## **Global Cycles**

- Your package includes diagrams from:
  - Brasseur
  - Manahan
  - Safe (unpublished)
- Will consider global cycles for:
  - Energy
  - Water (Hydrologic cycle)
  - Carbon
  - Nitrogen
  - Oxygen
  - Phosphorous
  - Sulphur
- All these cycles are coupled:
  - To each other
  - To anthropogenic impacts
  - To climatic impacts

# **Energy Cycle**

- The two main sources of energy are:
  - The Sun
  - The Earth
- Each of these may be treated as a blackbody radiator:

$$\rho(\lambda;T)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} d\lambda$$

• This integrates to:

$$\int_{0}^{\infty} \rho(\lambda; T) d\lambda = \frac{8\pi^{5}}{15} \frac{(kT^{4})}{(hc)^{3}} = \eta T^{4}$$

- Radiation from the sun that reaches the earth is insolation and is expressed as radiative flux in units of W m<sup>-2</sup> where 1 W = 1 J s<sup>-1</sup>
  - Energy flux intercepted by the earth is 1370 W m<sup>-2</sup>
  - $\bullet\,$  Energy flux captured by the earth is 342 W m  $^{-2}$
- The energy cycle is coupled to the hydrologic cycle by the thermal properties of water.
  - Water requires energy to undergo phase transitions.

$$\Delta H_{fus} = 6.008 \text{ kJ mol}^{-1}$$
$$\frac{C_p(l)}{R} = 12.16 - 1.943 \times 10^{-2}T + 3.042 \times 10^{-5}T^2$$

 $\Delta H_{vap} = 40.66 \text{ kJ mol}^{-1}$  $C_p(g) = 33.59 \text{ J mol}^{-1} \text{ K}^{-1}$ 

- The energy cycle is coupled to the carbon cycle by:
  - Photosynthesis (which is also essential for nitrogen and phosphorous fixation.
  - Burning of fossil fuels.
- Sources of energy are well-defined
  - $\bullet\,$  Sun and earth
- Sinks of energy include:
  - Photosynthesis
  - Thermal absorption
  - $\bullet$  Chemical
  - Mechanical
  - Reflection
  - Scattering
- The atmosphere has a significant role in the energy cycle because it is where absorption and scattering occur.

## Water Cycle (or Hydrologic cycle)

- In the energy cycle we have already discussed the thermodynamic properties of water.
  - Because of these thermodynamic properties, water acts as a thermal buffer, especially at temperatures near the freezing point.
- Examination of a phase diagram for water indicates the temperature and pressure for coexistence of phases.
  - It is from this diagram that relative humidity, dew point and frost point may be determined.
  - For a given T, the relative humidity is:

$$\frac{P_{actual}(H_2O)}{P_{equilibirum}(H_2O)}$$

- The dew point or the frost point is the temperature at which the ambient  $P(H_2O)$  becomes the  $P_{equilibirum}(H_2O)$
- As a saturated air mass cools it must lose water by precipitation.
- Reservoirs and fluxes for the hydrologic cycle include:

Reservoir	$10^{6} \rm ~km^{+3}$	Fluxes
Ground water	8	precipitation
Surface water	0.1 (Lakes) 0.1 (Salt lakes)	evaporation

## 0.001 (Rivers)

Snow & Ice		transpiration.
Clouds & Vapour	0.013	cloud momentum
Oceans	1350	run off
Glaciers & icecaps	29	movement of moist air

## Soil Moisture 0.07

- The hydrosphere is defined as where water is found.
- The lithosphere is defined as the portion of the geosphere that is accessible to water.
- Water is a significant factor in human history.
  - Denial of access to water is a tool of war, siege, and oppression.
  - Movement of nomadic peoples often correlated with the availability of water.
  - Presence of water is a significant factor in human settlement patterns.
  - Increasing important issue in international trade.
- Water is an economic factor for:
  - Transport
  - Coolant
  - Raw Material
- Anthropogenic impacts on water include:
  - Contamination
  - Warming
  - Salinization

