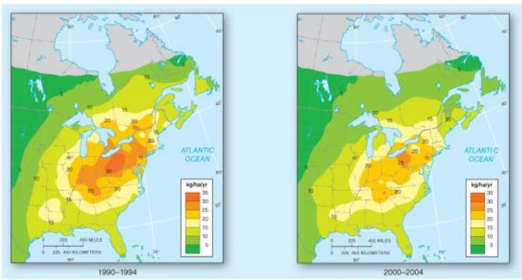
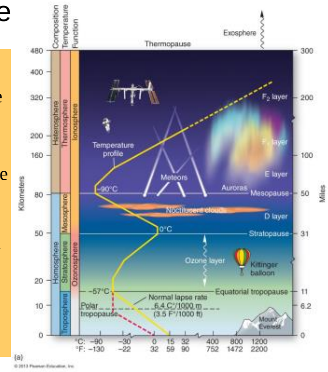


Fig. 2.2.2

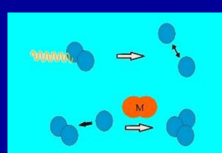
The Stratosphere

- Extends from the tropopause (~15km) to a height of 50km above Earth's surface
- Temperature increases at higher altitudes because the stratosphere absorbs uv light from the Sun to produce ozone
- Although ozone is only a trace gas in the stratosphere, it protects us from incoming uv radiation from the Sun

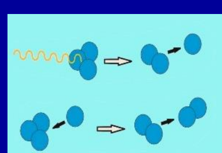


Ozone In The Stratosphere

Ozone Formation: The O-O bond of an oxygen molecule is broken by uv light. The formed O atom reacts with O_2 (and for energetic reasons a collision partner M) and forms ozone (O_3).



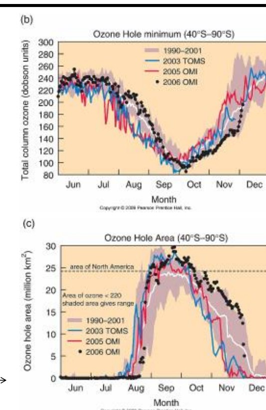
In an analogous way, ozone is destroyed by photolysis, if the O-O bond in an ozone molecule is split by sunlight. In this case the formed O atom reacts with another ozone molecule and forms two oxygen molecules O_2.



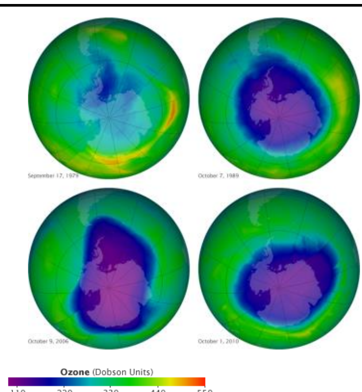
Ozone Depletion

- Ozone in the stratosphere:
  - Protects us from Sun's ultraviolet light
  - Formed by natural processes
- Significant thinning of the ozone layer has occurred in polar regions over the last few decades

Southern Hemisphere Ozone 2002-2003



Growth of Ozone Hole Over Antarctica



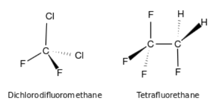
Images from NASA's Total Ozone Mapping Spectrometer (TOMS) instruments (1979–2003) and Royal Netherlands Meteorological Institute's Ozone Monitoring (OMI) Instrument (2004 – Present)

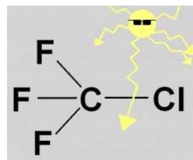
Causes of Ozone Depletion

- **High-energy particles from solar flares and sunspots bombard our atmosphere and may also affect ozone**
- **Volcanic gases and ash particles react with ozone to break it down**
- **Release of CFC's into the atmosphere**

Discovery of CFC's in Stratosphere

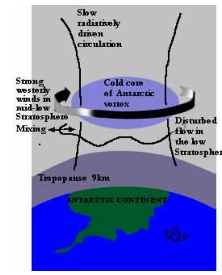
- In 1974, CFC's (Chlorine-Fluorine-Carbon) compounds were detected in stratosphere:
- Major sources of CFCs:
  - Air conditioning and refrigeration
  - Production of foam
  - Aerosol sprays
  - Solvents in electronics industry
- A single chlorine atom can destroy 100,000 ozone molecules





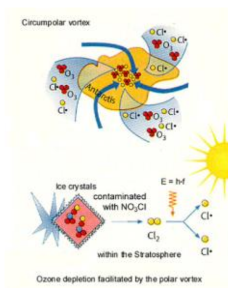
Formation of Antarctic Ozone Hole

- CFCs from northern hemisphere are transported southward by atmospheric winds and concentrated over Antarctica
- During the Antarctic winter, polar stratospheric clouds form under dark, extremely cold conditions:
  - Strong westerly winds start to circulate around the continent, creating an atmospheric container (vortex) that traps and chills the air
  - Low temperatures form ice crystals that trap compounds

