Atmospheric Pollution

Lecture 12

Sahraei
Physics Department
Razi university

http://www.razi.ac.ir/sahraei

Vertical Pollutant Transport

Pressure systems affect vertical air motions and, therefore, pollutant dispersion by forced and free convection .

In a semipermanent low-pressure system, for example, near-surface winds converge and rise, dispersing near-surface pollutants upward.

In a semipermanent high-pressure system, winds aloft converge and sink, confining near-surface pollutants. Both cases illustrate forced convection.

In thermal low-pressure systems, surface warming causes near-surface air to become buoyant and rise.

Thermodynamics of Dry Air

Dry Air

The First Law of Thermodynamics states that a small amount of heat, dQ, added to unit mass of a system (which here is a small parcel of air) can be used to change the internal energy, dU, and to do work, dW, against the surroundings.

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W$$

Where the work done by the viscous forces can be neglected, the work is communicated only by the pressure force $p\mathrm{d}a_{parcel}$.

we can write $\mathrm{d}W = p\mathrm{d}a$, which is the work done by expansion, and a is the specific volume. For dry air $\mathrm{d}U = C_v\mathrm{d}T$. Thus, the first law can be written:

$$\mathrm{d}Q = C_v\,\mathrm{d}T + p\,\mathrm{d}\alpha \qquad \text{[dry air(1)]}$$

Hence, heat added to the system may cause a change in volume of the gas, or it may result in a change in temperature of the gas, or both.

Air behaves nearly like a perfect gas, so we may use the perfect gas equation

$$p\alpha = RT \qquad R = C_p - C_v$$

and write the first law in the form

$$\mathrm{d}Q = C_p\,\mathrm{d}T - (1/\rho)\,\mathrm{d}p \qquad \text{[dry air (2)]}$$

An adiabatic process is one in which no heat enters or leaves the system, thus

$$\mathrm{d}Q = 0$$

$$\boxed{C_v\,\mathrm{d}T = -p\,\mathrm{d}\alpha}$$

$$C_p\,\mathrm{d}T = \alpha\,\mathrm{d}p$$

Hence, an expansion (da > 0) will cause a reduction in the internal energy of the gas and therefore a decrease in temperature (dT < 0).

Alternatively we see that an decrease in temperature results in a decrease in pressure (dp < 0).

Dry Adiabatic Lapse Rate (DALR)

In atmospheric flow, we have a significant built-in vertical variation in the pressure, the air density, and the temperature.

A baseline for this variation is the adiabatic change with respect to height. Density changes over short height differences are small.

Thus using a constant density approximation, we can calculate the vertical adiabatic temperature change as a function of the pressure change.

This temperature profile is called the dry adiabatic lapse rate.

$$C_p \, \mathrm{d}T = \alpha \, \mathrm{d}p$$

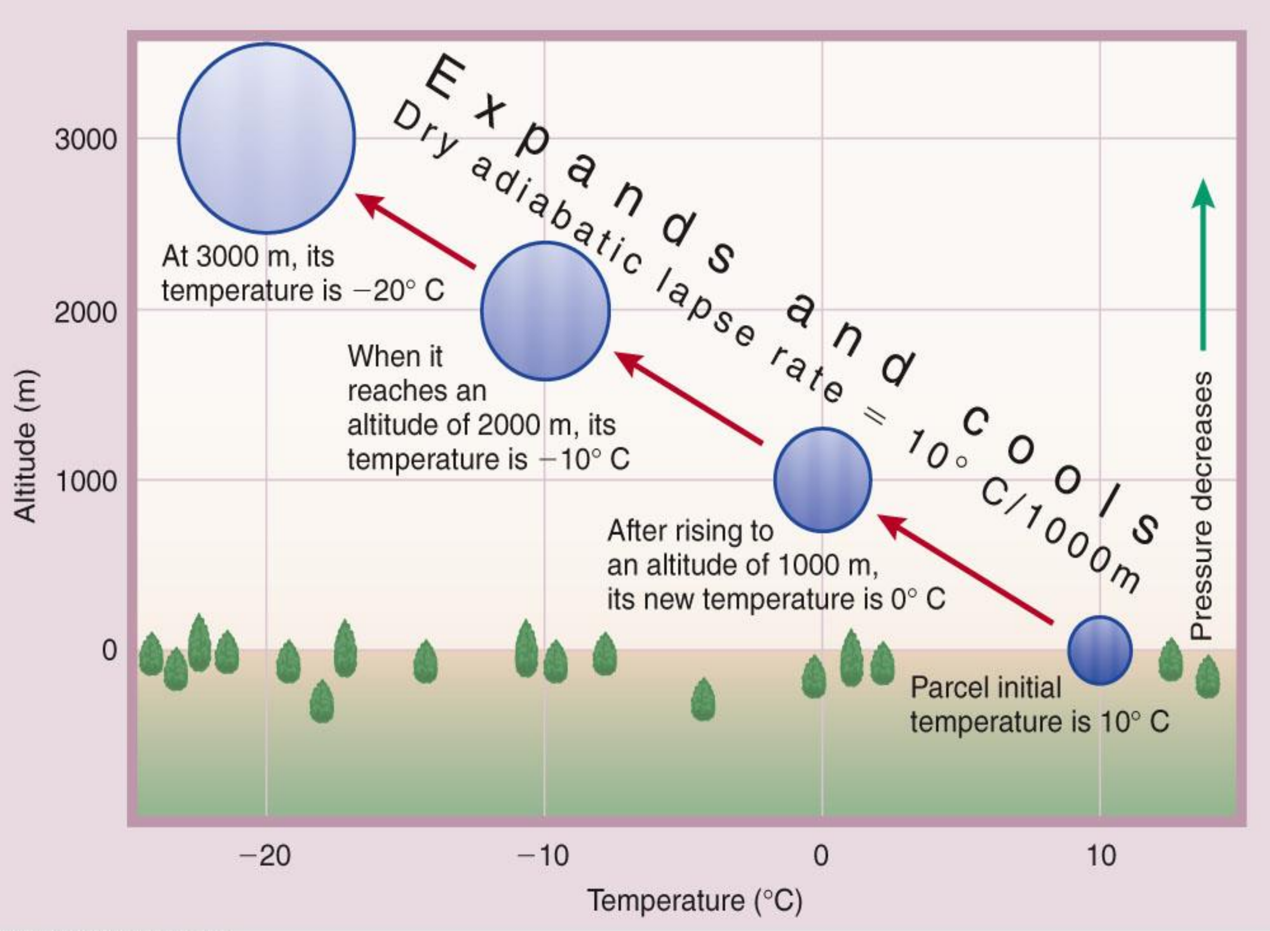
$$\alpha \frac{dp}{dz} = -g$$

Assuming p = const, we obtain

$$-\left(\frac{\partial T}{\partial z}\right)_{DALR} = \frac{g}{C_p}$$

We denote $(\partial T/\partial z)_{DALR}$ by γ_d and call it the dry adiabatic lapse rate (**DALR**):

$$-\left(\frac{\partial T}{\partial z}\right)_{DALR} \equiv \Gamma_d$$


Expands and cools
Dry adiabatic lapse rate = 10° C/1000m
At 3000 m, its temperature is −20° C
When it reaches an altitude of 2000 m, its temperature is −10° C
After rising to an altitude of 1000 m, its new temperature is 0° C
Parcel initial temperature is 10° C
Pressure decreases
Altitude (m)
3000
2000
1000
0
−20
−10
0
10
Temperature (°C)

Adiabatic and Environmental Lapse Rates

Whether air rises or sinks buoyantly in a thermal pressure system depends on atmospheric stability, which depends on adiabatic and environmental lapse rates