#### Impact of Water Usage

- For the United States of America
  - Precipitation is  $1.48 \times 10^{13} \text{ L day}^{-1}$
  - Evaporation is  $1.02 \times 10^{13} \text{ L day}^{-1}$
  - which leaves  $4.6 \times 10^{12} \text{ L day}^{-1}$
- Daily usage in the USA has evolved with time:

Usage	$L day^{-1}$	$L day^{-1} capita^{-1}$ (Domestic Use)
2002		1200
1990	$1.6\times10^{12}$	600
1900	$1.7 \times 10^{11}$	40

- This usage breaks down as:
  - 46 % agricultural
  - 46% industrial
  - 8% municipal
- The impact of this usage has caused:
  - The depletion of the Ogallala aquifer
  - Salinization of irrigated soils
  - Desertification
  - Deterioration of water quality
- Precipitation is irregularly distributed.
  - Linked to terrain and energy transfer.
- The likelihood of precipitation is linked to the thermal lapse rate.

Lapse Rate = 
$$\frac{\Delta T}{\Delta h}$$

where h is altitude.

- Warm air rises and cools.
- $\bullet\,$  For dry air undergoing an adiabatic expansion, the lapse rate is 10° C/km.
- $\bullet\,$  For moist air undergoing an adiabatic expansion, the lapse rate is 6° C/km.
- The difference is due to the heat capacity of water.
- The difference in lapse rates can contribute to the forming of thermal inversion as wet air moves over dry air.
- Inversions occur when warm air rest on top of cooler air.
  - Traps vertical circulation patterns.
  - Decreases mixing volumes for ground level emissions.
- Inversions can also be caused by the difference in the heat capacity of air and ground.
  - These are radiation inversions.
- Another type of inversion is a subsidence inversion when high air drops, compresses, and warms.
- Marine inversions are due to the difference in heat capacity of the ocean and land.
  - Land warms more rapidly than ocean.
  - Cool air from the ocean moves under the warmer air originally over the land mass.

## The Carbon Cycle

- Consider the oxidation states of carbon.
  - The range of oxidation states is determined by the ground state electronic configuration of the C atom,  $1s^22s^22p^2$ .
  - Carbon must either gain four electrons or lose four electrons to have a closed shell configuration.
  - Range of oxidation states is therefore +4 to -4.

- Some examples of oxidation state of carbon:
  - $CO_2$  is in oxidation state +4.
  - CO is in oxidation state +2.
  - HCO is in oxidation state +1.
  - H<sub>2</sub>CO, C(graphite), C(diamond) are in oxidation state 0.
  - $C_2H_2$  is in oxidation state -1.
  - $C_2H_4$  is oxidation state -2.
  - CH<sub>3</sub> is in oxidation state -3.
  - CH<sub>4</sub> is in oxidation state -4.
- Carbon fixation puts carbon into biologically available forms.
  - Photosynthesis uses 8 photons to drive the reaction:

$$8CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

which requires 2801.3 kJ per mole of glucose (467 kJ per mole of carbon).

- Photosynthesis is coupled to the energy cycle by the phosphorous cycle.
- The CO<sub>2</sub> cycle is coupled to the hydrologic and energy cycle.
  - Before 1800, the level of atmospheric CO<sub>2</sub> was about 280 ppm.
  - The 1800's saw the beginning of the industrial revolution and increased use of fossil fuel.
  - In 1994, atmospheric  $CO_2$  was observed to be 358 ppm.
- The global budget of CO<sub>2</sub> has not been fully determined.