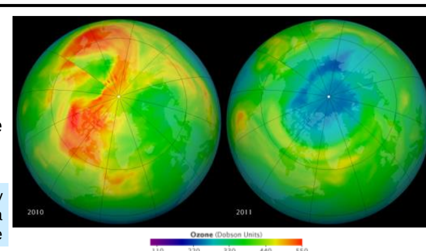


Formation of Antarctic Ozone Hole

- During Antarctic spring, emerging sunlight provides energy to drive photochemical reactions:
  - Photochemical reactions release trapped compounds
  - Chlorine is freed to take part in chemical reactions that lead to ozone destruction



Northern Hemisphere



Recorded by the Aura satellite

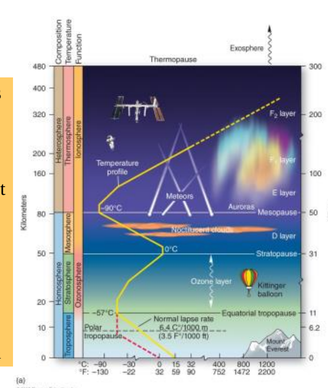
- Arctic ozone depletion detected between November and April:
  - Large depletion over the Arctic 15% below normal recorded in 1993
  - Record 45% loss during spring 1997
  - 40% loss during winter of 2011 described as "unprecedented" by the UN weather agency

What Can Be Done?

- **In 1987, 24 nations signed the Montreal Protocol:**
  - **Pledged to reduce CFCs by 1999**
- **Target amended five times since then**
- **CFC manufacturing has now been phased out**
- **In 2005, the IPCC (Intergovernmental Panel on Climate Change) summary report suggested that global average ozone depletion has now stabilized:**
  - **Ozone layer expected to begin to recover in the coming decades due to decline in CFC concentrations, assuming full compliance with the Montreal Protocol**
  - **Antarctic ozone layer not expected to return to 1980 global levels until 2050 and be completely eliminated by 2065**

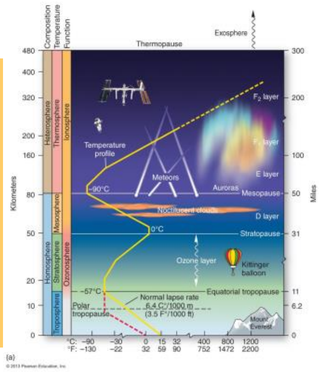
The Mesosphere

- The Mesosphere extends from 50 km (at the Stratopause) to 80 km above Earth's surface
- Temperature decreases at higher altitudes within the Mesosphere because of the decreasing influence of ozone
- Mesosphere does not absorb any significant portion of solar radiation



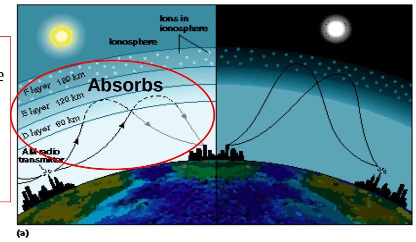
The Thermosphere

- Extends beyond 80 km above Earth's surface; Very low pressures (.005mb)
- Temperature increases upward because of interactions with solar wind
- Ionization (ionosphere) of atmospheric gases increases with sunlight (daytime)
- Near the poles, the earth's magnetic field concentrates the solar wind to form auroras



The Ionosphere

Ionosphere is composed of the D, E, and F layers: D layer is good at absorbing AM radio waves



(a)

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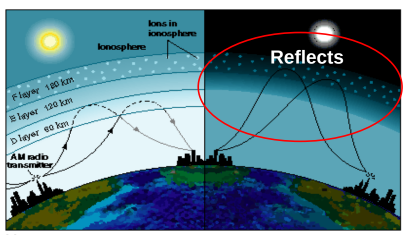
The Ionosphere

D layer disappears at night.... the E and F layers bounce the waves back to the earth



(a)

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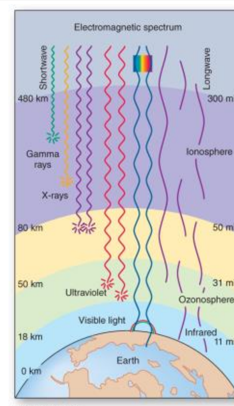
Earth's Atmosphere And The Electromagnetic Spectrum

- Incoming shortwave gamma and x-rays stopped by ionosphere
- UV radiation penetrates deeper but is mostly absorbed by the ozone layer (ozonosphere)
- Visible and infrared radiation reaches Earth's surface
- Earth's surface emits infrared radiation into the atmosphere



Ozone Depletion