Stability in Unsaturated Air

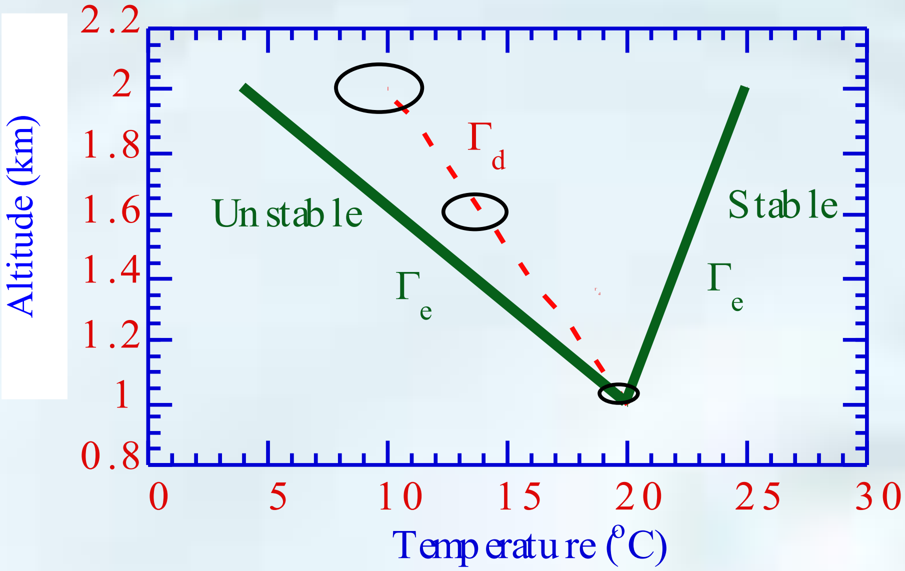


Figure 6.8

Stability in Saturated Air

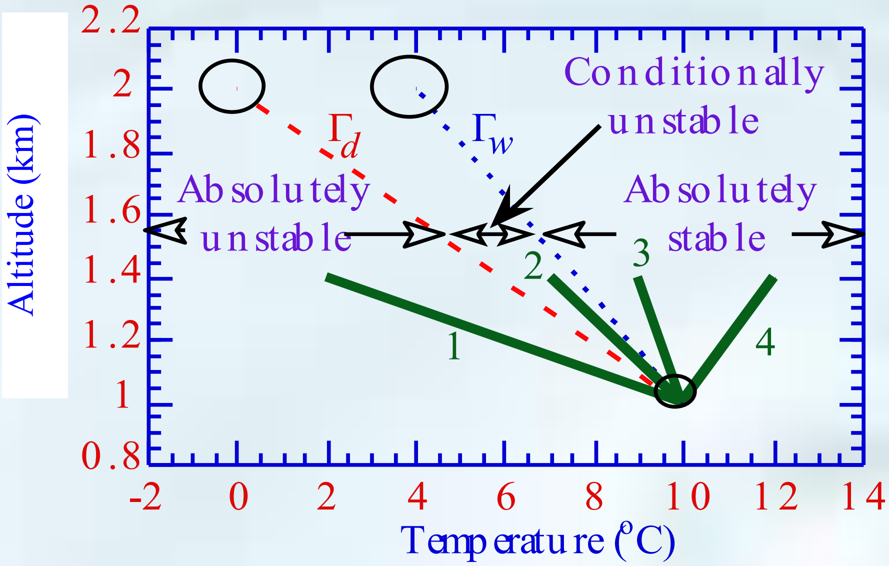


Figure 6.9

Temperature Inversion

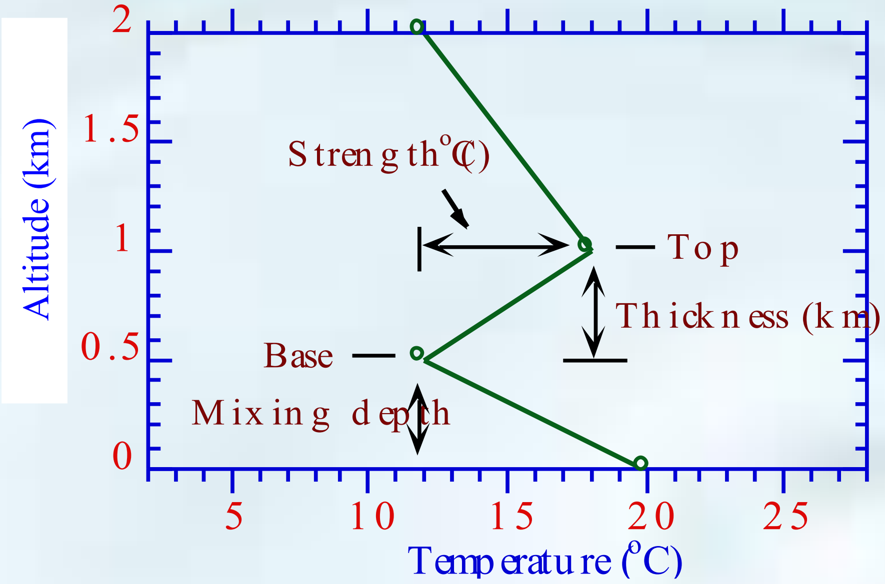


Figure 6.10

Trapping Pollutants Under an Inversion

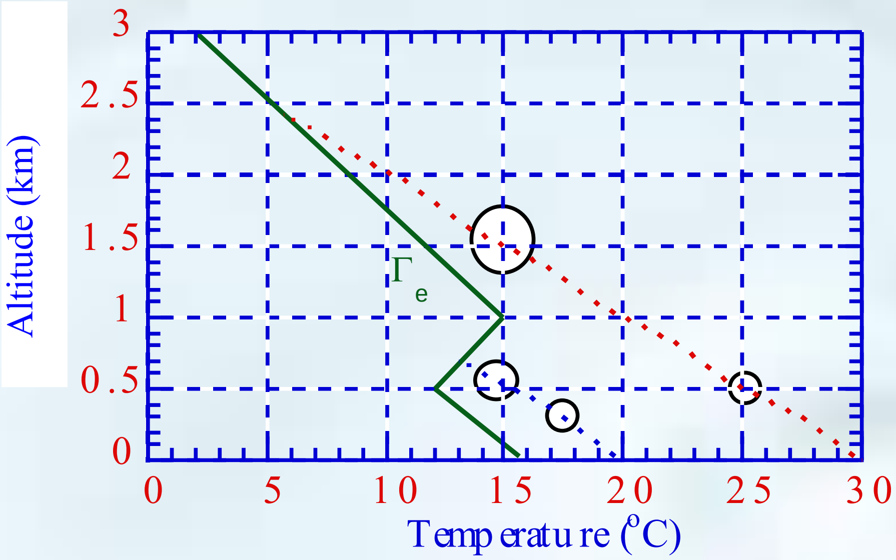


Figure 6.11

Morning and Afternoon Temperature Profiles

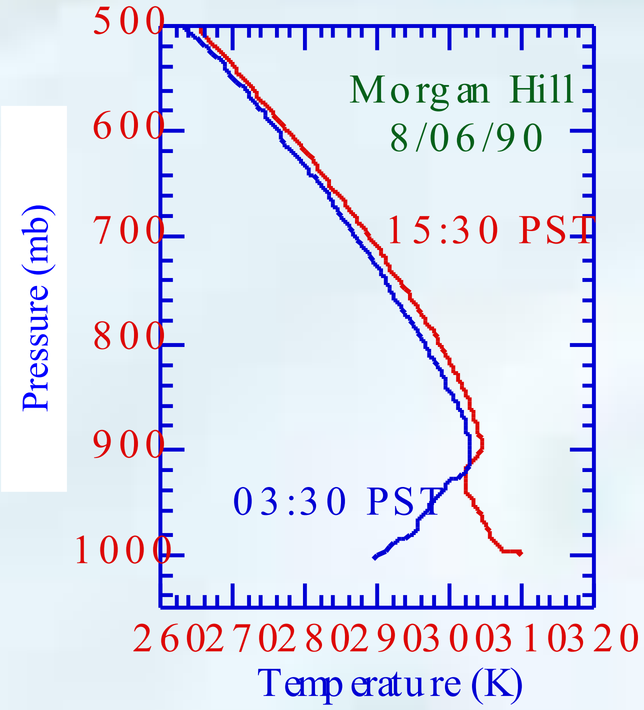


Figure 6.12

Formation of a Subsidence Inversion

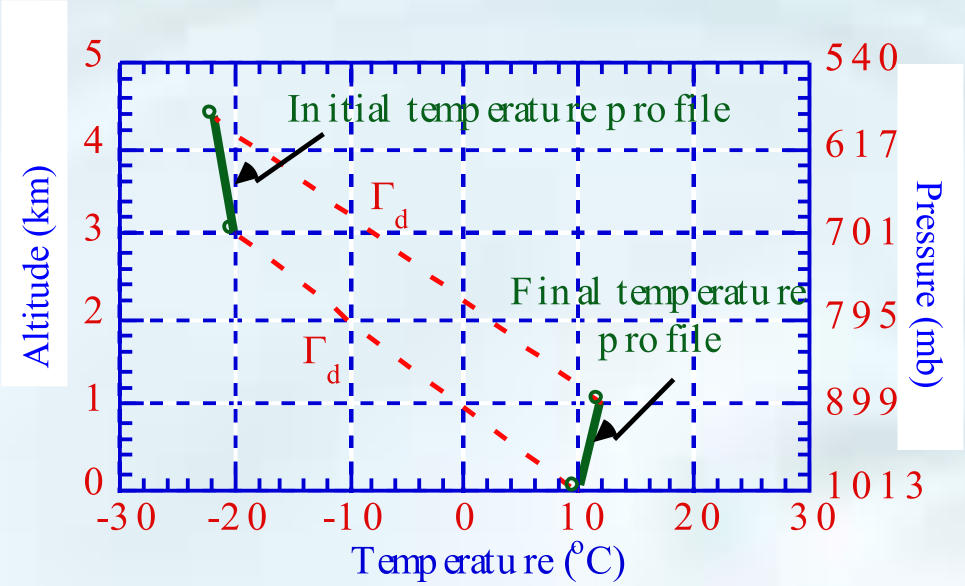


Figure 6.13

Change of Inversion Base Height During Day

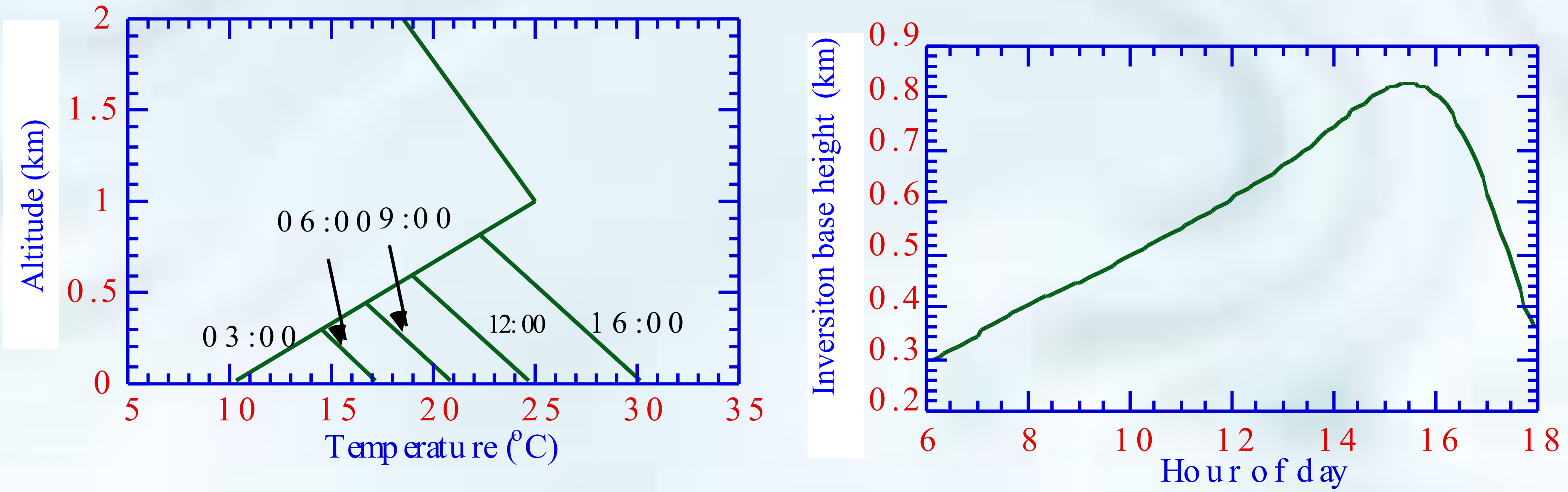


Figure 6.14

Change in Mixing Depth, Los Angeles, July 23, 2000

Noon

Late afternoon

Mark Z. Jacobson

Seasonal Variation of Inversions

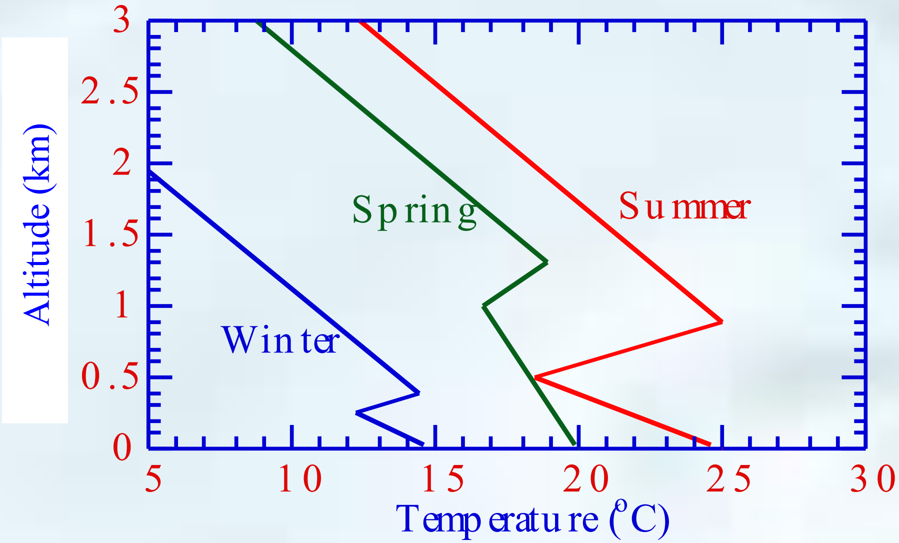


Figure 6.15

B. Chemical Composition

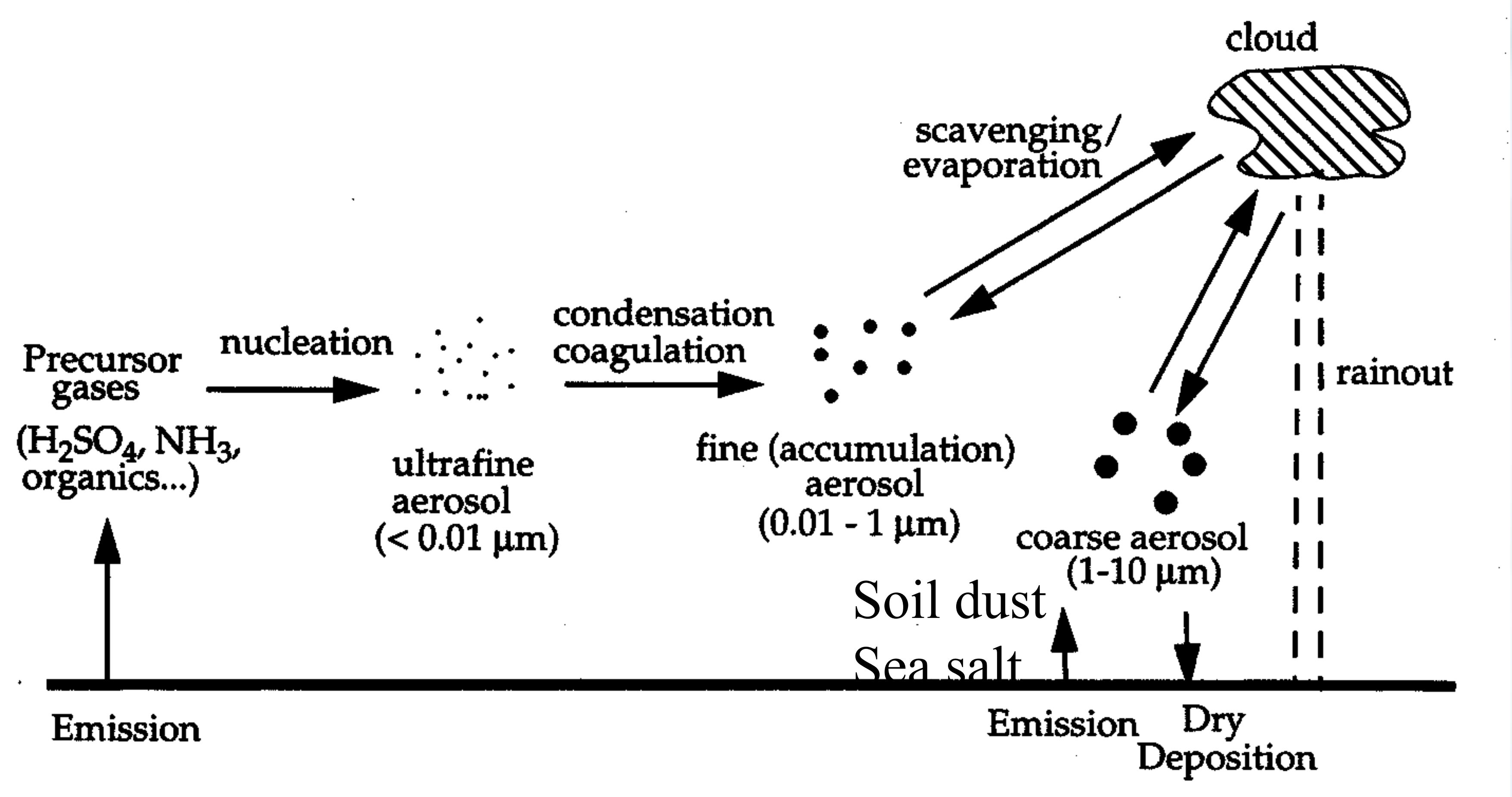
The bimodal nature of the size-number distribution of atmospheric particles suggests at least two distinct mechanisms of formation, and the chemical composition of the particles reflects their origins.

Fine particles have a diameter smaller than about 2.5 μm, and are produced by the condensation of vapors, accumulation, and coagulation. They have a chemical composition that reflects the condensable trace gases in the atmosphere: SO_2, NH_3, HNO_3, VOC's, and H_2O. The chemical composition is water with SO_4^{-2}, NO_3^-, NH_4^+, Pb, Cl^-, Br^-, C(soot), and organic matter; where biomass burning is prevalent, K^+.

Coarse Particles have a diameter greater than about 2.5 μm, are produced by mechanical weathering of surface materials. Their lifetimes, controlled by fallout and washout, are generally short. The composition of particles in this size range reflects that of the earth's surface - silicate (SiO_2), iron and aluminum oxides, $CaCO_3$ and $MgCO_3$; over the oceans , NaCl.

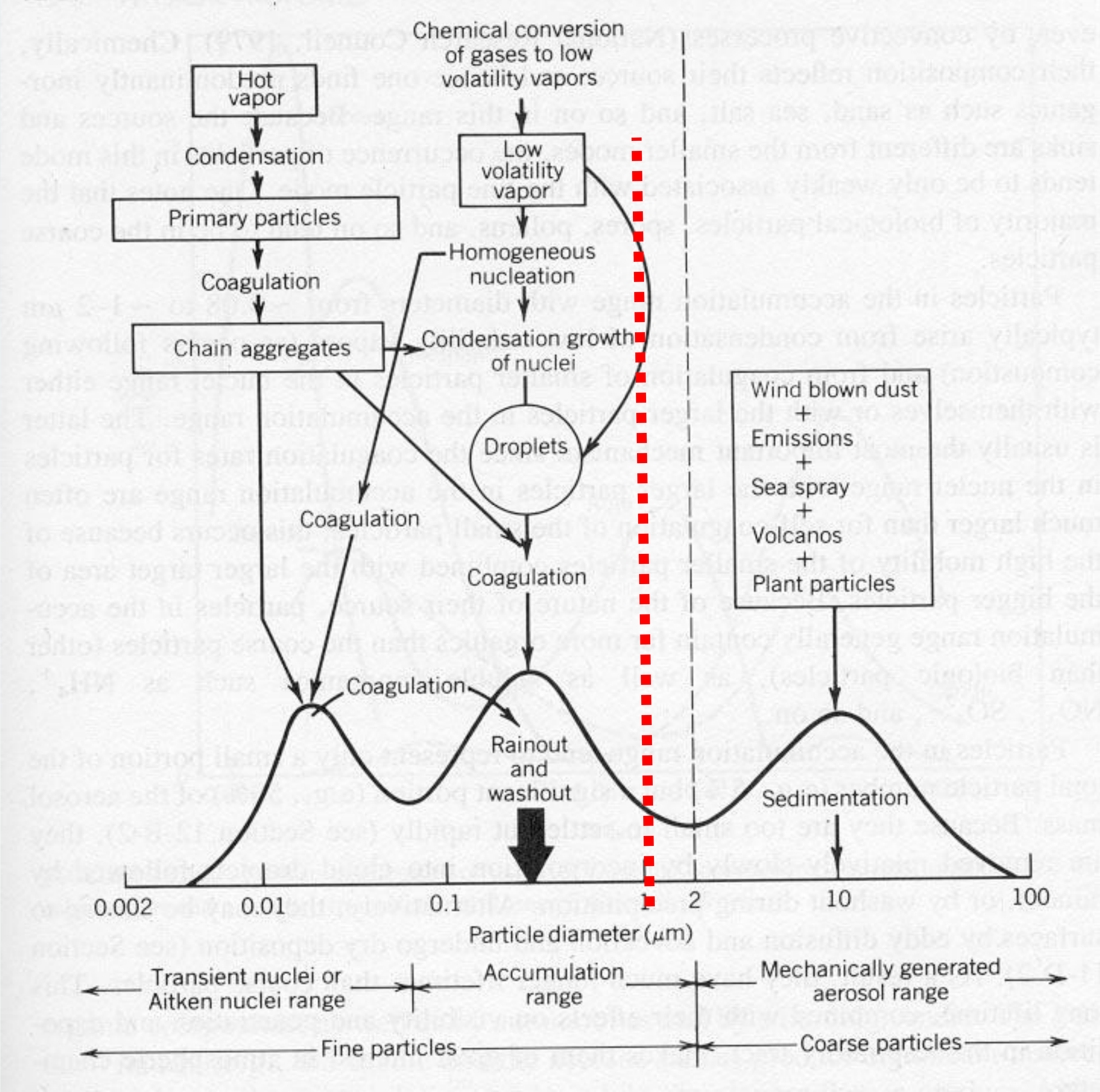
ORIGIN OF THE ATMOSPHERIC AEROSOL

Aerosol: dispersed condensed matter suspended in a gas
Size range: 0.001 µm (molecular cluster) to 100 µm (small raindrop)

