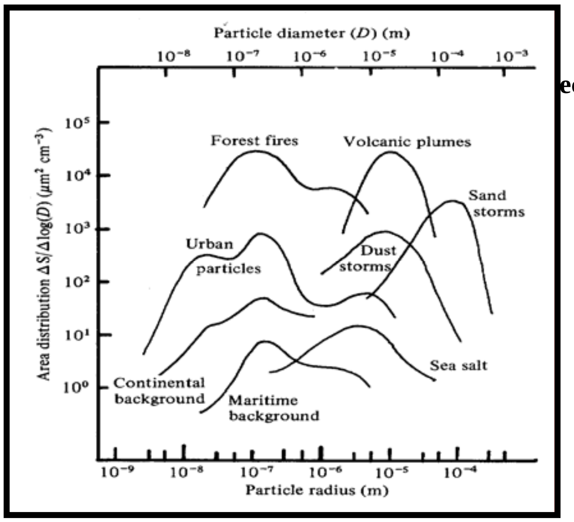
CH3041 Tutorial 4 Terrestrial Chemistry Answers

1. Discuss the chemistry in a raindrop using the **two-film model** for the transfer of gases into the drop.

Water is a present in the troposphere at 0.5 - 4% by volume. When small aerosol particles such as Aitken nuclei are present in air that is saturated with water vapour they act as Cloud Condensation Nuclei. Salt lowers the vapour pressure in these very small cloud drops and rapid condensation occurs as p_{vap} exceeds p_{sat} until the drops approach raindrop size (10^{-4} m).



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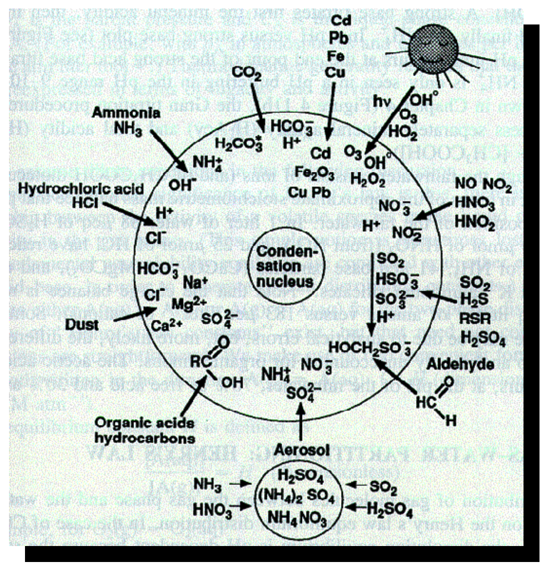


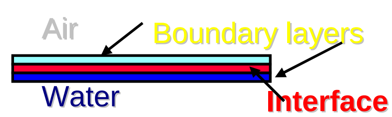
In the raindrop there is the central aerosol particle which is generally dust, sea salt sulphate or organic matter. This is in contact with the aqueous solution the outer boundary of which is then an interface between the gas phase and the liquid phase. Material that is present in the atmosphere as aerosol particles will deposit onto the surface of the raindrop and become incorporated in the drop in the process of 'wet deposition'.

Gases with limited solubility and low volatility will precipitate on the surface of the drop eg. Pb vapour, PAH (polyaromatic hydrocarbons). These materials can reduce the ability of soluble gases to transfer across the surface.

Soluble gases will dissolve into the raindrop according to Henry's Law $[i] = K_H p_i$.

Further reaction in the raindrop will reduce the concentration of the substance in the raindrop and so further amounts will dissolve, this will result in larger amounts going into solution than those based simply on Henry's Law alone.

Dissolution of a gas involves a two step process (1) fast transfer to the liquid and (2) slow mixing within the liquid The transfer process across the surface of the drop may be described by a Two-Film Model.



On either side of the surface turbulent diffusion is moving material by turbulent diffusion. At the surface there is a liquid boundary layer and a gas boundary layer.