 $CO_2(atmospheric) + H_2O \rightarrow solubilized speciated C(IV)$ 

$$CO_{2}(g) \rightleftharpoons CO_{2}(aq)$$
$$CO_{2}(aq) + H_{2}O \rightleftharpoons H_{2}CO_{3}(aq)$$
$$H_{2}CO_{3}(aq) \rightleftharpoons HCO_{3}^{-}(aq) + H^{+}(aq)$$
$$HCO_{3}^{-} \rightleftharpoons CO_{3}^{2-} + H^{+}$$

- $CO_3^{2-}$  precipitates and is incorporated into shells of aquatic animals such as coral.
- Organic carbon comprises oxidation states 0 to -4.
  - Living organic carbon may be represented as  $\{CH_2O\}$
  - Fossil organic carbon is reduced and may be represented as  $(CH_2)_n H_2$  and is produced by biogeochemical processes.
- Reservoirs of organic carbon include:
  - Oceans with  $5.8 \times 10^{14}$  moles of carbon in biomass,  $5 \times 10^{15}$  moles C as suspended {CH<sub>2</sub>O} particles,  $5.8 \times 10^{16}$  moles C as dissolved organic carbon.
  - By comparison, oceans contain  $3.2 \times 10^{18}$  moles of C as C(IV).
  - On land,  $4 \times 10^{16}$  moles C is found in living biomass with a residence time of 16 years.
  - On land, living and dead biomass combined account for  $1\times 10^{17}$  moles of C with a residence time of 40 years.

• The atmosphere provides a reservoir for a number of carbon containing species.

ppm	Species	mol C	au
1.7	$\mathrm{CH}_4$	$5.2 \times 10^{14}$	$3.6 \ \mathrm{yrs}$
0.1	СО	$1.9 \times 10^{13}$	$0.1 { m yr}$
360	$\mathrm{CO}_2$	$5 \times 10^{16}$	$4 \mathrm{yr}$

- In addition the atmosphere contains smog (smoky fog) and carbon containing particulates (such as soot) which account for  $2.9 \times 10^{14}$  mol of C.
- The atmospheric reservoirs are coupled to the biomass cycle.
- Recent sediments under the ocean are also significant reservoirs for carbon.
  - 50.8  $\times 10^{20}$  mol of C as  $CO_3^{2-}$
  - $10.4 \times 10^{20}$  mol of C as {CH<sub>2</sub>O}
  - Both of these have a lifetime 342 years.
- Sources for recent sediments are in the form of:
  - $6.1 \times 10^{12} \text{ mol C yr}^{-1}$  as {CH<sub>2</sub>O}
  - $11.8 \times 10^{12} \text{ mol C yr}^{-1} \text{ as CO}_3^{2-}$
- Sinks for recent sediments consist of transfer to old sediments (burial):
  - $2.5 \times 10^{12} \text{ mol C yr}^{-1}$  as {CH<sub>2</sub>O}
  - $15.4 \times 10^{12}$  mol C yr<sup>-1</sup> as CO<sub>3</sub><sup>2-</sup> in the form of CaCO<sub>3</sub> and MgCO<sub>3</sub>
  - These sinks are balanced by transfer from old to recent sediments.
- Anthropogenic activity extracts  $3.88 \times 10^{12}$  mol C yr<sup>-1</sup> as fossil fuel.
  - This is a net loss.

## Nitrogen Cycle

- Consider the oxidation states of nitrogen.
  - The range of oxidation states is determined by the ground state electronic configuration of the N atom,  $1s^22s^22p^3$ .
  - Nitrogen must either gain three electrons or lose five electrons to have a closed shell configuration.
  - Range of oxidation states is therefore +5 to -3.
- Some examples of oxidation state of nitrogen:
  - $NO_3^-$  and  $N_2O_5$  are in oxidation state +5.
  - NO<sub>2</sub> is in oxidation state +4.
  - N<sub>2</sub> is in oxidation state 0.
  - $NH_3$  and  $NH_4^+$  are in oxidation state -3.
- Nitrogen is essential to amino acids.
- The atmosphere is the main reservoir of nitrogen:
  - Contains  $3.9 \times 10^{18}$  N