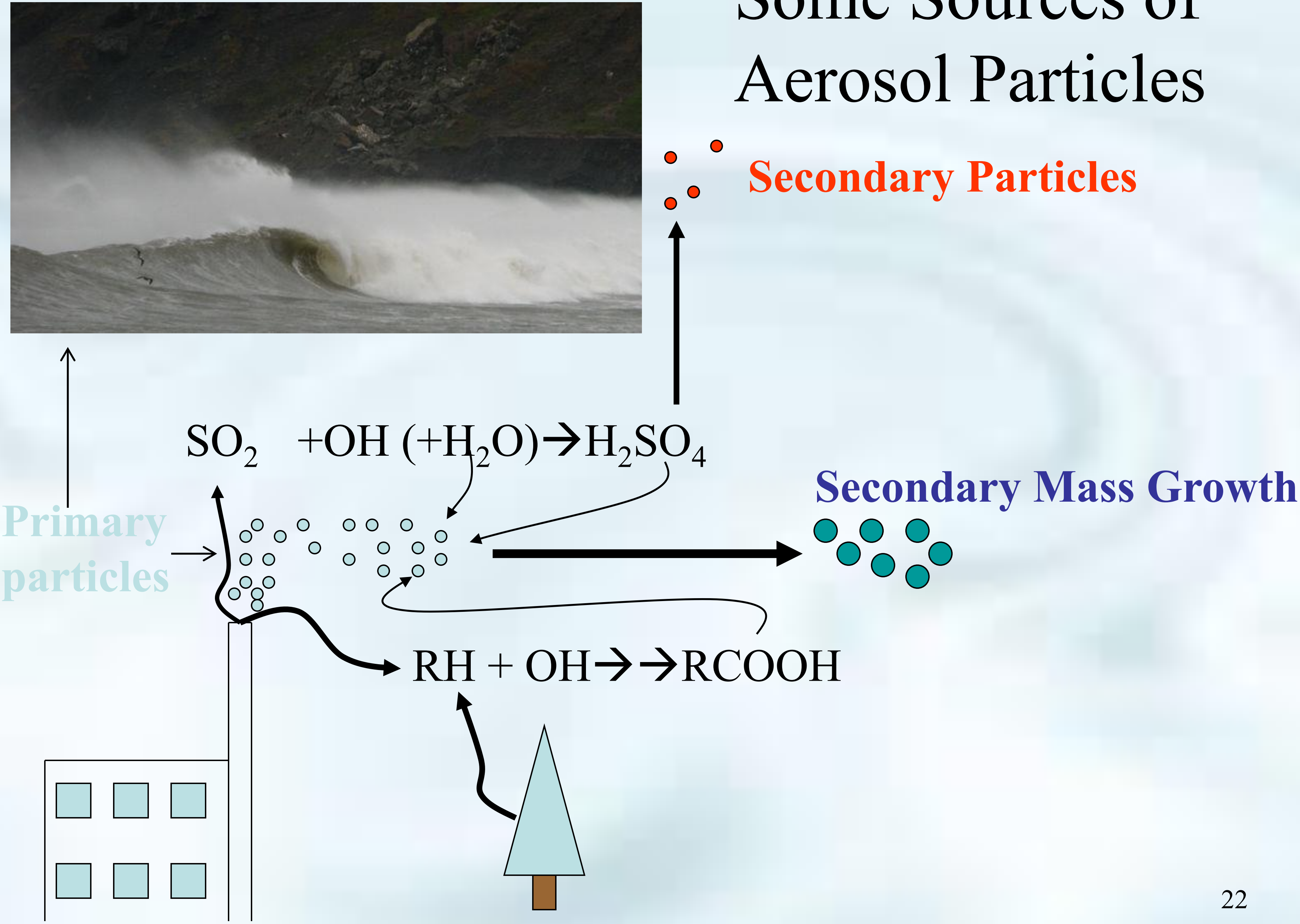


Environmental importance: health (respiration), visibility, radiative bala
cloud formation, heterogeneous reactions, delivery of nutrients…

Atmospheric Aerosols



Some Sources of Aerosol Particles



Secondary Particles

$SO_2 + OH (+H_2O) \rightarrow H_2SO_4$

Secondary Mass Growth

Primary particles

$RH + OH \rightarrow \rightarrow RCOOH$

Atmospheric Aerosol

❑ **Chemical Composition**

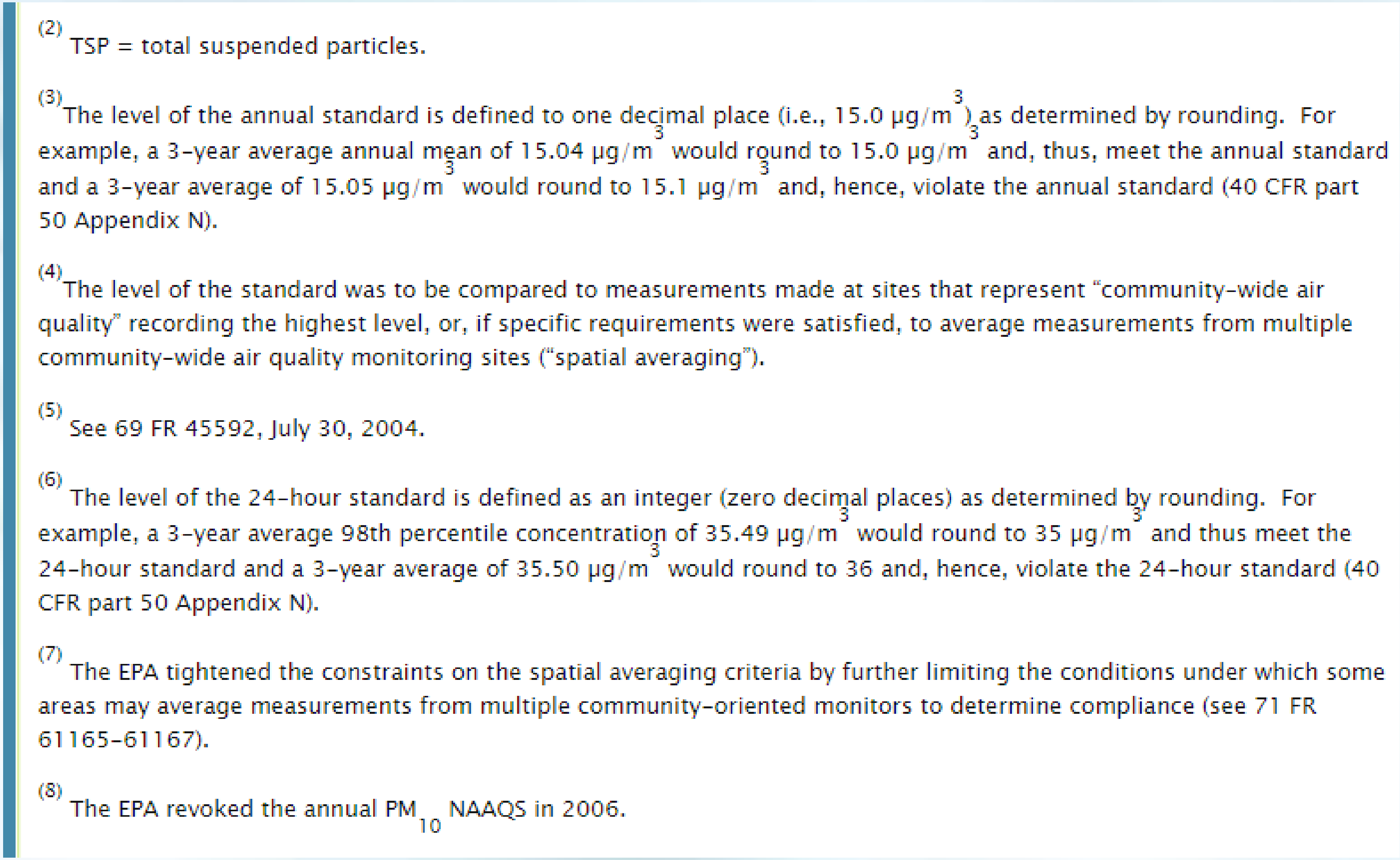
- Fine particles: acidic; sulfate, ammonium compounds, elemental carbon
- Coarse particles: basic; crustal materials and their oxides

1. What are the three major components of fine aerosols?
2. What are the four major components of coarse aerosols?

TABLE 3. Average composition of fine and coarse particles in μg/m³ at an urban and a rural site

	Urban		Rural	
	Fine	**Coarse**	**Fine**	**Coarse**
Total Mass	42	27	24	5.6
SO_4^-	17	1.1	12	—
NO_3^-	0.25	1.8	0.3	—
NH_4^+	4.3	<0.19	2.3	—
H^+	0.067	<0.01	0.114	—
C	7.6	3.3	3.3	1.3
Al	0.095	1.4	0.02	0.2
Si	0.2	3.8	0.038	0.58
S	—	—	3.7	0.2
Ca	0.15	3.1	0.016	0.32
Fe	0.17	0.73	0.028	0.12
Pb	0.48	0.13	0.097	0.014

Data from Finlayson-Pitts and Pitts, Atmospheric Chemistry: Fundamentals and Experimental Techniques, Wiley, New York, 1986.



(2) TSP = total suspended particles.

(3) The level of the annual standard is defined to one decimal place (i.e., 15.0 $\mu g/m^3$) as determined by rounding. For example, a 3-year average annual mean of 15.04 $\mu g/m^3$ would round to 15.0 $\mu g/m^3$ and, thus, meet the annual standard and a 3-year average of 15.05 $\mu g/m^3$ would round to 15.1 $\mu g/m^3$ and, hence, violate the annual standard (40 CFR part 50 Appendix N).

(4) The level of the standard was to be compared to measurements made at sites that represent "community-wide air quality" recording the highest level, or, if specific requirements were satisfied, to average measurements from multiple community-wide air quality monitoring sites ("spatial averaging").

(5) See 69 FR 45592, July 30, 2004.

(6) The level of the 24-hour standard is defined as an integer (zero decimal places) as determined by rounding. For example, a 3-year average 98th percentile concentration of 35.49 $\mu g/m^3$ would round to 35 $\mu g/m^3$ and thus meet the 24-hour standard and a 3-year average of 35.50 $\mu g/m^3$ would round to 36 and, hence, violate the 24-hour standard (40 CFR part 50 Appendix N).

(7) The EPA tightened the constraints on the spatial averaging criteria by further limiting the conditions under which some areas may average measurements from multiple community-oriented monitors to determine compliance (see 71 FR 61165-61167).

(8) The EPA revoked the annual PM_{10} NAAQS in 2006.

Ambient Size Distribution

Mode	Diameter Range (μm)
Nucleation	< 0.1
Accumulation	0.1 - 2
sub mode 1	~ 0.2
sub mode 2	~ 0.5 - 0.7
Coarse	> 2

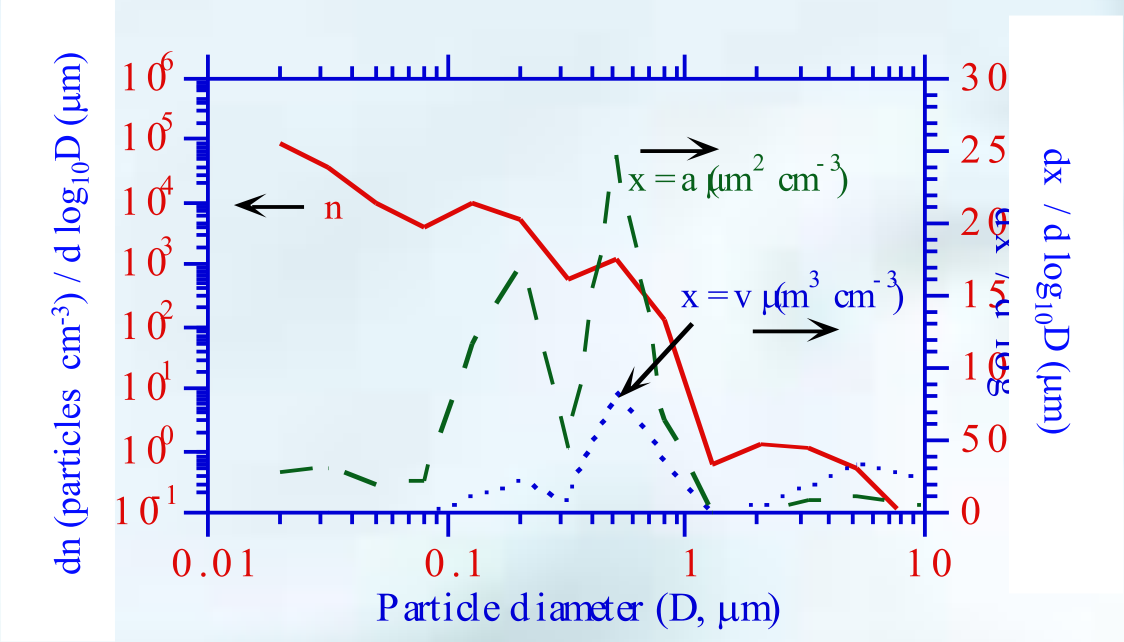


Figure 5.2, Distribution at Claremont, California, August, 1987

Aerosol Particle Composition vs. Size

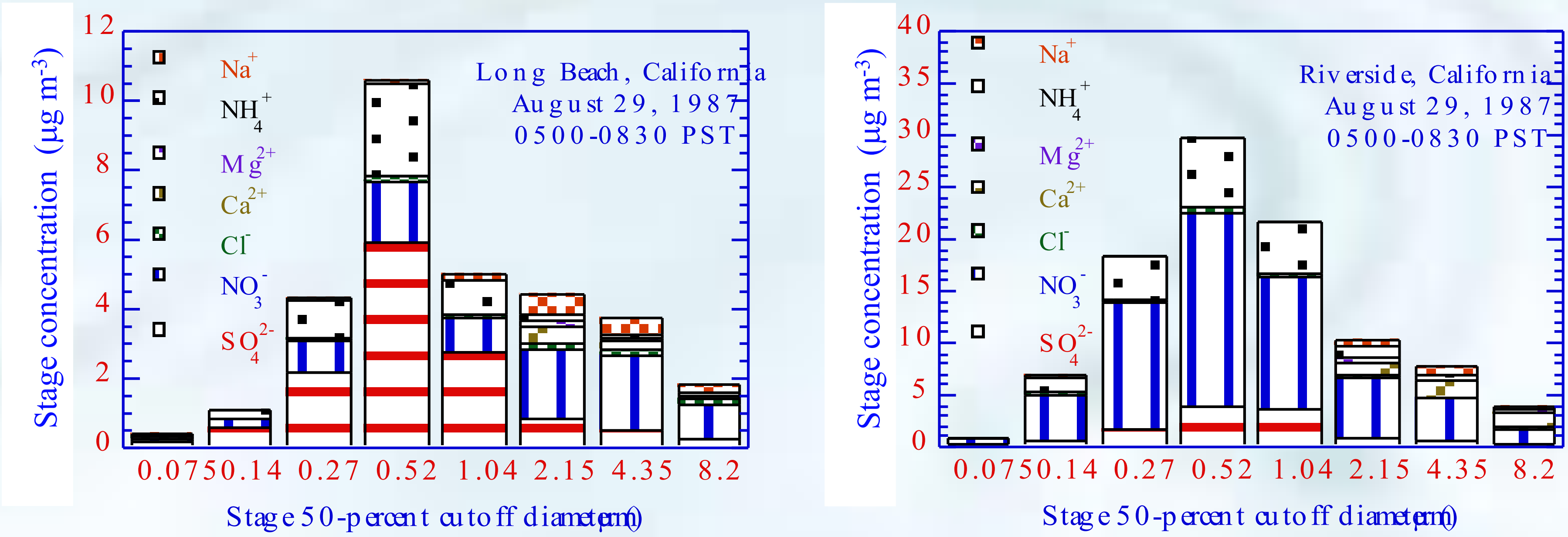


Figure 5.14

Composition and Sources of Particles

Nucleation Mode	Accumulation Mode	Coarse Mode
Nucleation $H_2O(aq)$, SO_4^{2-}, NH_4^+	Fossil-fuel emissions BC, OM, SO_4^{2-}, Fe, Zn	Sea-spray emissions H_2O, Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, Br^-, OM
Fossil-fuel emissions BC, OM, SO_4^{2-}, Fe, Zn	Biomass-burning emissions BC, OM, SO_4^{2-}, Cl^-, Fe, Mn, Zn, Pb, V, Cd, Cu, Co, Sb, As, Ni, Cr	Soil-dust emissions Si, Al, Fe, Ti, P, Mn, Co, Ni, Cr, Na^+, Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, Cl^-, CO_3^{2-}, OM
Biomass-burning emissions BC, OM, SO_4^{2-}, Cl^-, Fe, Mn, Zn, Pb, V, Cd, Cu, Co, Sb, As, Ni, Cr	Industrial emission BC, OM, Fe, Al, S, P, Mn, Zn, Pb, Ba, Sr, V, Cd, Cu, Co, Hg, Sb, As, Sn, Ni, Cr, H_2O, NH_4^+, Na^+, Ca^{2+}, K^+, SO_4^{2-}, NO_3^-, Cl^-, CO_3^{2-}	Biomass-burning ash, industrial fly-ash, tire-particle emissions
Condensation/ dissolution $H_2O(aq)$, SO_4^{2-}, NH_4^+, OM	Condensation/ dissolution $H_2O(aq)$, SO_4^{2-}, NH_4^+, OM	Condensation/ dissolution $H_2O(aq)$, NO_3^-
	Coagulation of all components from nucleation mode	Coagulation of all components from smaller modes

Table 5.6

Photostationary State Ozone

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \qquad (4.1)$$

Nitric oxide   Ozone   Nitrogen dioxide   Molecula oxygen

$$NO_2(g) + \nu h \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \qquad (4.2)$$

Nitrogen dioxide   Nitric oxide   Atomic oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g \qquad (4.3)$$

Ground-   Molecular   Ozon
state atomic oxygen
oxygen

Photostationary State Ozone

$$\chi_{O_3} = (J/N_d k_1)(\chi_{NO_2(g)}/\chi_{NO(g)}) \qquad (4.4)$$

Example 4.1.

