

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 - Safe (unpublished)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^{-2} where $1 \text{ W} = 1 \text{ J s}^{-1}$
 - Energy flux intercepted by the earth is 1370 W m^{-2}
 - 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
 - Sun and earth
- Sinks of energy include:
 - Photosynthesis
 - Thermal absorption
 - 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:

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

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

Reservoir	10^6 km^3	Fluxes
Ground water	8	precipitation
Surface water	0.1 (Lakes) 0.1 (Salt lakes) 0.001 (Rivers)	evaporation
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 1.48×10^{13} L day⁻¹
 - Evaporation is 1.02×10^{13} L day⁻¹
 - which leaves 4.6×10^{12} 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	1.6×10^{12}	600
1900	1.7×10^{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.

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

where h is altitude.

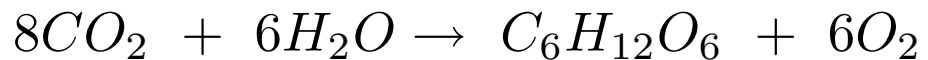
- Warm air rises and cools.
- For dry air undergoing an adiabatic expansion, the lapse rate is 10° C/km.
- For moist air undergoing an adiabatic expansion, the lapse rate is 6° C/km.

- 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

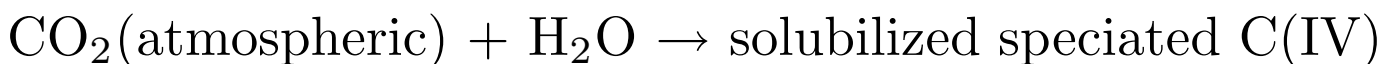
- Consider the oxidation states of carbon.
 - The range of oxidation states is determined by the ground state electronic configuration of the C atom, $1s^2 2s^2 2p^2$.
 - Carbon must either gain four electrons or lose four electrons to have a closed shell configuration.
 - Range of oxidation states is 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_2CO , 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_3 is in oxidation state -3.
 - CH_4 is in oxidation state -4.

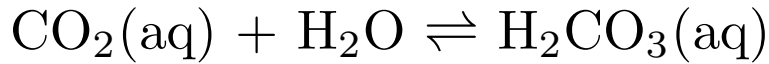
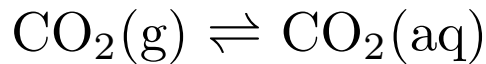
- Carbon fixation puts carbon into biologically available forms.
 - Photosynthesis uses 8 photons to drive the reaction:



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 CO₂ cycle is coupled to the hydrologic and energy cycle.
 - Before 1800, the level of atmospheric CO₂ was about 280 ppm.
 - The 1800's saw the beginning of the industrial revolution and increased use of fossil fuel.
 - In 1994, atmospheric CO₂ was observed to be 358 ppm.
- The global budget of CO₂ has not been fully determined.





- 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 $\{\text{CH}_2\text{O}\}$
 - Fossil organic carbon is reduced and may be represented as $(\text{CH}_2)_n\text{H}_2$ and is produced by biogeochemical processes.
- Reservoirs of organic carbon include:
 - Oceans with 5.8×10^{14} moles of carbon in biomass, 5×10^{15} moles C as suspended $\{\text{CH}_2\text{O}\}$ particles, 5.8×10^{16} moles C as dissolved organic carbon.
 - By comparison, oceans contain 3.2×10^{18} moles of C as C(IV).
 - On land, 4×10^{16} moles C is found in living biomass with a residence time of 16 years.

- On land, living and dead biomass combined account for 1×10^{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	τ
1.7	CH ₄	5.2×10^{14}	3.6 yrs
0.1	CO	1.9×10^{13}	0.1 yr
360	CO ₂	5×10^{16}	4 yr

- In addition the atmosphere contains smog (smoky fog) and carbon containing particulates (such as soot) which account for 2.9×10^{14} mol of C.
- The atmospheric reservoirs are coupled to the biomass cycle.
- Recent sediments under the ocean are also significant reservoirs for carbon.
 - 50.8×10^{20} mol of C as CO_3^{2-}
 - 10.4×10^{20} mol of C as $\{\text{CH}_2\text{O}\}$