- 78% of the atmosphere
- $\tau \sim 10^7$  years
- In order to be biologically available, N must be fixed.
  - 2  $\times$  10^{11} kg N fixed a year.
  - Anthropogenic fixation accounts for 5  $\times$  10<sup>10</sup> kg N y<sup>-1</sup>.
- Biological fixation of nitrogen is coupled to the carbon cycle.

$$3 {CH_2O} + 2 N_2 + 3 H_2O + 4 H^+ \rightarrow 3 CO_2 + 4 NH_4^+$$

- If the pH is sufficiently high, NH<sub>3</sub> is released.
- Fixation of nitrogen may be considered from a redox perspective:

$$\begin{split} N_2 + 8 H^+ + 6 e^- &\rightarrow 2 N H_4^+ \\ \{ C H_2 O \} + H_2 O &\rightarrow C O_2 + 4 e^- \end{split}$$

• Biological fixation occurs with

• Aquatic	organism	such	as	Azobacter,
Clostridium,	and	$C_{2}$	yanobacter	(formerly
known as bluegree	n algae).			

- Terrestial organism Rhizobium in symbiosis with legumes (peas, beans, peanuts). The Rhizobium infect root hairs to draw on the legumes organic carbon from photosynthesis.
- Not enough nitrogen is fixed annually to satisfy the current biomass requirements.
- Anthropogenic fixation occurs by the Haber Process:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

- The process is catalyzed by Fe,  $K_2O$ , and  $Al_2O_3$
- The process is endothermic with  $\Delta H = 92.6 \text{ kJ mol}^{-1} \text{ N}_2$ .
- Used to form  $NH_4NO_3$  for fertilizer and explosives.
- Organically bound N occurs in humus (N/C  $\approx 1/10)$  and can be released on a time scale similar to that of plant growth.
- Nitrification is the process of transforming N(-3) to N(+5):
  - From a redox perspective:

$$\begin{aligned} \mathrm{NH}_4^+ &+ 3 \; \mathrm{H}_2\mathrm{O} \to \mathrm{NO}_3^- + 10 \; \mathrm{H}^+ + 8 \; \mathrm{e}^- \\ &4 \; \mathrm{H}^+ + 4 \; \mathrm{e}^- + \mathrm{O}_2 \to 2 \; \mathrm{H}_2\mathrm{O} \end{aligned}$$

$$NH_4^+ + 2 O_2 \rightarrow NO_3^- + H_2O + 2 H^+$$

- Nitrification is a thermodynamically favoured process with  $K = 10^{60.72} = 5.25 \times 10^{60}$ .
- $NO_3^-$  may be absorbed by plants.
- Nitrification can occurs naturally as a two step process mediated by bacteria:
  - $\mathrm{NH}_4^+ \to \mathrm{NO}_2^-$  is mediated by nitrosomonas.
  - $\mathrm{NO}_2^- \to \mathrm{NO}_3^-$  is mediated by nitrobacter.
  - $\bullet\,$  Both are obligate aerobes that require  ${\rm O}_2$  for the oxidation process.

- This is why aeration of soil is important.
- $NO_3^-$  may act as an oxygen source for anaerobes.
  - Do not want nitrification to occur during sewage treatment because of subsequent denitrification.
- Thunderstorms may contribute to the production of NO<sub>3</sub><sup>-</sup>.

$$\begin{array}{ccc} N_2 + O_2 \rightarrow 2 NO \\ NO \rightarrow \cdots \rightarrow HNO_3 \end{array}$$
 is scavenged efficiently by cloud

- droplets.
  Decay of biomass leads to the mineralization of nitrogen in the form of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>.
- Denitrification is the removal of nitrogen from the biologically available forms.
  - Returns N<sub>2</sub> to the atmosphere.