Estimate ozone mixing ratio when

$p_d = 1013$ mb

$T = 298$ K

$\chi_{NO(g)} = 5$ pptv

$\chi_{NO_2(g)} = 10$ pptv

$k_1 = 1.8\text{x}10^{-14}$ cm^3 molec.$^{-1}$ s^{-1}

$J = 0.01$ s^{-1}

----> $N_{O_3(g)} = 1.1 \text{ x } 10^{12}$ molec. cm^{-3}

----> $N_d = 2.46 \text{ x } 10^{19}$ molec. cm^{-3}

----> $\chi_{O_3(g)} = 44.7$ ppbv

Daytime Nitrogen Oxide Removal

$$NO_2(g) + OH(g) \xrightarrow{M} HNO_3(g$$

Nitrogen Hydroxyl Nitric
dioxide radical acid

(4.5)

Hydroxyl Radical Production

$$\underset{\text{Ozone}}{O_3(g)} + h\nu \longrightarrow \underset{\text{Molecular oxygen}}{O_2(g)} + \underset{\text{Excited atomic oxygen}}{O(^1D)(g)} \qquad \lambda < 310 \qquad (4.6)$$

$$\underset{\text{Excited atomic oxygen}}{O(^1D)(g)} + \underset{\text{Water vapor}}{H_2O(g)} \longrightarrow \underset{\text{Hydrox radical}}{2\,OH(g} \qquad (4.7)$$

Nighttime Nitrogen Chemistry

$$NO_2(g) + O_3(g) \longrightarrow NO_3(g) + O_2(g) \qquad (4.8)$$

Nitrogen dioxide | Ozone | Nitrate radical | Molecula oxyge

$$NO_2(g) + NO_3(g) \overset{M}{\rightleftharpoons} N_2O_5(g) \qquad (4.9)$$

Nitrogen dioxide | Nitrate radical | Dinitrog pentoxi

$$N_2O_5(g) + H_2O(aq) \longrightarrow 2HNO_3(aq) \qquad (4.10)$$

Dinitrogen pentoxide | Liquid water | Dissolved nitric acid

Ozone Production From Carbon Monoxide

$$CO(g) + OH(g) \longrightarrow CO_2(g) + H(g \qquad (4.11)$$

Carbon Hydroxyl Carbon Atomic
monoxide radical dioxide hydrog

$$H(g) + O_2(g) \xrightarrow{M} HO_2(g) \qquad (4.12)$$

Atomic Molecular Hydropero
hydrogen oxygen radical

$$NO(g) + HO_2(g) \longrightarrow NO_2(g) + OH(g) \qquad (4.13)$$

Nitric Hydroperoxy Nitrogen Hydrox
oxide radical dioxide radical

$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \qquad (4.14)$$

Nitrogen Nitric Atomic
dioxide oxide oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g \qquad (4.15)$$

Ground-Molecular Ozon
state atomic oxygen
oxygen

Ozone Production From Methane

$$CH_4(g) + OH(g) \longrightarrow CH_3(g) + H_2O(g) \tag{4.16}$$

Methane Hydroxyl Methyl Water
radical radical vapor

$$CH_3(g) + O_2(g) \xrightarrow{M} CH_3O_2(g) \tag{4.17}$$

Methyl Molecular Methylpero
radical oxygen radical

$$NO(g) + CH_3O_2(g) \longrightarrow NO_2(g) + CH_3O(g) \tag{4.18}$$

Nitric Methylperoxy Nitrogen Methox
oxide radical dioxide radical

$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \tag{4.19}$$

Nitrogen Nitric Atomic
dioxide oxide oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g) \tag{4.20}$$

Ground-Molecular Ozone
state atomic oxygen
oxygen

Ozone Production From Ethane

$$C_2H_6(g) + OH(g) \longrightarrow C_2H_5(g) + H_2O(g \tag{4.26}$$

Ethane
Hydroxyl radical
Ethyl radical
Water vapo

$$C_2H_5(g) + O_2(g) \xrightarrow{M} C_2H_5O_2\ (g \tag{4.27}$$

Ethyl radical
Molecular oxygen
Ethylpero radical

$$NO(g) + C_2H_5O_2(g) \longrightarrow NO_2(g) + C_2H_5O(g \tag{4.28}$$

Nitric oxide
Ethylperoxy radical
Nitrogen dioxide
Ethox radical

$$NO_2\ (g) + h\nu \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \tag{4.29}$$

Nitrogen dioxide
Nitric oxide
Atomic oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g \tag{4.30}$$

Ground-state atomic oxygen
Molecular oxygen
Ozone

Production of Formaldehyde and Acetaldehyde

Formaldehyde (4.21)

$$CH_3O(g) + O_2(g) \longrightarrow HCHO(g) + HO_2(g)$$

Methoxy radical	Molecular oxygen	Formal-dehyde	Hydropero radical

Acetaldehyde (4.22)

$$C_2H_5O(g) + O_2(g) \longrightarrow CH_3CH(=O) + HO_2(g)$$

Ethoxy radical	Molecular oxygen	Acetaldehyde	Hydropero radical

Ozone From Formaldehyde

$$\underset{\text{Formaldehyde}}{\mathrm{HCHO(g)}} + h\nu \longrightarrow \begin{cases} \underset{\text{Formyl radical}}{\mathrm{HCO(g)}} + \underset{\text{Atomic hydrogen}}{\mathrm{H(g)}} & \lambda < 334 \\[2ex] \underset{\text{Carbon monoxide}}{\mathrm{CO(g)}} + \underset{\text{Molecular hydrogen}}{\mathrm{H_2(g)}} & \lambda < 370 \end{cases} \qquad (4.22)$$

$$\underset{\text{Formaldehyde}}{\mathrm{HCHO(g)}} + \underset{\text{Hydroxyl radical}}{\mathrm{OH(g)}} \longrightarrow \underset{\text{Formyl radical}}{\mathrm{HCO(g)}} + \underset{\text{Water vapor}}{\mathrm{H_2O(g)}} \qquad (4.23)$$

$$\underset{\text{Formyl radical}}{\mathrm{HCO(g)}} + \underset{\text{Molecular oxygen}}{\mathrm{O_2(g)}} \longrightarrow \underset{\text{Carbon monoxide}}{\mathrm{CO(g)}} + \underset{\text{Hydropero radical}}{\mathrm{HO_2(g)}} \qquad (4.24)$$

$$\underset{\text{Atomic hydrogen}}{\mathrm{H(g)}} + \underset{\text{Molecular oxygen}}{\mathrm{O_2(g)}} \xrightarrow{M} \underset{\text{Hydropero radical}}{\mathrm{HO_2(g)}} \qquad (4.25)$$

--> Form O_3 from both CO and HO_2

PAN Production From Acetaldehyde

$$CH_3CH(=O)(g) + OH(g) \longrightarrow CH_3C(=O)(g) + H_2O(g) \qquad (4.32)$$

Acetaldehyde Hydroxyl radical Acetyl radical Water vapo

$$CH_3C(=O)(g) + O_2(g) \xrightarrow{M} CH_3C(=O)O_2(g \qquad (4.33)$$

Acetyl radical Molecular oxygen Peroxyacety radical

$$CH_3C(=O)O_2(g) + NO_2(g) \overset{M}{\rightleftharpoons} CH_3C(=O)O_2NO_2(g) \qquad (4.34)$$

Peroxyacetyl radical Nitrogen dioxide Peroxyacetyl nit (PAN)

Ozone Production From Acetaldehyde

$$\underset{\text{Peroxyacetyl radical}}{CH_3C(=O)O_2(g)} + \underset{\text{Nitric oxide}}{NO(g)} \longrightarrow \underset{\text{Acetyloxy radical}}{CH_3C(=O)O(g)} + \underset{\text{Nitroge dioxid}}{NO_2(g)} \qquad (4.35)$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO(g)} + h\nu \longrightarrow \underset{\text{Methyl radical}}{CH_3(g)} + \underset{\text{Formyl radical}}{HCO(} \qquad (4.36)$$

--> Form O_3 from NO_2, CH_3, and HCO

Photochemical Smog Formation

$$NO(g) + RO_2(g) \longrightarrow NO_2(g) + RO(g \quad (4.37)$$

Nitric oxide | Organic peroxy radical | Nitrogen dioxide | Organi oxy radical

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \quad (4.38)$$

Nitric oxide | Ozone | Nitrogen dioxide | Molecula oxyge

$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \quad (4.39)$$

Nitrogen dioxide | Nitric oxide | Atomic oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g \quad (4.40)$$

Ground-state atomic oxygen | Molecular oxygen | Ozon

Source/Receptor Regions in Los Angeles

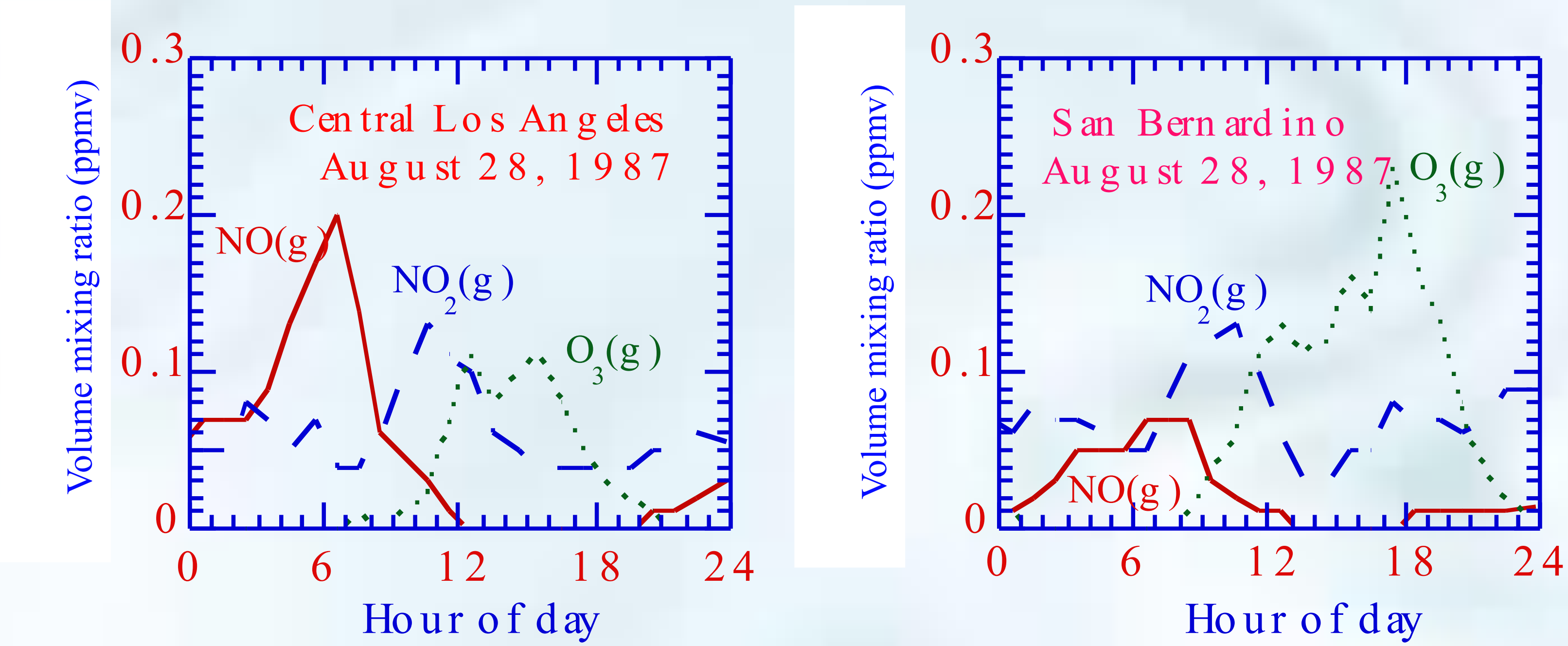


Figure 4.10

Daily Emissions in Los Angeles (1987)

Substance	Emissions (tons day^{-1})	Percent of total
Carbon monoxide [CO(g)]	**9796**	**69.3**
Nitric oxide [NO(g)]	754	
Nitrogen dioxide [NO_2(g)]	129	
Nitrous acid [HONO(g)]	6.5	
Total NO_x(g) + HONO(g)	**889.5**	**6.3**
Sulfur dioxide [SO_2(g)]	109	
Sulfur trioxide [SO_3(g)]	4.5	
Total SO_x(g)	**113.5**	**0.8**
Alkanes	1399	
Alkenes	313	
Aldehydes	108	
Ketones	29	
Alcohols	33	
Aromatics	500	
Hemiterpenes	47	
Total ROGs	**2429**	**17.2**
Methane [CH_4(g)]	**904**	**6.4**
Total Emissions	**14,132**	**100**

Table 4.1, Allen and Wagner, 1992

Percent Emission by Source

Source Category	CO(g)	NO_x(g)	SO_x(g)	ROG
Stationary	2	24	38	50
Mobile	98	76	62	50
Tota l	100	100	100	100

Table 4.2, Chang et al., 1991

Lifetimes of Organic Gases in Urban Air

[OH(g)]

5× × × × ×

ROG Species Photolysis

trans-*2*-Butene	---	52 m	4 y	6.3 d	4 m	17 m
Acetylene	---	3.0 d	---	2.5 y	---	200 d
Formaldehyde	7 h	6.0 h	1.8 h	2.5 y	2.0 d	3200 y
Acetone	23 d	9.6 d	---	---	---	---
Ethanol	---	19 h	---	---	---	---
Toluene	---	9.0 h	---	6 y	33 d	200 d
Isoprene	---	34 m	---	4 d	5 m	4.6 h

Table 4.3

Most Abundant Species in Terms of Abundance and Reactivity

1. *m*- and *p*-Xylene
2. Ethene
3. Acetaldehyde
4. Toluene
5. Formaldehyde
6. *i*-Pentane
7. Propene
8. *o*-Xylene
9. Butane
10. Methylcyclopentane