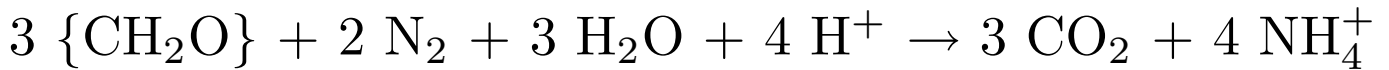
- Both of these have a lifetime 342 years.
- Sources for recent sediments are in the form of:
 - $6.1 \times 10^{12} \text{ mol C yr}^{-1}$ as $\{\text{CH}_2\text{O}\}$
 - $11.8 \times 10^{12} \text{ mol C yr}^{-1}$ as CO_3^{2-}
- Sinks for recent sediments consist of transfer to old sediments (burial):
 - $2.5 \times 10^{12} \text{ mol C yr}^{-1}$ as $\{\text{CH}_2\text{O}\}$
 - $15.4 \times 10^{12} \text{ mol C yr}^{-1}$ as CO_3^{2-} in the form of CaCO_3 and MgCO_3
 - These sinks are balanced by transfer from old to recent sediments.
- Anthropogenic activity extracts $3.88 \times 10^{12} \text{ mol C yr}^{-1}$ as fossil fuel.
 - This is a net loss.

Nitrogen Cycle

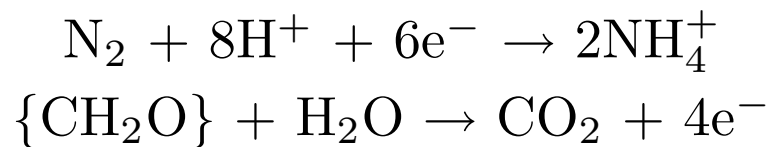
- Consider the oxidation states of nitrogen.
 - The range of oxidation states is determined by the ground state electronic configuration of the N atom, $1s^2 2s^2 2p^3$.

- 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_2 is in oxidation state +4.
 - N_2 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 3.9×10^{18} N
 - 78% of the atmosphere
 - $\tau \sim 10^7$ years
- In order to be biologically available, N must be fixed.
 - 2×10^{11} kg N fixed a year.
 - Anthropogenic fixation accounts for 5×10^{10} kg N y^{-1} .

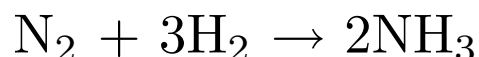
- Biological fixation of nitrogen is coupled to the carbon cycle.



- If the pH is sufficiently high, NH_3 is released.
- Fixation of nitrogen may be considered from a redox perspective:



- Biological fixation occurs with
 - Aquatic organism such as Azobacter, Clostridium, and Cyanobacter (formerly known as bluegreen algae).
 - Terrestrial 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:



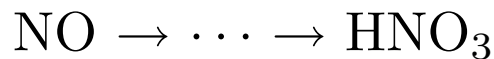
- The process is catalyzed by Fe, K₂O, and Al₂O₃
- The process is endothermic with $\Delta H = 92.6 \text{ kJ mol}^{-1} \text{ N}_2$.
- Used to form NH₄NO₃ for fertilizer and explosives.
- Organically bound N occurs in humus (N/C \approx 1/10) and can be released on a time scale similar to that of plant growth.
- Nitrification is the process of transforming N(-3) to N(+5):
 - From a redox perspective:

$$\text{NH}_4^+ + 3 \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^-$$

$$4 \text{H}^+ + 4 \text{e}^- + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$$

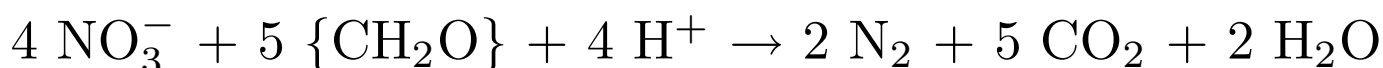
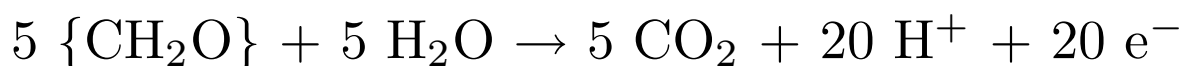
$$\text{NH}_4^+ + 2 \text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2 \text{H}^+$$
 - Nitrification is a thermodynamically favoured process with $K = 10^{60.72} = 5.25 \times 10^{60}$.
- NO₃⁻ may be absorbed by plants.
- Nitrification can occurs naturally as a two step process mediated by bacteria:

- $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ is mediated by nitrosomonas.
- $\text{NO}_2^- \rightarrow \text{NO}_3^-$ is mediated by nitrobacter.
- Both are obligate aerobes that require 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_3^- .