• HNO<sub>3</sub>

- Involves the reduction of NO<sub>3</sub><sup>-</sup> and the oxidation of NH<sub>3</sub>.
- Reduction of  $NO_3^-$  produces  $N_2O$  and NO, both of which are greenhouse gases.
- If reduction of NO<sub>3</sub><sup>-</sup> occurs during sewage treatment, it is undesirable.
- Denitrification can also occur during sewage treatment:  $4 \text{ NO}_3^- + 24 \text{ H}^+ + 20 \text{ e}^- \rightarrow 2 \text{ N}_2 + 12 \text{ H}_2\text{O}$

 $5 {CH_2O} + 5 H_2O \rightarrow 5 CO_2 + 20 H^+ + 20 e^-$ 

 $4 \text{ NO}_3^- + 5 \{\text{CH}_2\text{O}\} + 4 \text{ H}^+ \rightarrow 2 \text{ N}_2 + 5 \text{ CO}_2 + 2 \text{ H}_2\text{O}$ 

•  $N_2$  and  $CO_2$  bubbles are formed and prevent settling.

#### Phosphorous Cycle

- Consider the oxidation states of phosphorous.
  - The range of oxidation states is determined by the ground state electronic configuration of the P atom,  $1s^22s^22p^63s^23p^3$ .
  - Phosphorous must either gain three electrons or lose five electrons to have a closed shell configuration.
  - 3d orbitals available for contribution expanded octet configurations.
  - Range of oxidation states is therefore +5 to -3.
- Some examples of oxidation state of phosphorous:
  - $PH_3$  is in oxidation state +3
  - $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^{-}$ ,  $H_3PO_4$  and associated polyphosphates are in oxidation state +5.
- In many cases, P is the limiting element in biological uptake.
  - C:N:P are taken up in the ratio 100:15:1
  - P is essential to ADP and ATP in organisms.
- The primary reservoir is the geosphere as various forms of phosphate.
  - There is no gas phase reservoir for P.

- The solubility of phosphates is strongly pH dependent.
- Phosphates in the geosphere include insoluble mineral forms of phosphate:
  - Hydroxyapatite is very insoluble ( $K_{sp} = 10^{-59} M^9$ )

$$Ca_5(PO_4)_3OH \rightleftharpoons 5 Ca^{2+} + 3 PO_4^{-3} + OH^{-}$$

- Hydroxyapatite is also found in tooth enamel.
- Occluded phosphorous is not biologically available.
  - $\bullet\,$  Soil contains  ${\rm Fe_2O_3}$  and  ${\rm Al_2O_3}$  and aluminosilicates.
  - The associated hydrates form an amorphous matrix, with orthophosphate (monophosphate) contained within the matrix.
- Non-occluded phosphorous is primarily in the form of orthophosphate bound to surface silicate (SiO<sub>2</sub>) or CaCO<sub>3</sub>.
  - Depending on pH, this is more soluble than occluded phosphorous
- Anthropogenic environmental impact of phosphorous compounds is of most concern in aquatic reservoirs.
- Solubility of phosphates are closely connected to their speciation.
  - Consider rock phosphate,  $Ca_3(PO_4)_2$ , which has a  $K_{sp} = 10^{-24} M^5$

$$Ca_3(PO_4)_2 \rightleftharpoons 3 Ca^{2+} + 2 PO_4^{2-}$$

• This equilibrates with  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^{-}$  in according with pH, the above  $K_{sp}$  and  $K_{a1}$ ,  $K_{a2}$ , and  $K_{a3}$ .