Table 4.4, Lurmann et al., 1992

Early Morning Source of OH in Polluted Air

$$\mathrm{HONO(g)} + \nu h \longrightarrow \mathrm{OH(g)} + \mathrm{NO(g)} \qquad \lambda < 400\ 1 \qquad (4.42)$$

Nitrous acid

Hydroxy radical

Nitric oxide

Mid-Morning Source of OH in Polluted Air

$$HCHO(g) + h\nu \longrightarrow HCO(g) + H(g) \qquad \lambda < 334 \qquad (4.43)$$

Formal-dehyde	Formyl radical	Atomic hydrogen

$$H(g) + O_2(g) \xrightarrow{M} HO_2(g) \qquad (4.44)$$

Atomic hydrogen	Molecular oxygen	Hydropero radical

$$HCO(g) + O_2(g) \longrightarrow CO(g) + HO_2(g) \qquad (4.45)$$

Formyl radical	Molecular oxygen	Carbon monoxide	Hydropero radical

$$NO(g) + HO_2(g) \longrightarrow NO_2(g) + OH(g) \qquad (4.46)$$

Nitric oxide	Hydroperoxy radical	Nitrogen dioxide	Hydrox radical

Afternoon Source of OH in Polluted Air

$O_3(g) + h\nu \longrightarrow O_2(g) + O(^1D)(g) \qquad \lambda < 310$ (4.47)

Ozone

Molecular oxygen

Excited atomic oxygen

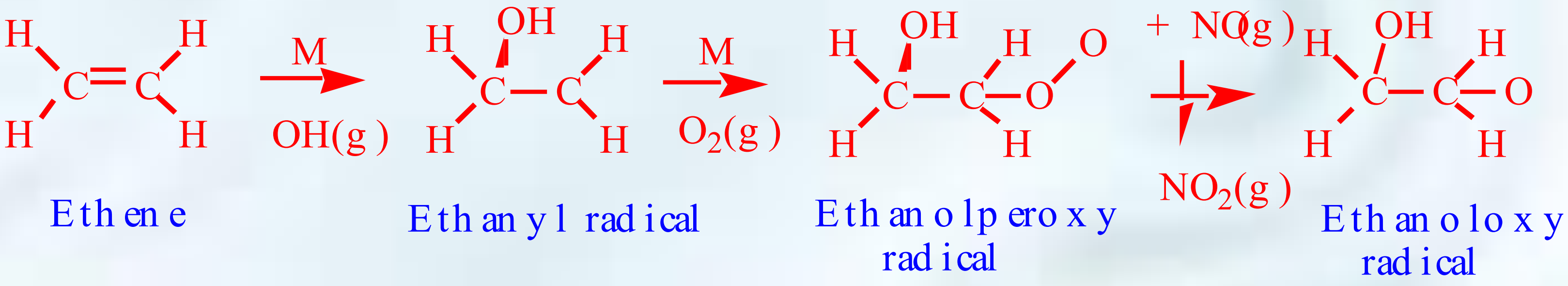
$O(^1D)(g) + H_2O(g) \longrightarrow 2\,OH(g$ (4.48)

Excited atomic oxygen

Water vapor

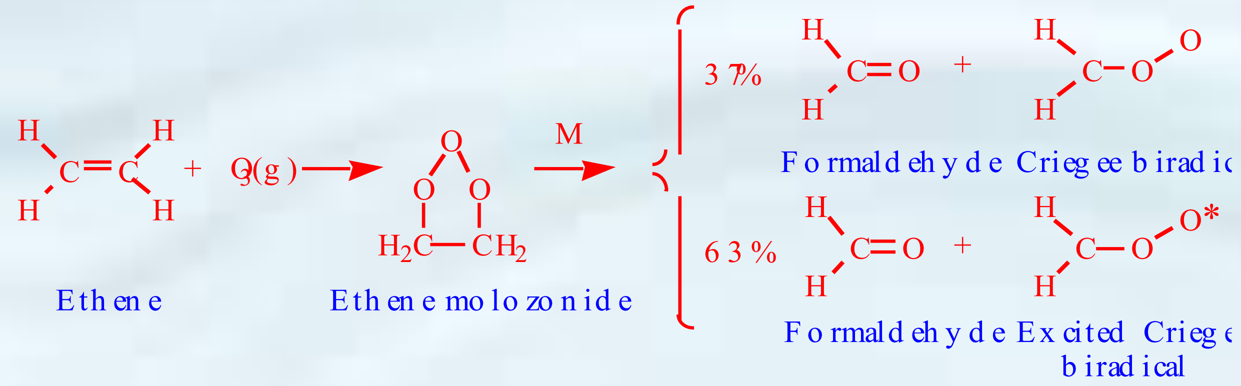
Hydrox radical

Alkene Reaction with OH



(4.49)

Alkene Reaction with Ozone

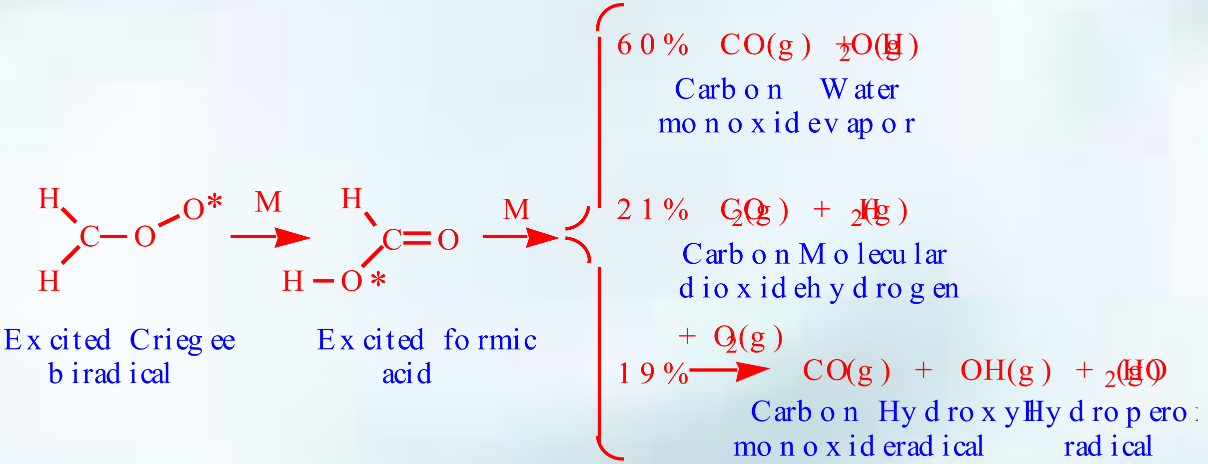


(4.50)

$$H_2COO(g) + NO(g) \rightarrow HCHO(g) + NO_2(g)$$

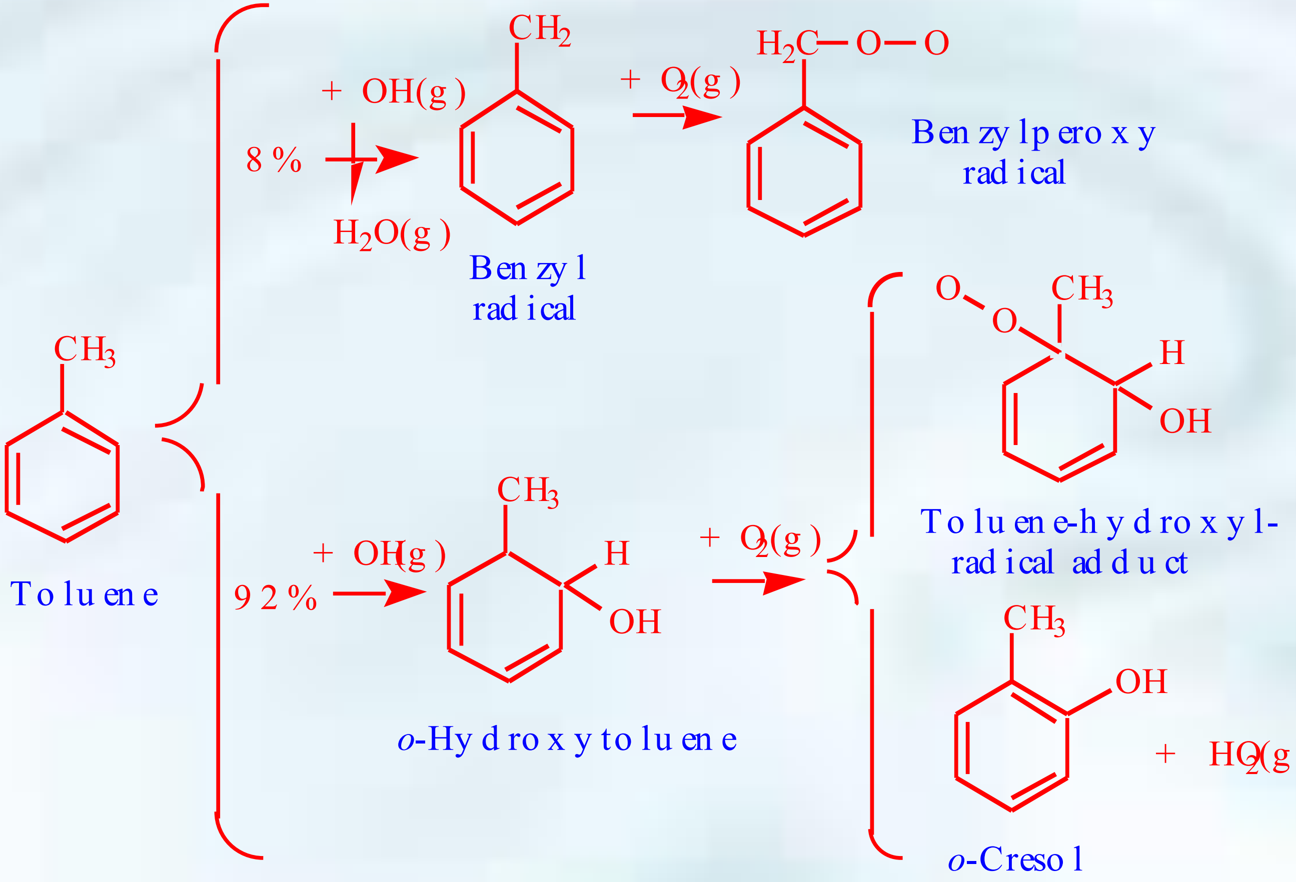
Criegee biradical — Nitric oxide — Formal- dehyde — Nitroge dioxid

(4.51)



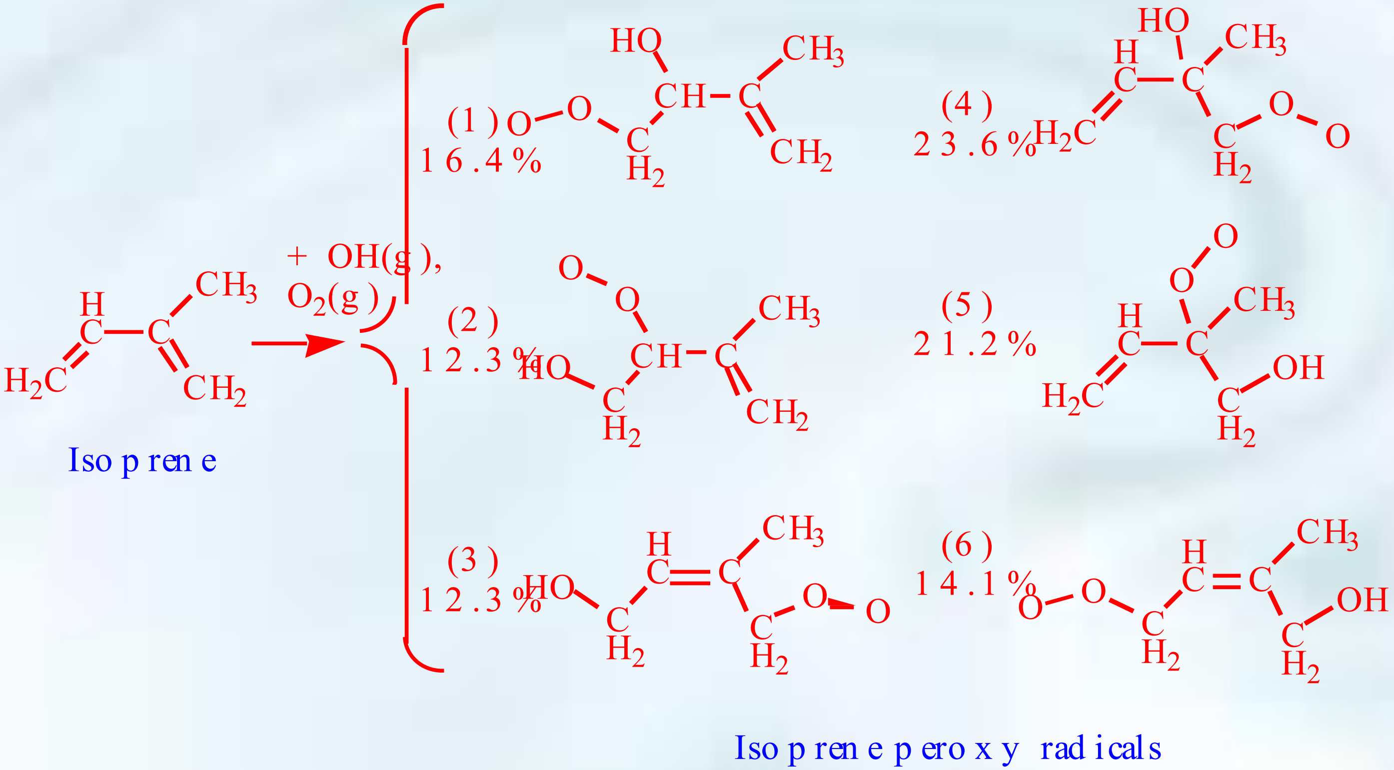
(4.52)

Toluene Reaction with OH



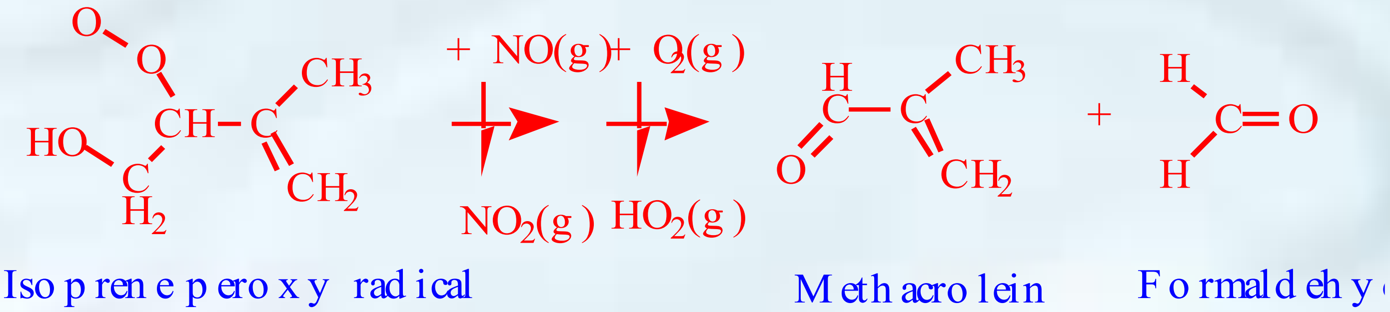
(4.53)