Slow transfer of material occurs across the boundary layers by diffusion.

The movement of material across a boundary layer is described by the flux expression $F = 1/r\ \Delta[i]$ where 1/r is the resistance of the boundary layer to diffusion of the substance through the layer and the difference in concentrations is the other term.

One of the resistance terms normally dominates, for instance diffusion of a high solubility gas will generally have the gas phase resistance dominating.

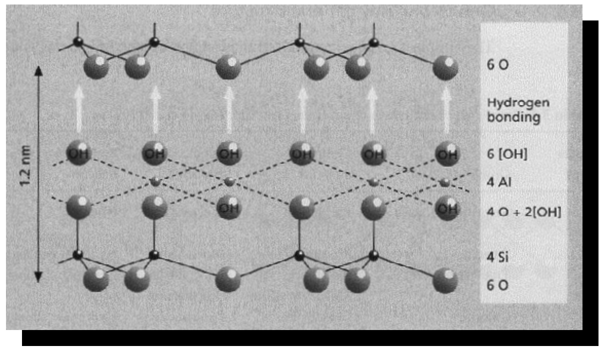
The soluble gases that transfer into the raindrop will include CO_2 which will make the pH of the drop slightly acid, H2S/DMS/SO_2/SO_3/H_2SO_4 , HCl and NO_x/HNO_3 all of which will increase the acidity.

Ammonia which will be protonated to form NH_4^+ in the raindrop. Organic gases which may either increase or decrease the pH.

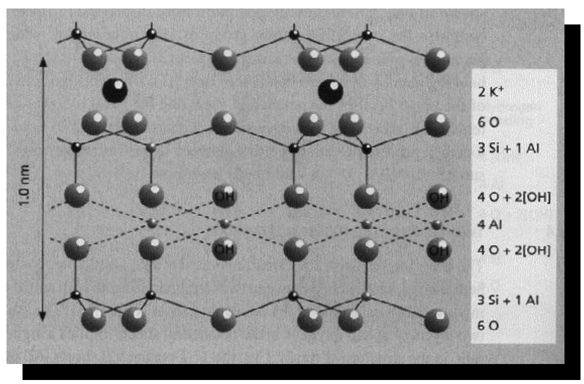
2. Provide chemical formulae and structural diagrams for three common aluminosilicate minerals.

Feldspar **$KAlSi_3O_8$** quartz structure, 3-D network covalent solid aluminium substitutes every 4th Si site.

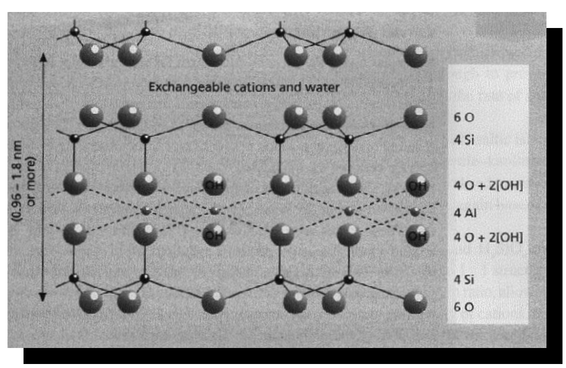
Kaolinite a 1 : 1 mineral
$Si_4Al_4O_{10}(OH)_8$