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+; K_{a1} = 7.5 \times 10^{-3} M$$
  
 $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+; K_{a2} = 6.2 \times 10^{-8} M$   
 $HPO_4^- \rightleftharpoons PO_4^{3-} + H^+; K_{a3} = 4.8 \times 10^{-13} M$ 

- Solubility of CaHPO<sub>4</sub> and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> can be calculated from the above reactions.
- It is the protonated forms that are effective for biological uptake.
- Phosphate for fertilizer is prepared by mixing sulphuric acid with rock phosphate.
- Anthropogenic impact on P levels is due to:
  - Phosphate fertilizers
  - sewage
  - detergents
- Phosphate in detergents was primarily in the form of sodium tripolyphosphate or STP,  $Na_3H_2P_3O_{10}$ .
  - STP was added as a "builder", or a source of hydroxide ion, but does not precipitate Ca<sup>2+</sup>
  - This keeps the pH high enough that the detergent molecules are in their ionic form.
  - The ionic form of a detergent or soap is active as a surfactant.

- In addition to detergent (or soap) and a builder, laundry detergent products may contain bleach, zeolites, non-ionic surfactants, and bluing or brightening agents.
- Use of STP in detergents has been restricted since the late 1970's. In Canada and Europe the sodium salt of nitrilotriacetic acid (NTA) is used as a builder instead of STP.
- Discharge of phosphates can lead to algal blooms in lakes and can promote eutrophication.
  - Treatment of sewage removes phosphates by precipitation with Ca<sup>2+</sup> at high pH.
- Biologically, phosphate is found in:
  - Nucleic acids
  - ADP/ATP
  - bones and teeth

• Phosphorothionate and phosophorodithionate pesticides do not bioaccumulate.

#### **Oxygen Cycle**

- Electronic configuration of oxygen is  $1s^22s^22p^4$ .
  - Oxidation states are 0,-1, and -2.
- Some examples of oxidation states of oxygen are:
  - Oxidation state 0:  $O_2$
  - Oxidation state -1: OH radical, peroxides HOOH, ROOH.
  - Oxidation state -2: H<sub>2</sub>O, oxides, and organic compounds.
- Coupled to the energy cycle and the carbon cycle by photosynthesis.
  - All atmospheric O<sub>2</sub> comes from photosynthesis.
- Primary reservoir is the atmosphere.
  - $\bullet$  O, O<sub>2</sub>, and O<sub>3</sub> are involved in the Chapman Cycle and are found in the mesosphere, stratosphere, and troposphere.
- Many oxygen containing species in the atmosphere.
  - Nitrogen oxide species  $NO_x$  and  $NO_y$  include NO,  $NO_2$ ,  $NO_3$ , and  $N_2O$ .
  - Sulphur containing species  $SO_x$  refers to  $SO_2$  which can be further oxidized.
  - Hydrogen containing species  $HO_x$  refers to OH and  $HO_2$ , which are important free radicals in atmospheric chemistry.
  - Oxygen is also found in atmospheric organic compounds, known as VOCs or volatile organic carbon
- Sinks for oxygen include weathering and the formation of metal oxides.
  - These processes are exothermic and spontaneous.
  - In constrast, the smelting of metals (reducing the oxide to the pure metal) is endothermic.
- Properties and reactivity of atmospheric oxygen have their origins in the electronic structure with unpaired electrons in both the atom and diatom.
  - Two common electronic states of the atom are the ground state (<sup>3</sup>P) and the excited state (<sup>1</sup>D).

- Two common electronic states of the molecule are the ground state  $({}^{3}\Pi)$  and the excited state  $({}^{1}\Delta)$ .
- The main source of atmospheric OH is:

$$O(^1D) + H_2O \rightarrow 2OH$$

• The source of  $O(^1D)$  is the photolysis of ozone:

$$O_3 + h\nu \to O(^1D) + O_2(^1\Delta)$$

• Ozone also photolyzes to the ground states:

$$O_3 + h\nu \rightarrow O(^{3}P) + O_2(^{3}\Pi)$$

• Photons of wavelength 310 nm or shorter required.