Isoprene Reaction with OH

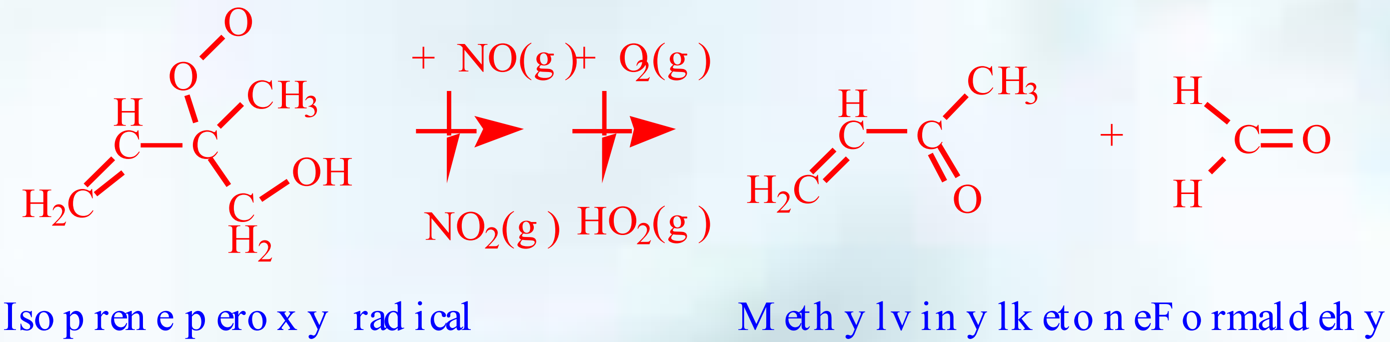


(4.54)

Methacrolein and Methyvinylketone Production

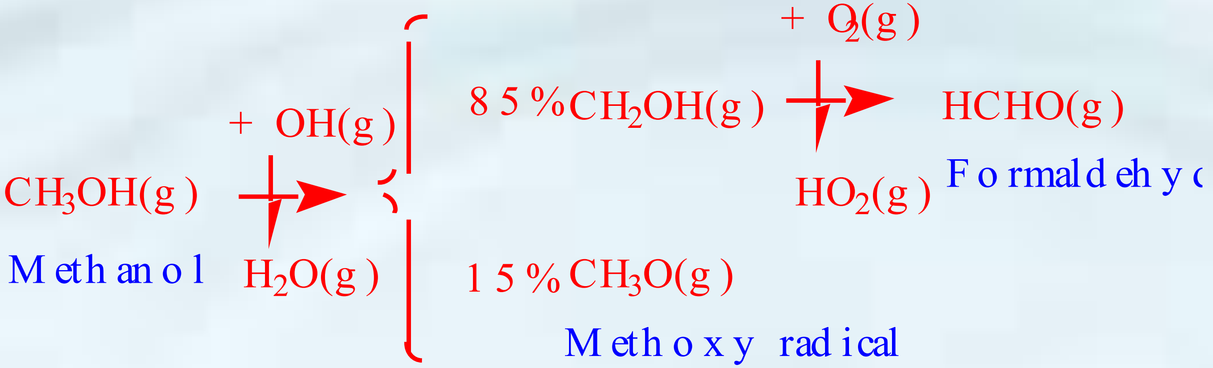


(4.55)



(4.56)

Alcohol Reactions with OH

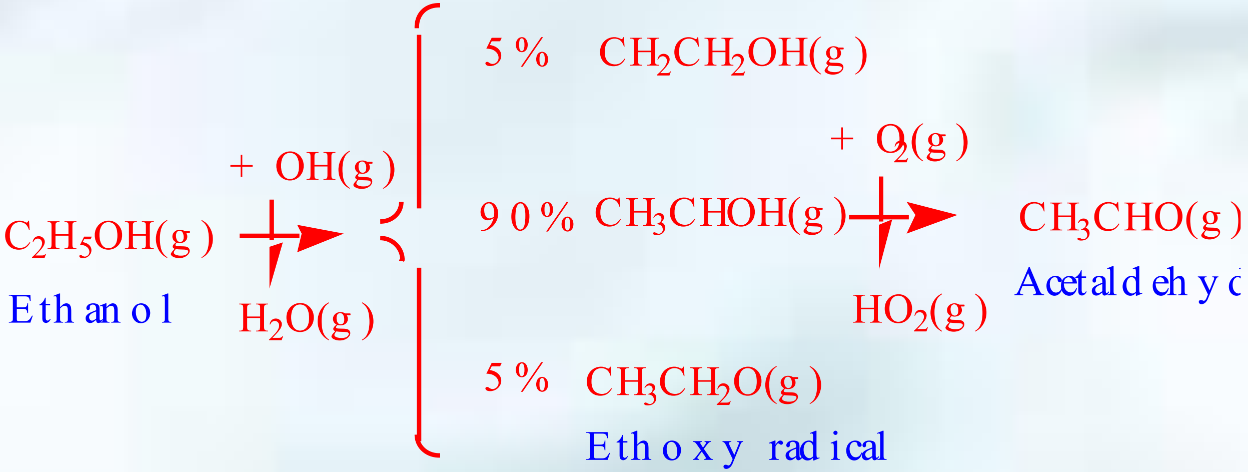


$CH_3OH(g)$ Methanol $\xrightarrow[H_2O(g)]{+\ OH(g)}$

85% $CH_2OH(g) \xrightarrow[HO_2(g)]{+\ O_2(g)} HCHO(g)$ Formaldehy

15% $CH_3O(g)$ Methoxy radical

(4.57)



$C_2H_5OH(g)$ Ethanol $\xrightarrow[H_2O(g)]{+\ OH(g)}$

5% $CH_2CH_2OH(g)$

90% $CH_3CHOH(g) \xrightarrow[HO_2(g)]{+\ O_2(g)} CH_3CHO(g)$ Acetaldehy

5% $CH_3CH_2O(g)$ Ethoxy radical

(4.58)

Chapter 2:

The Sun, the Earth, and the Evolution of the Earth's Atmosphere

Origin of the Sun

15 billion years ago (bya). Big bang. All mass in universe compressed to single point 10^9 kg m^{-3} density, $T=10^{12}$ K

Aggregates of ejected material collapsed gravitationally to form earliest stars.

Temperatures in cores increased due to compressional heating

When temperatures reached 10 million K, nuclear fusion of H into He and other elements began, releasing energy to power the stars.

As early stars aged, they ultimately exploded, ejecting elements to the universe around

Cosmic Abundance of Hydrogen Relative to Other Elements

Element	Atomic Mass	Abundance of H Relative to Element
Hydrogen	1.01	1:1
Helium	4.00	14:1
Oxygen	16.0	1400:1
Carbon	12.0	2300:1
Nitrogen	14.0	11,000:1
Magnesium	24.3	24,000:1
Silicon	28.1	26,000:1
Iron	55.8	29,000:1
Aluminum	27.0	306,000:1
Sodium	23.0	433,000:1

Table 2.1

Origin of the Sun

4.6 bya interstellar material aggregated to form cloudy mass, the solar nebula

Sun formed from gravitational collapse of solar nebula

Today's Sun (90% H, 9.9% He)
- Core (8-15 million K)
- Intermediate interior (5-8 million K)
- Hydrogen convection zone (HCZ) (6400 K - 5 million K)
  - 10 million years for photon to travel from core to top of HCZ
- Photosphere (4000-6400 K, effective 5785 K)
- Chromosphere (4000 K - 1 million K. H energized and decays)
- Corona (1 - 2 million K. Consists of ionized gases)
- Solar wind --> Aurora Borealis and Aurora Australis on Earth
  - 300-1000 km/s, 200,000 K at Earth

Structure of the Sun

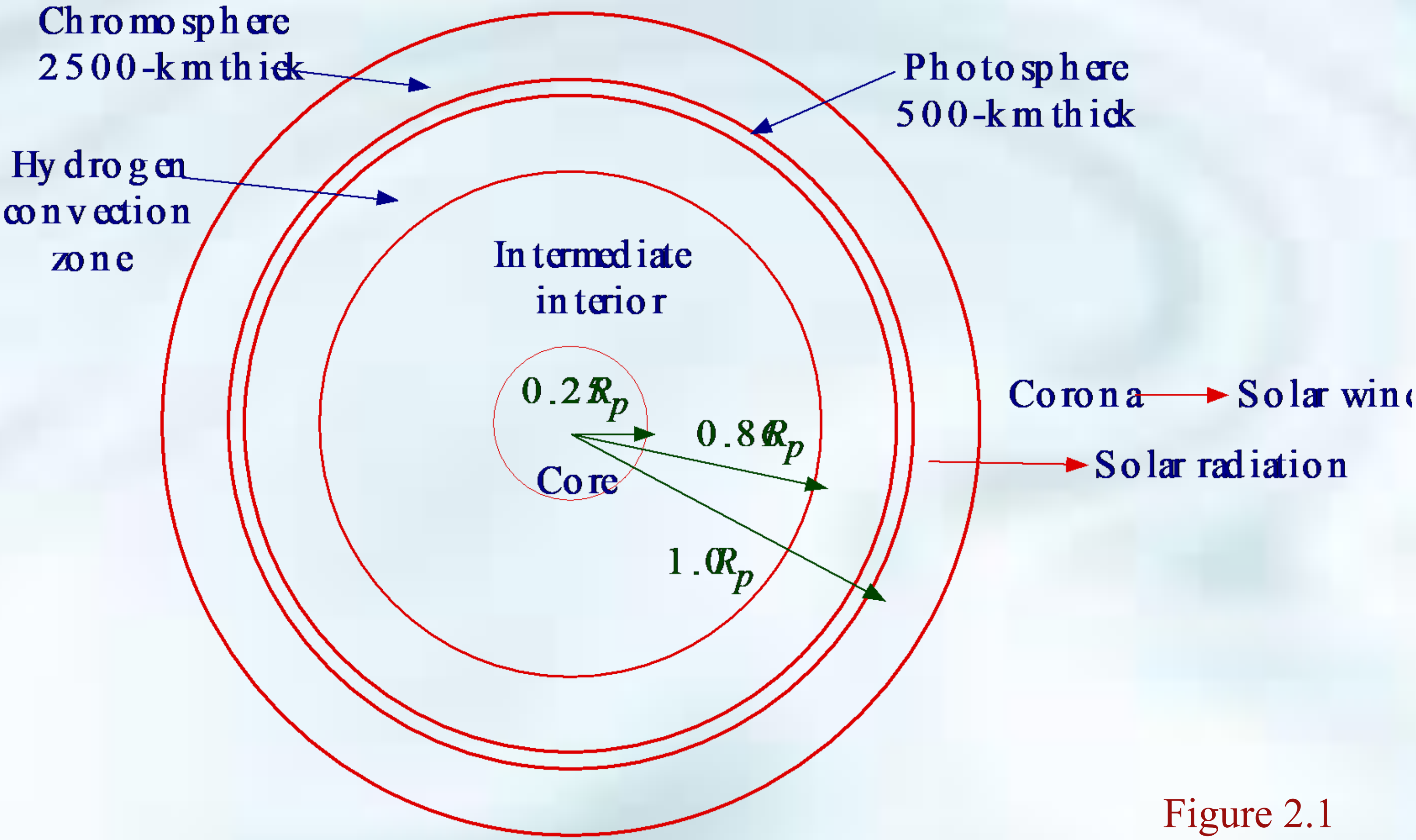


Figure 2.1

Aurora Australis

David Miller, National Geophysical Data Center, available from NOAA Central Library

Radiation Spectra

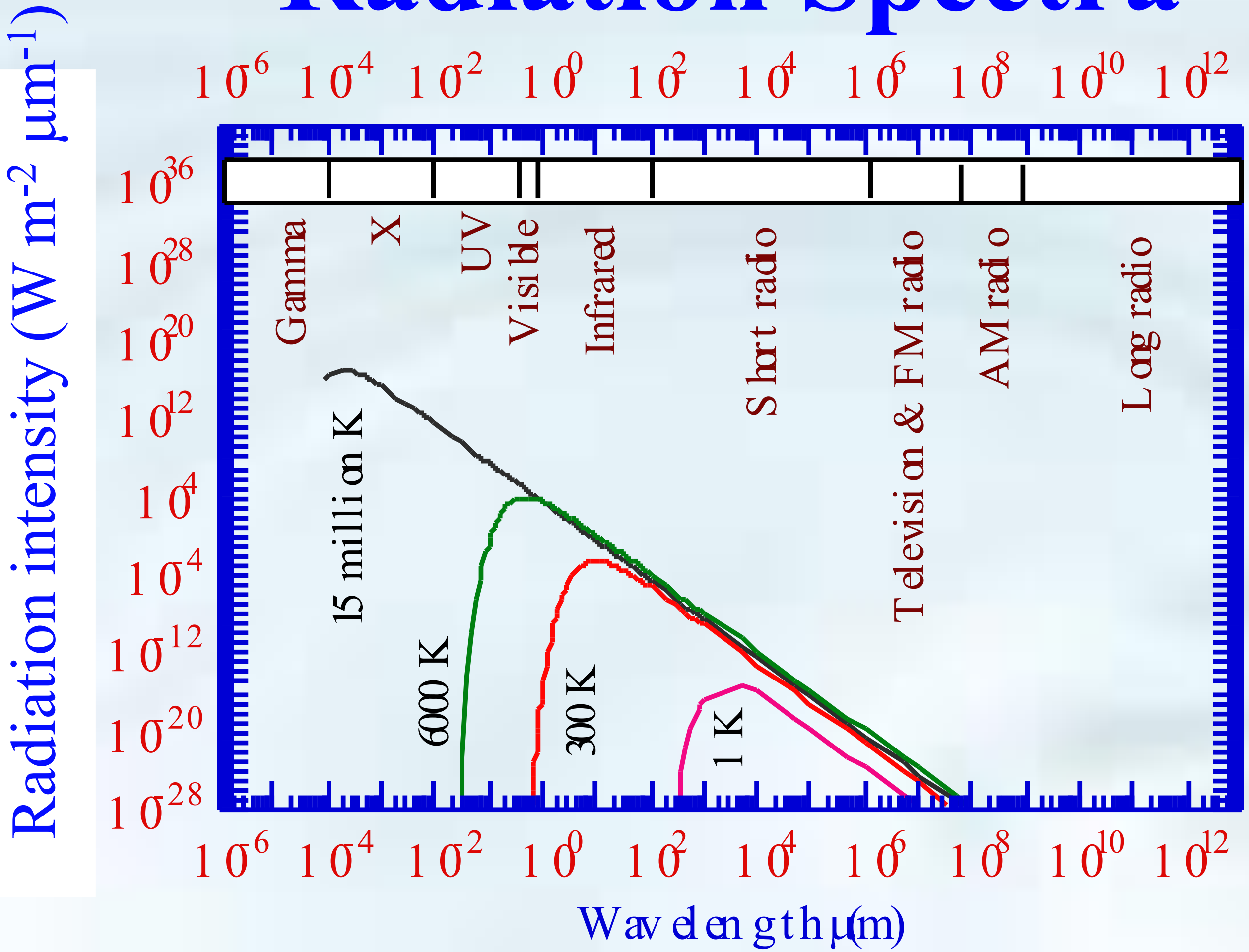


Figure 2.3

Wien's Law (2.1)

$\lambda_p(\mu m) = 2897/T(K)$

Stefan-Boltzmann Law (2.2)