- HNO_3 is scavenged efficiently by cloud droplets.
- Decay of biomass leads to the mineralization of nitrogen in the form of NO_2^- and NO_3^- .
- Denitrification is the removal of nitrogen from the biologically available forms.
 - Returns N_2 to the atmosphere.
 - Involves the reduction of NO_3^- and the oxidation of NH_3 .

- Reduction of NO_3^- produces N_2O and NO , both of which are greenhouse gases.
- If reduction of NO_3^- occurs during sewage treatment, it is undesirable.
- Denitrification can also occur during sewage treatment:



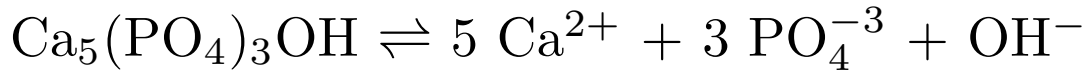
- N_2 and CO_2 bubbles are formed and prevent settling.

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, $1s^2 2s^2 2p^6 3s^2 3p^3$.
 - 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 ($K_{sp} = 10^{-59} \text{ M}^9$)

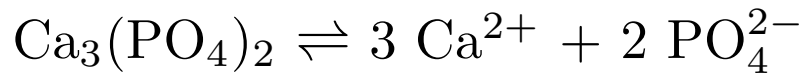


- Hydroxyapatite is also found in tooth enamel.
- Occluded phosphorous is not biologically available.
 - Soil contains Fe_2O_3 and Al_2O_3 and aluminosilicates.
 - The associated hydrates form an amorphous matrix, with orthophosphate (monophosphate) contained within the matrix.
- Non-occluded phosphorous is primarily in the form of orthophosphate bound to surface silicate (SiO_2) or CaCO_3 .
 - Depending on pH, this is more soluble than occluded phosphorous
- Anthropogenic environmental impact of phosphorous compounds is of most concern in aquatic reservoirs.
 - Soluble forms of phosphate include orthophosphate, linear polyphosphate

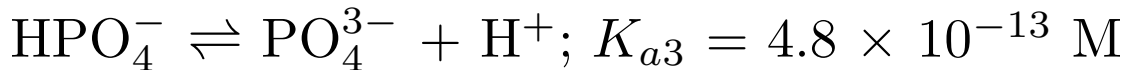
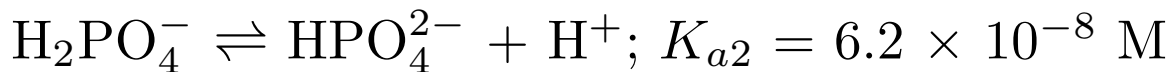
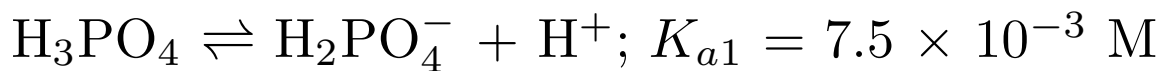
$(\text{P}_3\text{O}_{10}^{5-})$ and cyclic polyphosphates
 $(\text{P}_3\text{O}_9^{3-})$

- Solubility of phosphates are closely connected to their speciation.

- Consider rock phosphate, $\text{Ca}_3(\text{PO}_4)_2$, which has a $K_{sp} = 10^{-24} \text{ M}^5$



- This equilibrates with HPO_4^{2-} and H_2PO_4^- in according with pH, the above K_{sp} and K_{a1} , K_{a2} , and K_{a3} .