## Sulphur Cycle

- Electronic configuration of sulphur is  $1s^22s^22p^63s^23p^4$ .
  - Oxidation states range from +6 to -2.
- Some examples of the oxidation states of sulphur:
  - $SO_3$ ,  $H_2SO_4$ ,  $HSO_4^-$ , and  $SO_4^{2-}$  are in oxidation state +6.
  - $SO_2$ ,  $H_2SO_3$ ,  $HSO_3^-$ , and  $SO_3^{2-}$  are in oxidation state +4.
  - $S_8$  is in oxidation state 0.
  - $S_2^{2-}$  and FeS<sub>2</sub> (pyrite) are in oxidation state -1.
  - $H_2S$  and  $Fe_2S_3$  contain S in oxidation state -2.
- The S cycle is coupled to the O cycle.
- The geosphere is an important reservoir with S found in:
  - Sulphate salts
  - Sulphite salts
  - metal disulfide ores
  - metal sulphide ores.
  - Since proteins contain S, fossil fuels will contain S.
- Anthropogenic impacts are most significant in the atmospheric reservoir.
- Atmospheric species include:
  - Sulphur dioxide, SO<sub>2</sub>
  - Dimethyl sulphide or DMS, CH<sub>3</sub>SCH<sub>3</sub>
  - Dimethyl disulphide or DMDS, CH<sub>3</sub>SSCH<sub>3</sub>
  - Carbonyl sulphide or OCS, O=C=S
  - Carbon disulphide, S=C=S
  - Hydrogen sulphide or (H<sub>2</sub>S)
- Anthropogenic emissions are three times natural emissions.
  - $\bullet\,$  Most anthropogenic emissions are as  $\mathrm{SO}_2$  from smelting of metals and combustion of fossil fuels.

- In contrast, most natural emissions are reduced forms of sulphur since anaerobic organisms use S(VI) as a source of oxygen.
- Natural emissions include DMS, CS<sub>2</sub>, and OCS from the reduction of amino acids.
- With the exception of OCS, the reduced species can be oxidized in the troposphere.
- OCS is transported to the stratosphere where it is photolyzed.
- Volcanic emissions include SO<sub>2</sub>, H<sub>2</sub>S, and OCS.
  - May be injected directly into the stratosphere.
- Atmospheric oxidation of  $H_2S$  proceeds by the sequence:

$$\begin{array}{l} \mathrm{H_2S} + \mathrm{OH} \rightarrow \mathrm{HS} + \mathrm{H_2O} \\ \mathrm{HS} + \mathrm{O_2} \rightarrow \mathrm{OH} + \mathrm{SO} \\ \mathrm{SO} + \mathrm{O_2} \rightarrow \mathrm{SO_2} + \mathrm{O} \end{array}$$

- Atmospheric oxidation of SO<sub>2</sub> proceeds by several routes.
  - Direct gas phase oxidation is too slow to be significant.

$$SO_2 + O_2 \rightarrow SO_3 + O$$

- Gas phase oxidation can occur with photochemical oxidants formed in photochemical smog by nonmethane
   (NMHC). These oxidants includes
   OH,
   HO<sub>2</sub>, O, O<sub>3</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, ROO, and RO.
- Aqueous phase oxidation inside cloud droplets is the dominant route.
  - SO<sub>2</sub> is effectively scavenged by cloud droplets as are oxidants such as O<sub>2</sub>, O<sub>3</sub>, HO, H<sub>2</sub>O<sub>2</sub>, ROOH, CH<sub>3</sub>OOH, and CH<sub>3</sub>(CO)OOH (peroxyacetic acid or PAA).
  - Aqueous phase oxidation with  $O_2$  is catalyzed by  $Fe^{2+}$ ,  $Mn^{2+}$  and C.
  - Aqueous phase oxidation with O<sub>3</sub>, OH, and H<sub>2</sub>O<sub>2</sub> is pH sensitive and is connected with the S(IV) speciation. HSO<sub>3</sub><sup>-</sup> is more easily oxidized than other species of S(IV).
- A major anthropogenic source of SO<sub>2</sub> is the roasting of metal ores. For example:

$$NiS + \frac{3}{2}O_2 \rightarrow NiO + SO_2$$