$F_b\,(W/m^2) = \varepsilon\sigma T(K)^4$

Emission Spectra of the Sun and Earth

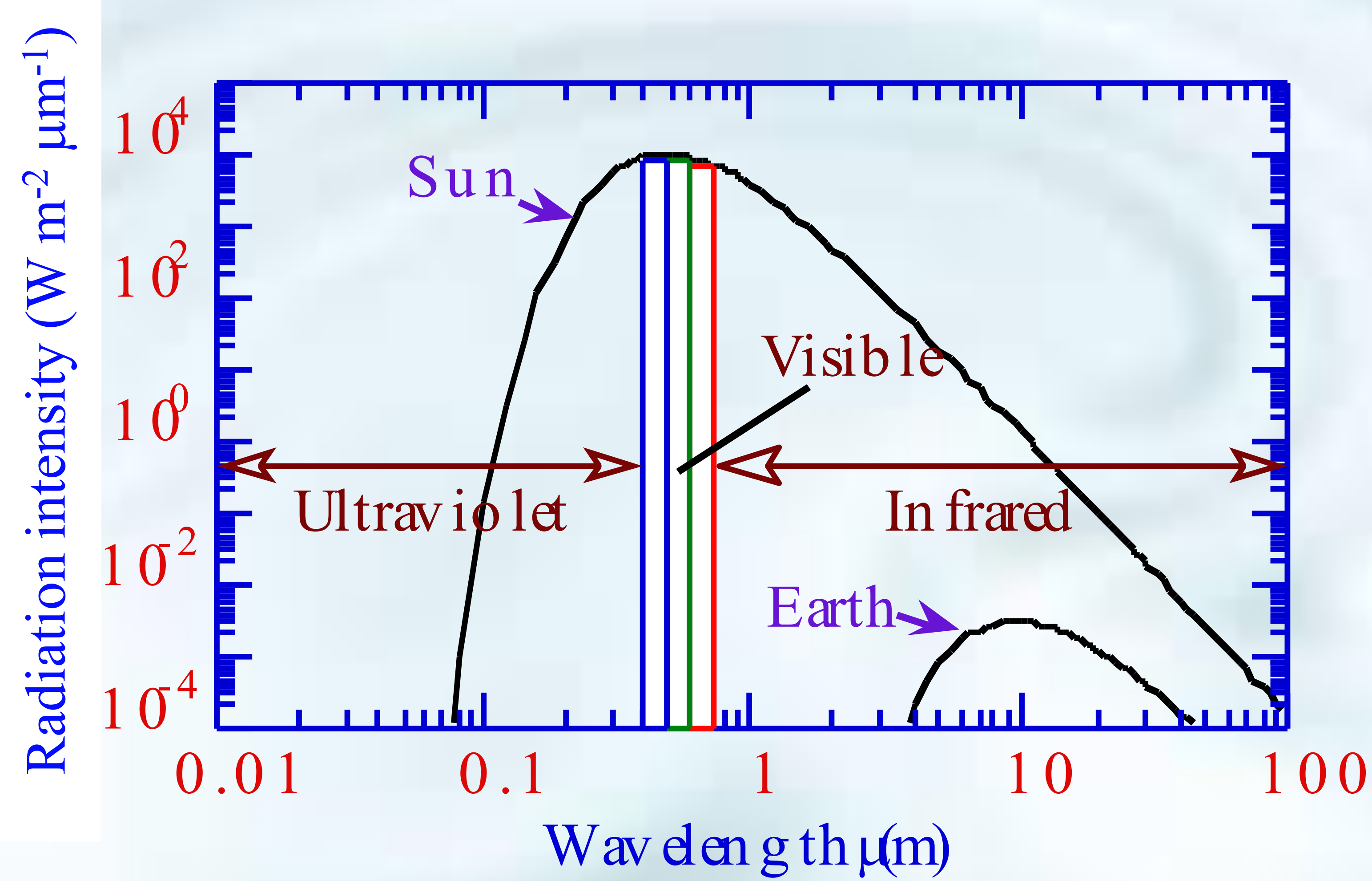


Figure 2.4

Ultraviolet and Visible Spectra of the Sun

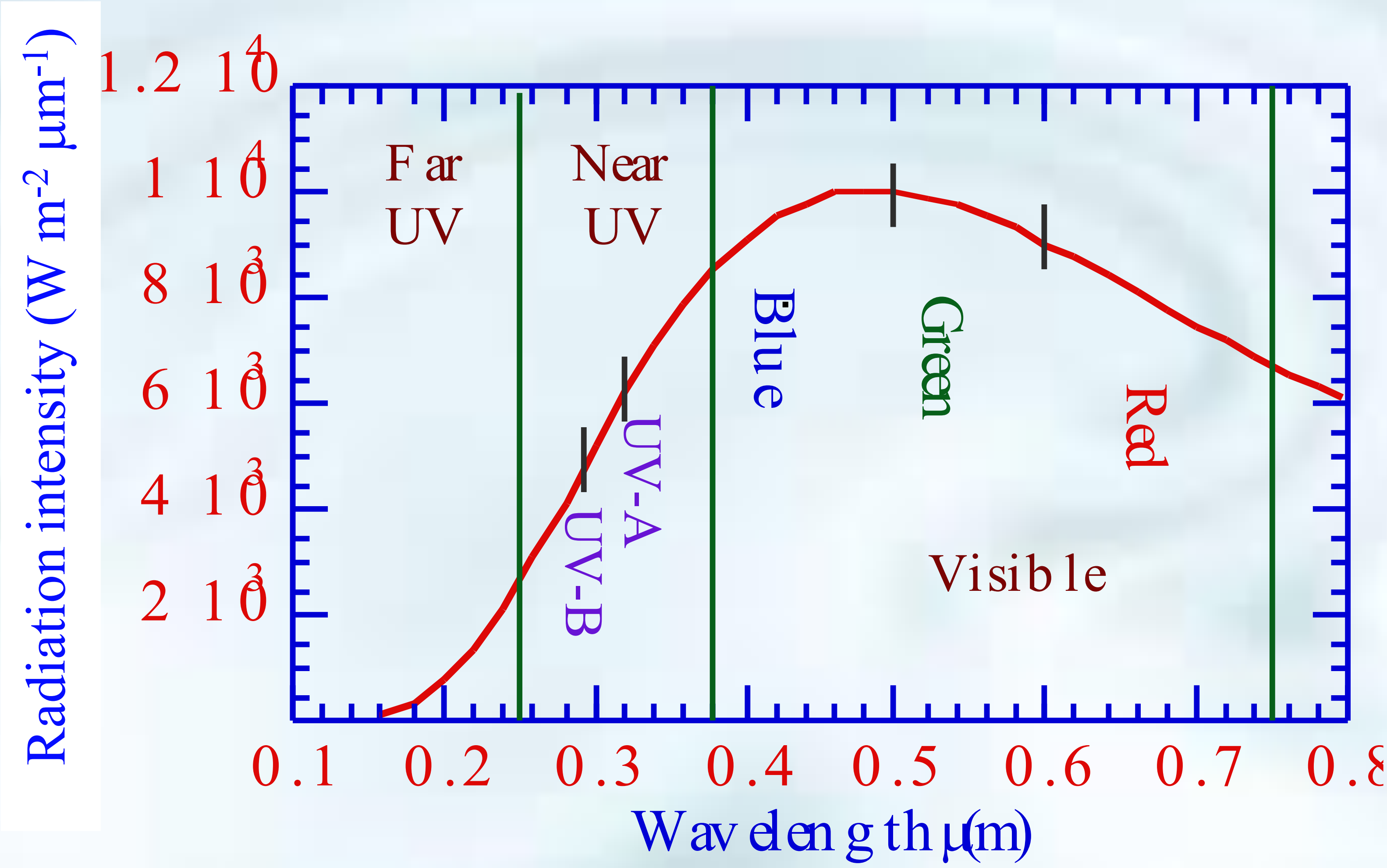


Figure 2.5

Origin of the Earth

4.6 bya, rock-forming elements, which were gases at high temperature in solar nebula, condensed into small solid grains as nebula cooled.

Grains accreted to planetesimals, such as asteroids and comets.

Asteroid: rocky body 1-1000 km in size that orbits sun.

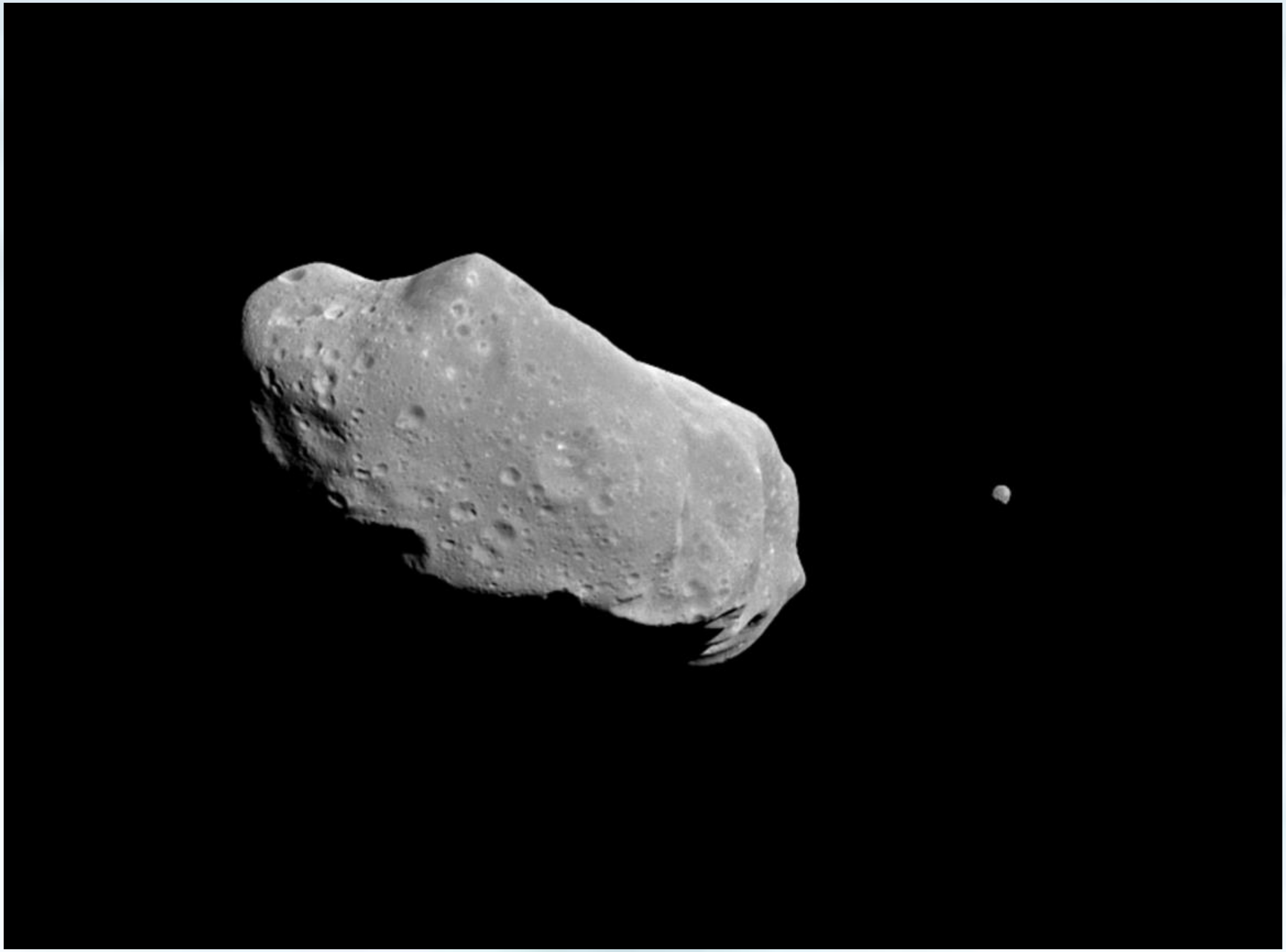
Comet: a small frozen mass that orbits sun

Planetesimals accreted to form the Earth

Meteorite bombardment over 500 million years aided Earth’s growth.

Meteorite: Solid mineral or rock that reaches a planet’s surface without vaporizing.

Asteroid Ida and its Moon, Dactyl



National Space Science Data Center

Meteorite Impacts

Meteorites contained rock-forming elements (Mg, Si, Fe, Al, Ca, Na, Ni) that condensed in solar nebula and noncondensable elements (H, He, O, C, Ne, N, S, Ar, P).

How did noncondensable elements enter meteorites?

They chemically reacted as gases to form high molecular-weight compounds that condensed.

Upon impact with Earth, some noncondensable elements (volatiles) evaporated (volatilized) on impact. Others have volatilized over time and have been outgassed through volcanos, fumaroles, steam wells, geysers.

Composition of Stony Meteorites, Total Earth, and Earth’s Crust

	<---- Mass percent of element in --->			
Element	Stony Meteorites	Total Earth	Soil Crust	Ocean Crust
Oxygen	33.24	29.50	46.6	45.4
Iron	27.24	34.60	5.0	6.4
Silicon	17.10	15.20	27.2	22.8
Magnesium	14.29	12.70	2.1	4.1
Sulfur	1.93	1.93	0.026	0.026
Nickel	1.64	2.39	0.075	0.075
Calcium	1.27	1.13	3.6	8.8
Aluminum	1.22	1.09	8.1	8.7
Sodium	0.64	0.57	2.8	1.9

Table 2.2

Formation of the Earth's Crust

4.5-4 bya, Earth's core hotter than today. Only mechanism of energy escape was conduction (transfer of energy molecule to molecule).

Because conduction is slow, internal energy could not dissipate, so entire Earth became molten and surface was magma ocean.

At that point, energy could be transferred to the surface by convection, the mass movement of molecules.

Convection allowed energy release and cooling at the surface, forming the Earth's crust 4.3-3.8 bya.

Dense elements (Fe, Ni) settled to core. Light ones (Si, Al, Na, Ca) rose to surface. Certain Mg, Fe silicates settled to mantle.

Today, land crust granite (quartz, potassium feldspar). Ocean crust basalt (plagioclase feldspar, pyroxene). Outer core liquid Fe, Ni; inner core solid Fe, Ni

The Earth’s Interior

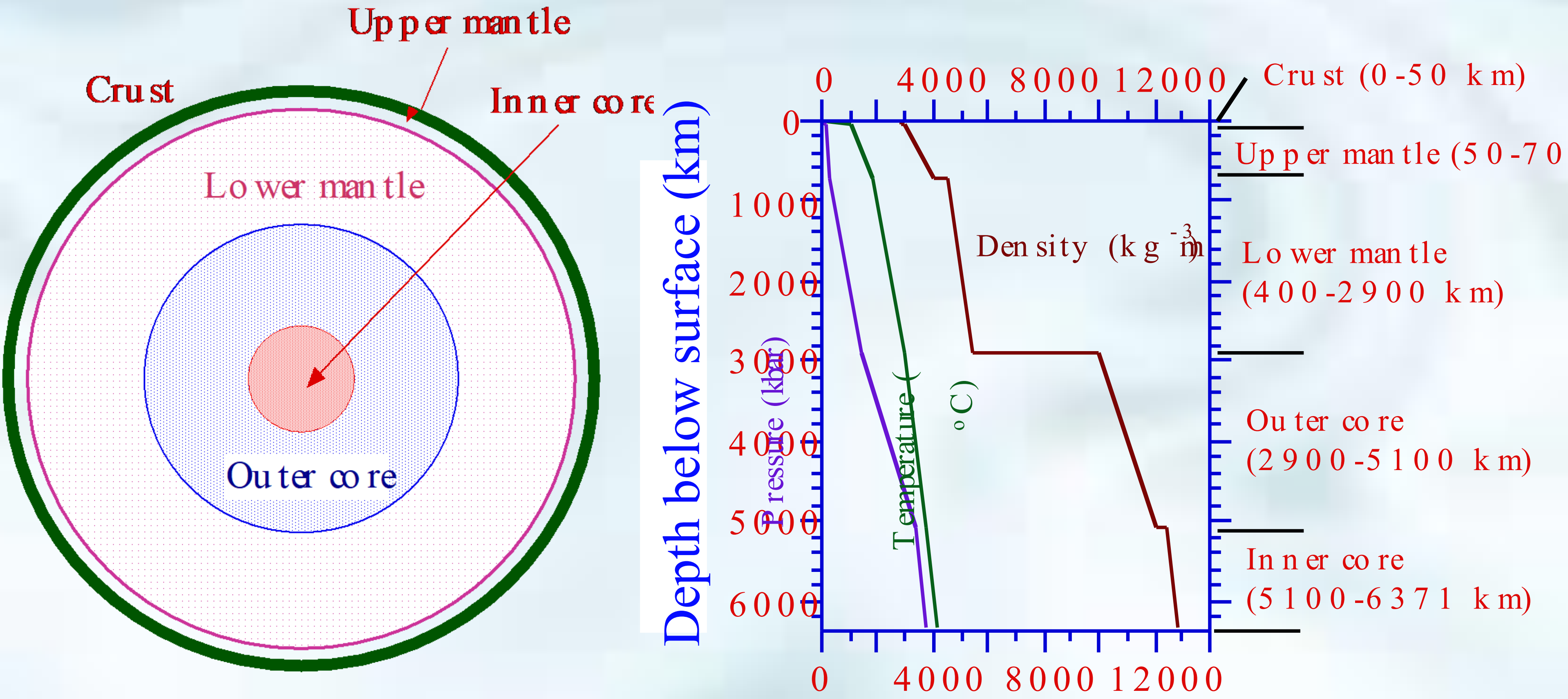


Figure 2.7

Earth's First Atmosphere

Consisted mostly of H, He

During birth of the Sun, nuclear reactions are enhanced, increasing solar wind speeds and densities (T-Tauri stage of solar evolution).