Muscovite **$[KAl_3Si_3O_{10}(OH)_2]_2$**

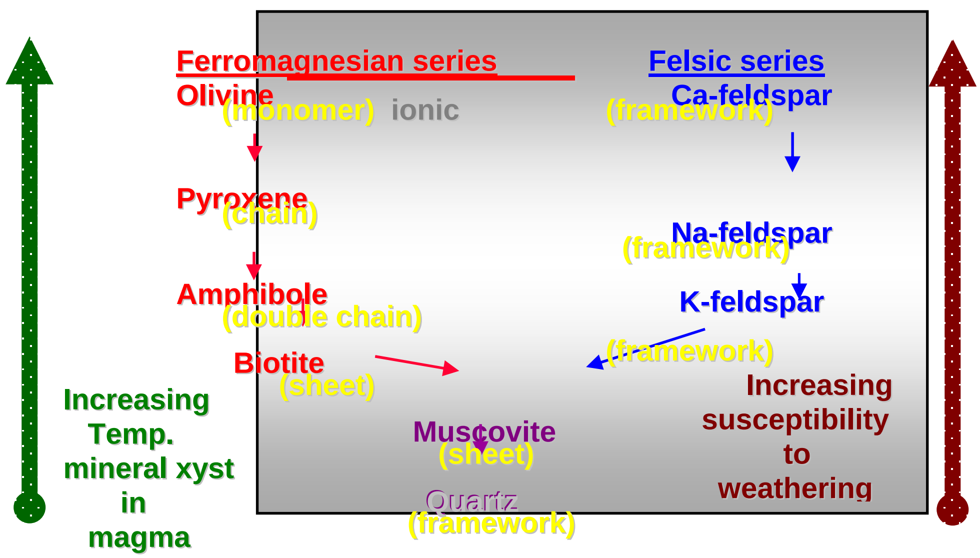


Smectite
$[M_0(Al_2)(Si_4)O_{10}(OH)_2]_2$



3. Discuss the mechanisms for **weathering** of primary minerals to form secondary minerals in soil.
   Why is quartz found in high percentage in the sedimentary rocks?

A primary mineral is formed under conditions of high temperature and pressure, rock forming conditions.
A secondary mineral is formed from primary minerals by alteration (either chemical or physical conditions) in the course of weathering.
As primary conditions are formed under anaerobic reducing conditions they are not thermodynamically stable under oxic conditions found at the Earth's surface.
Bowen's reaction series illustrates the relationship between the conditions of formation of a mineral and the propensity to weather, this then is an indication of the propensity of a primary mineral to weather based on the structural type of the mineral. A monomer silicate is formed under high temperature of crystallisation and as a result a thermodynamically less stable structure is formed under these conditions the lack of interconnection between monomer units allows ready weathering, the stability of quartz is due the converse.
The Felsic series is based on the aluminosilicate 3D framework silicate structure which contains internal cage structures. These cages are most stable when they contain K^+ and least stable when they contain Ca^{2+} and this again relates to the ease of weathering.
Mechanisms of chemical weathering:
1) Dissolution: $Mg_2SiO_4 + H_2O \rightarrow Mg^{2+}_{(aq)} + H_4SiO_{4(aq)}$
2) Oxidation: $4FeS_2+15O_2+14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4$
3) Acid hydrolysis: $2NaAlSi_3O_{8(s)} + 2H_2CO_3 + 9H_2O \rightarrow 2Na^+ + 2HCO_3^- + 4H_4SiO_{4(aq)} + Al_2Si_2O_5(OH)_{4(s)}$
4) Complexation: muscovite + oxalate $KAl_3Si_3O_{10}(OH)_2 + 3C_2O_4^{2-} + 10H^+ \rightarrow 3AlC_2O_4^+ + 3Si(OH)_4 + K^+$



The secondary minerals such as the clay minerals form from the primary minerals under conditions of low pressure and temperature and high oxygen partial pressure. The primary minerals are weathered at surface sites that possess defects or are broken by physical weathering. Once the surface area to particle size ratio becomes high then weathering proceeds at a rapid rate. The pits that form in the defect sites are eroded away by the weak organic acids from humic materials and the carbonic acid in the C horizon of the soil. The Al:Si ratio will increase with time as the $Al(OH)_3$ is quite insoluble under most pH regimes while the silicic acid may be removed as the framework of the primary silicate mineral is broken down. Reformation of a clay mineral occurs as the solublised silcate content and the available base cations recombine.
Quartz is a 3D-network covalently bonded silicate, which means that it has a particularly stable structure. As it is both thermodynamically & kinetically a stable mineral slow physical weathering is a major mechanism for the breakdown of quartz and this means it is usually found in this form in sedimentary rocks.

4. Illustrate the main features of the nitrogen cycle and explain the processes **denitrification** and **nitrogen fixation**.

STABILITY (ΔG_f^o)

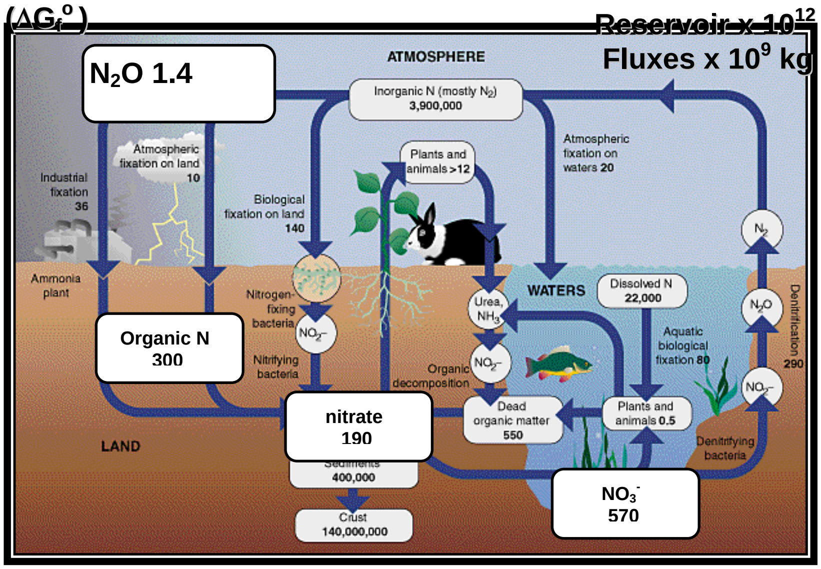
N_2 (O) nitrogen

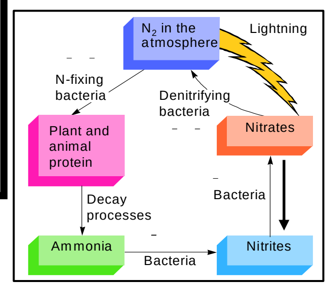
NH_3 (-3) ammonia

NO_2^- (+3) nitrite

NO_3^- (+5) nitrate

Reservoir x 10^{12} kg N
Fluxes x 10^9 kg N/a





Dintrogen is the main reservoir of N and for organisms to use this as a source of N (Redfield protoplasm has the formula **$C_{106}H_{263}O_{110}N_{16}P_1$)** they must either use this or a product derived from it. The entry point of N into the biological cycle is the Nitrogen fixation reaction and the major return is denitriication.

Nitrogenase is a 2 protein enzyme that catalyses the reduction of N_2.
One of the proteins has 2 Mo atoms which coordinate to the N_2 molecule and help to break the triple bond which has a energy of activation of 950 kJ/mol.
Nitrogen fixation: In the case of the *Rhizobium* bacteria it is symbiotic relation-ship the bacteria gets E from the plant (legume nodules $\rightarrow$ photosynthetically produced sugars), the plant gets NH_4^{++}

Nitrogen fixation $\qquad N_2 + 8H^+ + 6e^- \rightarrow 2NH_4^+$

ΔG -120 kJ/mol $\qquad$ 'CH$_2$O'+ $H_2O \rightarrow CO_2 + 4H^+ + 4e^-$

3{'CH$_2$O'}+ $3H_2O + 2N_2 + 4H^+ \rightarrow 3CO_2 + 4NH_4^+$
- this links the C cycle to the N cycle.

2) Denitrification: a major N_2 return pathway which *Rhizobium* will also use as a source of metabolic energy.

$$NO_3^- + 5/4\{\text{'CH}_2\text{O'}\} + H^+ \rightarrow \tfrac{1}{2}N_2 + 7/4H_2O + 5/4CO_2$$