CH3041 Tutorial 4 Terrestrial Chemistry Answers

- 1. As a raindrop falls it readily absorbs soluble gases which increase in concentration inside the drop.
 - Calculate the concentration of aqueous **sulphur dioxide** in a **raindrop** that is in a parcel of air (just above sea-level) containing a gas-phase concentration of SO₂ of 3 ppm. The Henry's Law constant for SO₂ is 1.470 mol dm⁻³ atm⁻¹.
 - Explain how apparent aqueous SO₂ concentrations **higher** than those predicted by Henry's Law may be obtained.

$$\begin{split} [SO_{2(aq)}] &= p_{SO2} \; K_{H} = \; 3 \; x \; 10^{-6} \; x \; 1.470 \; mol \; dm^{-3} \\ &= 4.41 \; x \; 10^{-6} \; mol \; dm^{-3} \\ &= 4 \; x \; 10^{-6} \; mol \; dm^{-3} \end{split}$$

 SO_2 may react on the inside of the rain drop to form SO_3 which may then react further to form H_2SO_4 . This will lead to the reduction of the equilibrium concentration of SO_2 inside the raindrop and to restore this further SO_2 will be absorbed into the rain drop.

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



- 3. Bowen's reaction series is useful in predicting the ordering of mineral weathering.
 - Draw a sketch of Bowen's series with illustrative formulae for the minerals at each step.
 - What physical basis is behind the success of Bowen's series.



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 formation conditions are high pressure anaerobic reducing conditions these minerals are not thermodynamically stable under the low pressure oxic conditions found at the Earth's surface.

Bowen's series was developed to explain the propensity of different minerals to crystallise from magma at different temperatures. Bowen's reaction series also 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 slower low temperature crystallisation process in the mineral formation process will lead to a more stable framework of bonding in the mineral, which as a result will make the mineral more resistant to weathering.

eg. a monomer silicate forms rapidly at a high temperature of crystallisation and as a result is a thermodynamically less stable structure. When formed under these conditions the lack of interconnection between the monomer units allows ready weathering. The stability of quartz is due to the converse argument.

The Felsic series is based on an aluminosilicate 3D framework which contains internal cage structures, all are feldspars. This series is referred to as a continuous series as each feldspar has occupation of the cationic sites with either Ca^{2+} , Na^+ or K^+ but the proportion of each varies depending on the temperature of crystallisation. 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 chemical weathering. Ionic sizes : Ca^{2+} 100pm, Na^+ 102pm, K^+ 138pm

The Ferromagnesian series is based on the SiO_4 tetrahedral monomeric unit. The extent of polymerisation of this monomeric unit increases the lower the temperature of crystallisation with a progression from monomer silicates (olivines) through to sheet silicates (micas).

This series is referred to as a discontinuous series as each mineral type has a discrete formula and one mineral then turns into another at a particular temperature.

The minerals at the top of the series have less extensive polymerisation and as result are more weakly bonded, this in turns mean they are more susceptible to chemical weathering.

Mechanisms of chemical weathering:

 $\begin{array}{l} \text{K-feldspar}\\ 1) \text{ Dissolution: } \text{ KAlSi}_{3}\text{O}_{8(s)} + 8\text{H}_{2}\text{O} \rightarrow \text{Al}(\text{OH})_{4}^{+}{}_{(aq)} + 3\text{Si}(\text{OH})_{4(aq)} + \text{K}^{+}{}_{(aq)}\\ 2) \text{ Acid hydrolysis: } \text{ KAlSi}_{3}\text{O}_{8(s)} + \text{H}^{+}{}_{(aq)} + 7\text{H}_{2}\text{O}_{(1)} \rightarrow \text{K}^{+}{}_{(aq)} + 3\text{Si}(\text{OH})_{4(aq)} + \text{Al}(\text{OH})_{3(s)}\\ 3) \text{ Complexation: muscovite + oxalate } \text{ KAl}_{3}\text{Si}_{3}\text{O}_{10}(\text{OH})_{2} + 3\text{C}_{2}\text{O}_{4}^{-2} + 10\text{H}^{+} \rightarrow 3\text{AlC}_{2}\text{O}_{4}^{+} + 3\text{Si}(\text{OH})_{4} + \text{K}^{+}\\ \end{array}$

The reduction in stability between muscovite $KAl_3Si_3O_{10}(OH)_2$ and biotite $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$ comes about from the reduced aluminium content in the biotite. Instead there are a high proportion of the soluble cations $(Mg^{2+}, Ca^{2+}, Fe^{2+})$ which are required to balance the negative charge on the silicate framework . Formation of a clay mineral occurs as the solubilised silicate 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.

Secondary minerals (such as the clay minerals smectite, kaolinite) 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 (most weathering occurs in the vadose zone). The Al:Si ratio will increase with time as the Al(OH)₃ (gibbsite) 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.

4. Define the following types of soils (a) a **sodic soil** (b) a **saline soil**.

• What measurements would you carry out to confirm the nature of these soils.

Sodic soils have primarily exchangeable Na⁺ available - not free Na⁺ (saline soils). A sodic soil will not have a high conductivity (EC) it will typically be < 4 mS/cm

Exchangeable Sodium Percentage (ESP) is used to assess sodicity. ESP / (100 - ESP) = 0.015 SAR ESP > 15 is sodic

SodiumAdsorptionRatio - obtained by AA analysis of Na, Ca and Mg on a 1:5 soil/water extract. $SAR = [Na^{+}] / \sqrt{\{([Ca^{2+}] + [Mg^{2+}]) / 2\}}$

Saline soils have mainly free Na⁺ due to salt being input into the system. The conductivity of the supernatant of a 1:5 soil/dist. water paste > 4 mS/cm indicates the soil is saline. (S = mSiemens or mmho), a conductivity meter has 2 plates 1cm apart)