Enhanced solar wind stripped off most H, He from the Earth.

Additional H, He lost by escape from Earth's gravitational field.

Earth's Second Atmosphere

Initially due to outgassing by volcanos, fumaroles, steam wells, geysers.

Hydroxyl molecules (OH) bound in crustal minerals, became detached and converted reduced gases to oxidized gases:

$H_2(g) + OH \dashrightarrow \ldots \dashrightarrow H_2O(g)$

$CH_4(g) + OH \dashrightarrow \ldots. \dashrightarrow CO_2(g)$

$NH_3(g) + OH \dashrightarrow \ldots \dashrightarrow NO(g), NO_2(g)$

$N_2(g) + OH \dashrightarrow \ldots \dashrightarrow NO(g), NO_2(g)$

$H_2S(g) + OH \dashrightarrow \ldots \dashrightarrow SO_2(g)$

Second atmosphere dominated initially by $CO_2(g)$, $H_2(g)$

Outgassed water vapor condensed to form the oceans.

Timeline of Earth’s Evolution

4.6 bya	Formation of the Earth
3.5 bya	Abiotic synthesis, 1953 Miller and Urey

$H_2(g)+H_2O(g)+CH_4(g)+NH_3(g)+H_2O(aq)+$
electricity or UV --> complex organics, amino acids

--> first prokaryotes
single strand of DNA but no nucleus
conventional heterotrophs

Classification of Organisms

Energy Source

Sunlight	Phototroph
Oxidation of inorganic material	Lithotroph
Oxidation of organic material	Conventional heterotroph

Carbon source

Carbon dioxide	Autotroph
Organic material	Heterotroph

*Conventional heterotrophs obtain
Energy and carbon from organic material

Table 2.3

Classification of Organisms

Photoautotrophs

- Green plants, most algae, cyanobacteria, some purple and green bacteria

Photoheterotrophs

- Some algae, most purple and green bacteria, some cyanobacteria

Lithotrophic autotrophs

- Hydrogen bacteria, colorless sulfur bacteria, methanogenic bacteria, nitrifying bacteria, iron bacteria

Lithotrophic heterotrophs

- Some colorless sulfur bacteria

Conventional heterotrophs

- Animals, fungi, protozoa, most bacteria

Table 2.4

Hot Sulfur Springs in Lassen National Park

Lithotrophic autotrophs oxidize $H_2S(aq)$ to $H_2SO_4(aq)$, which dissolves minerals into a “mud pot.” Alfred Spormann, Stanford University

CO_2(g) and CH_4(g) From Bacteria

Anaerobic respiration: production of energy from food where electron acceptor is not oxygen.

CO_2(g) by fermentation (2.3)

$$C_6H_{12}O_6(aq) \longrightarrow 2\,C_2H_5OH(aq) + 2\,CO_2(g$$

Glucose Ethanol Carbo
dioxi

CH_4(g) by methanogenesis (lithotrophic autotrophs) (2.4)

$$4\,H_2(g) + CO_2(g) \longrightarrow CH_4(g) + 2\,H_2O(aq)$$

Molecular hydrogen Carbon dioxide Methane Liqui
water

Evolution of Molecular Nitrogen

4.6 bya $N_2(g)$ by ammonia photolysis (2.5-2.6)

$$NH_3(g) + h\nu \longrightarrow N(g) + 3H$$

Ammonia

Atomic nitrogen

Atomic hydrog

$$N(g) + N(g) \xrightarrow{M} N_2(g)$$

Atomic nitrogen

Molecula nitrogen

Evolution of Molecular Nitrogen

3.2 bya Denitrification: 2-step process

$N_2(g)$ by anaerobic respiration (2.7-2.8)
(conventional heterotrophs)

Organic compound $+ NO_3^- \rightarrow CO_2(g) + NO_2^- +$

Nitrate ion Carbon dioxide Nitrite ion

Organic compound $+ NO_2^- \rightarrow CO_2(g) + N_2(g) +$

Nitrite ion Carbon dioxide Molecular nitrogen

Photosynthesis

Anoxygenic photosynthesis (photoautotrophs)   (2.9)

$$CO_2(g) + 2H_2S(g) + h\nu \longrightarrow CH_2O(aq) + H_2O(aq) + 2S($$

Carbon dioxide	Hydrogen sulfide	Carbo- hydrate	Liquid water	Atomi sulfur

2.3 bya   Oxygenic photosynthesis (cyanobacteria)   (2.10)

1.4 bya   Oxygen levels still 1% of today

0.395-0.43 bya   Green plant photosynthesis

$$6CO_2(g) + 6H_2O(aq) + h\nu \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

Carbon dioxide	Liquid water	Glucose	Molecul oxygen

Photsynthesis in chlorophylls *a*,*b* :pigments that absorb visible

Chlorophyll *a*. Absorbs red more efficiently

Chlorophyll *b*. Absorbs blue more efficiently

Hot Spring in Yellowstone National Park

Different colored photosynthetic cyanobacteria grow at in hot spring due to different temperatures. Alfred Spormann, Stanford University

Aerobic Respiration

O_2(g) reacts with organic cell material to produce energy during cellular respiration, which is oxidation of organics in living cells.

$$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(aq) \qquad (2.12)$$

Glucose	Molecular oxygen	Carbon dioxide	Liquid water

Aerobic respiration developed first in prokaryotes (bacteria, blue-green algae), but spread with the advent of eukaryotes.

Eukaryote. Cell containing DNA surrounded by a true membrane-enclosed nucleus. Cells of higher organisms all eukaryotic.

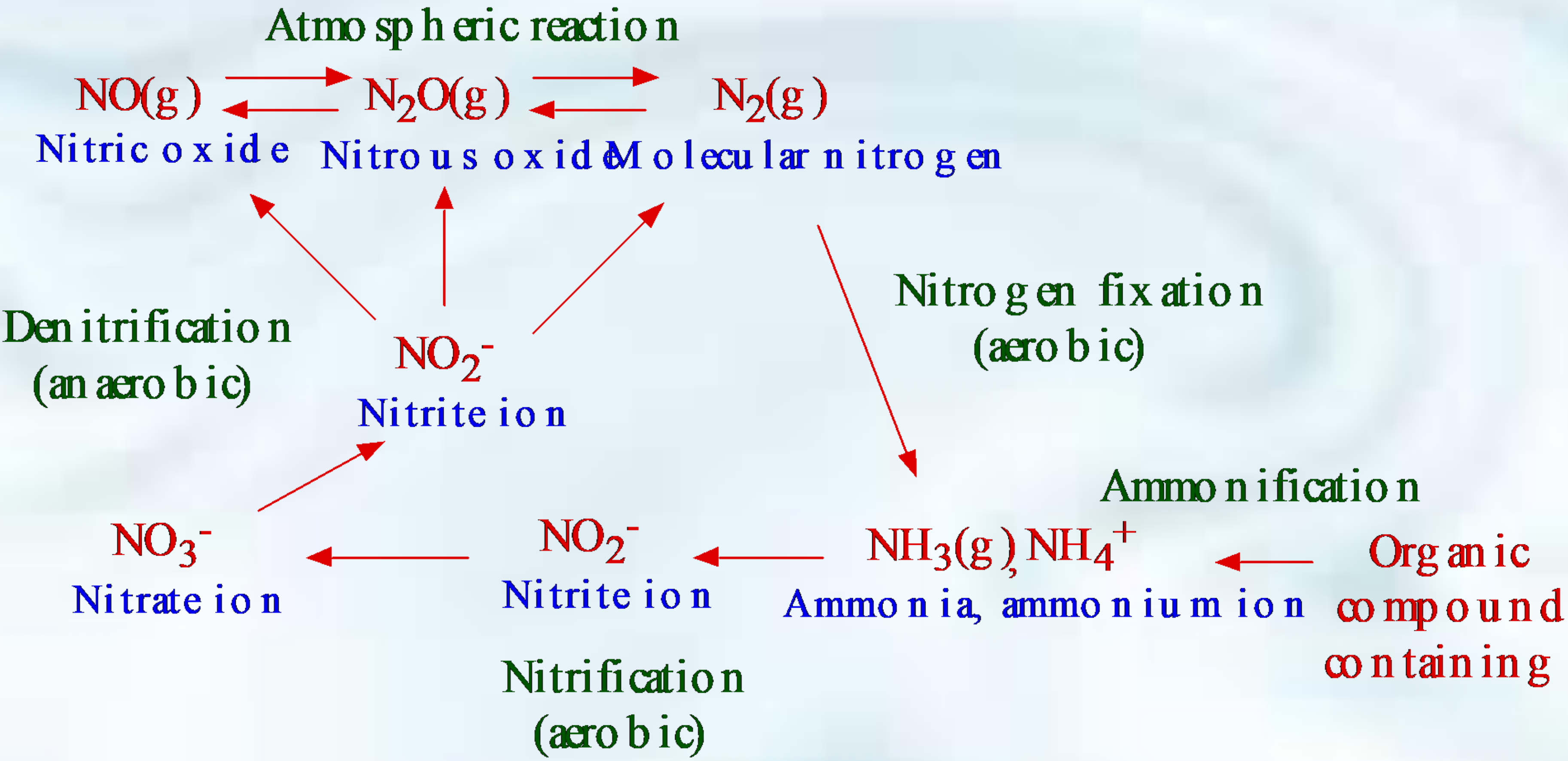
Eukaryotic cells usually switch from fermentation to aerobic respiration when oxygen reaches 1% of present levels --> Eukaryotes developed about 1.4 bya, after oxygen rose to 1%

Timeline of Earth’s Evolution

4.6 bya	Formation of the Earth
3.5 bya	Abiotic synthesis,
3.2 bya	Denitrification
2.3 bya	Oxygen-producing photosynthesis by cyanobacteria
	Start of ozone formation
1.8 bya	Nitrification (aerobic)
1.5 bya	Nitrogen fixation (aerobic)
1.4 bya	Earliest eukaryotes
0.57 bya	First shelled invertebrates
0.43-0.5 bya	Primitive fish
0.395-0.43 bya	First land plants -- oxygen and ozone increase

Figure 2.8

The Nitrogen Cycle



Atmospheric reaction

$NO(g)$
Nitric oxide

$N_2O(g)$
Nitrous oxide

$N_2(g)$
Molecular nitrogen

Denitrification
(anaerobic)

NO_2^-
Nitrite ion

Nitrogen fixation
(aerobic)

Ammonification

NO_3^-
Nitrate ion

NO_2^-
Nitrite ion

$NH_3(g)$, NH_4^+
Ammonia, ammonium ion

Organic
compound
containing

Nitrification
(aerobic)

Figure 2.11

Evolution of the Earth's Second Atmosphere

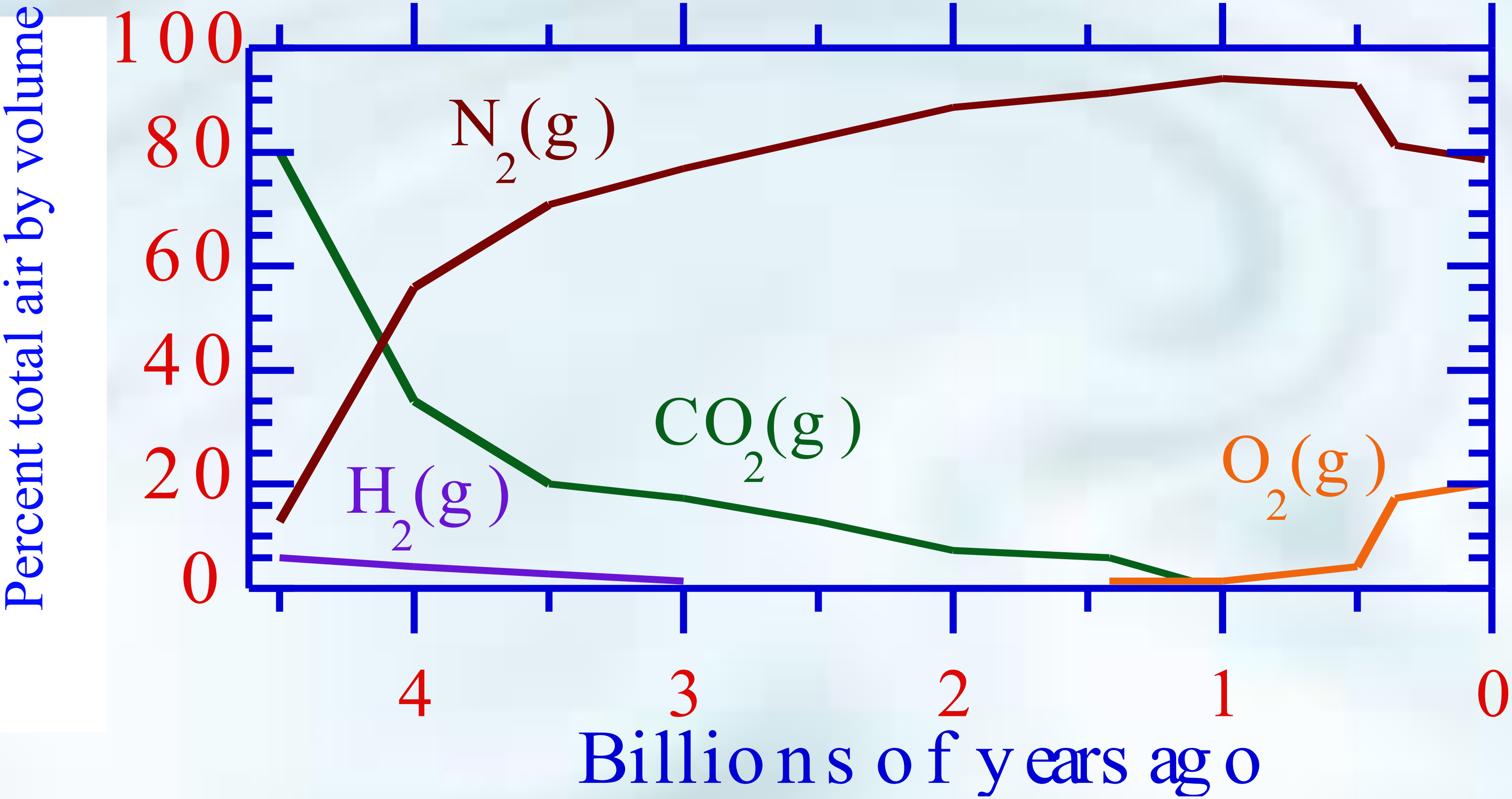


Figure 2.12