- Solubility of CaHPO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ 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, $\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10}$.
 - STP was added as a “builder”, or a source of hydroxide ion, but does not precipitate Ca^{2+}
 - 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^{2+} at high pH.
- Biologically, phosphate is found in:
 - Nucleic acids
 - ADP/ATP
 - bones and teeth
- Phosphorothionate and phosphorodithionate pesticides do not bioaccumulate.

Oxygen Cycle

- Electronic configuration of oxygen is $1s^2 2s^2 2p^4$.
 - 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 .

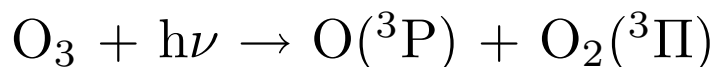
- Oxidation state -2: H_2O , oxides, and organic compounds.
- Coupled to the energy cycle and the carbon cycle by photosynthesis.
 - All atmospheric O_2 comes from photosynthesis.
- Primary reservoir is the atmosphere.
 - O , O_2 , and O_3 are involved in the Chapman Cycle and are found in the mesosphere, 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 contrast, 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 (^3P) and the excited state (^1D).
 - 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:

$$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$$
 - The source of $\text{O}(^1\text{D})$ is the photolysis of ozone:

$$\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2(^1\Delta)$$

- Ozone also photolyzes to the ground states:



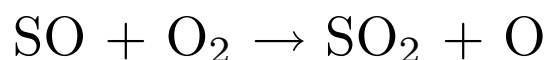
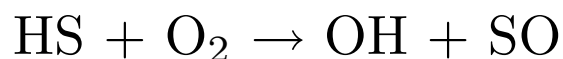
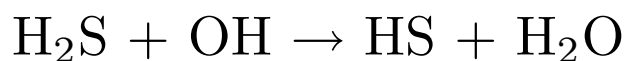
- Photons of wavelength 310 nm or shorter required.

Sulphur Cycle

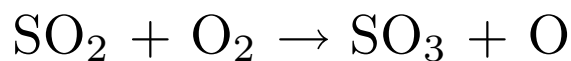
- Electronic configuration of sulphur is $1s^2 2s^2 2p^6 3s^2 3p^4$.
 - Oxidation states range from +6 to -2.
- Some examples of the oxidation states of sulphur:
 - SO_3 , H_2SO_4 , HSO_4^- , and SO_4^{2-} are in oxidation state +6.
 - SO_2 , H_2SO_3 , HSO_3^- , and SO_3^{2-} are in oxidation state +4.
 - S_8 is in oxidation state 0.
 - S_2^{2-} and FeS_2 (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_2
 - Dimethyl sulphide or DMS, CH_3SCH_3
 - Dimethyl disulphide or DMDS, CH_3SSCH_3
 - Carbonyl sulphide or OCS, $\text{O}=\text{C}=\text{S}$
 - Carbon disulphide, $\text{S}=\text{C}=\text{S}$
 - Hydrogen sulphide or (H_2S)

- Anthropogenic emissions are three times natural emissions.
 - Most anthropogenic emissions are as SO₂ 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, CS₂, 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 SO₂, H₂S, and OCS.
 - May be injected directly into the stratosphere.
- Atmospheric oxidation of H₂S proceeds by the sequence:



- Atmospheric oxidation of SO₂ proceeds by several routes.
 - Direct gas phase oxidation is too slow to be significant.



- Gas phase oxidation can occur with photochemical oxidants formed in photochemical smog by nonmethane hydrocarbons (NMHC). These oxidants includes OH, HO₂, O, O₃, NO₃, N₂O₅, ROO, and RO.
- Aqueous phase oxidation inside cloud droplets is the dominant route.
 - SO₂ is effectively scavenged by cloud droplets as are oxidants such as O₂, O₃, HO, H₂O₂, ROOH, CH₃OOH, and CH₃(CO)OOH (peroxyacetic acid or PAA).
 - Aqueous phase oxidation with O₂ is catalyzed by Fe²⁺, Mn²⁺ and C.
 - Aqueous phase oxidation with O₃, OH, and H₂O₂ is pH sensitive and is connected with the S(IV) speciation. HSO₃⁻ is more easily oxidized than other species of S(IV).

- A major anthropogenic source of SO₂ is the roasting of metal ores. For example:

