

THE LITHOSPHERE

1. Introduction

The lithosphere is constantly being modified by weathering mechanisms. These fall into a number of different categories, namely:

- Physical processes
- Chemical processes such as dissolution, carbonation, hydrolysis and redox
- Biological

However, the actual nature of the interactions is affected by the composition of the minerals involved and the pH. Therefore, this is an exceedingly complex situation.

2. Physical Weathering

Rocks which have been buried in the crust of the lithosphere can develop small cracks on exposure to the atmosphere. Water enters these cracks and if the temperature falls sufficiently for the water to freeze then the pressure of the expanding ice will extend the cracks, eventually causing the rock to split or flake. Note that expanding ice can exert a pressure of $150\text{kg}\cdot\text{cm}^{-2}$ while the tensile strength of rock is about $120\text{kg}\cdot\text{cm}^{-2}$.

Alternating hot and cold spells will speed up the disintegration of rocks, especially if the temperature variations are large and occur rapidly. In situations where rocks are partly submerged then the exposed surfaces will become heated during the day while the buried portions remain cool. The differential expansion that results will cause extensive cracking and the subsequent disintegration of the rock. Physical abrasion can be caused by the action of wind, running water and glaciers, while plant roots, penetrating cracks and crevices, force the rock apart.

All these factors combine to break down rock into ever smaller particles, so increasing its potential for reacting chemically with other materials in the environment. Thus, the rate of weathering is substantially increased. Also, the changes are now qualitative with the products of weathering being very different from the original rock.

3. Chemical Weathering

The principal weathering agents are water, oxygen and carbon dioxide. There are, of course many other substances in the environment which, because of their reactivity, will contribute to the weathering process. However, their effects are often local and/or relatively unimportant and so they will not be considered in any detail.

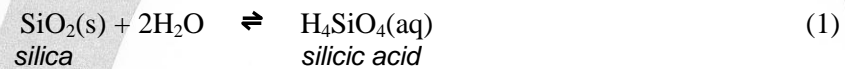
The mineral composition of natural water depends on the local environment; for example, coastal freshwater will contain more sodium and chloride ions than water further inland. It must be remembered also that the mineral composition of water changes as it percolates through the earth's crust. On average, rainwater contains $2.0\mu\text{g}\cdot\text{cm}^{-3}$ sodium ions, $0.3\mu\text{g}\cdot\text{cm}^{-3}$ potassium ions, $0.1\mu\text{g}\cdot\text{cm}^{-3}$ calcium ions, $3.8\mu\text{g}\cdot\text{cm}^{-3}$ chloride ions, $0.6\mu\text{g}\cdot\text{cm}^{-3}$ sulphate ions and $0.12\mu\text{g}\cdot\text{cm}^{-3}$ hydrogen carbonate ions. It has a pH of approximately 5.7 and the amount of carbon dioxide present is in equilibrium with the amount of carbon dioxide in the atmosphere. Once in contact with the land, however, this composition is likely to change dramatically. Organisms will extract the nutrient ions and replace them nitrate ions, ammonia and so on. In addition, the carbon dioxide content will increase as the water passes through areas where there is decaying organic matter. The amount of dissolved oxygen too will fluctuate considerably.

As mentioned before, the chemical weathering processes include:

- Dissolution
- Carbonation
- Hydrolysis
- Redox

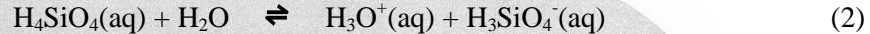
These will now be considered in greater detail.

Dissolution: This is the dissolving of materials in water. When this happens substances are in effect extracted from rocks and minerals and carried away. The act of dissolution is affected in the first place, of course, by the ability of materials to actually dissolve in water. Although much of the inorganic material in the earth's crust is ionic and so theoretically soluble, in fact solubilities vary widely. Thus, sodium chloride, derived from halite deposits and sodium-rich rocks, has a relatively high solubility ($350\text{g}\cdot\text{dm}^{-3}$). Calcium sulphate, occurring as gypsum and anhydrite, is considerably less soluble ($2.0\text{g}\cdot\text{dm}^{-3}$) while silica, which is not really ionic, is only sparingly soluble in water ($6.5\text{mg}\cdot\text{dm}^{-3}$). Actually, silica tends to undergo a **hydrolysis** reaction with the water to form silicic acid:



The direct hydrolysis of silicate minerals by water leads to there being rather more silicic acid present in water than would be suggested by the solubility of silica alone.

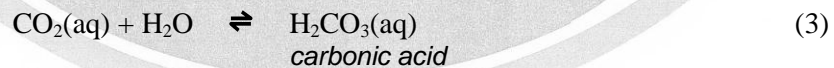
Silicic acid is a weak acid reacting with water as follows:



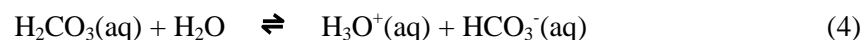
A moment's reflection will reveal that there are occasions when solubility is dependent on pH. For example, in an alkaline environment the dissolution of silica is going to be greater since the alkaline hydroxide ions are going to react with the acid hydronium ions in equation 2. This will cause both equilibrium equations, 1 and 2, to move to the right with the result that more silica goes into solution.

Finally, it must be pointed out that crystal structure can affect solubility. Thus, calcium carbonate in the form of aragonite is 16% more soluble in water than calcium carbonate as calcite.

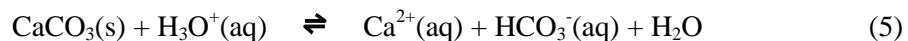
Carbonation: This is an important class of reaction and it is basically an acid-base reaction. In essence it involves the reaction of carbon dioxide, dissolved in water, with materials in the earth's crust. When it dissolves in water carbon dioxide reacts with water molecules to a certain extent forming **carbonic acid**:



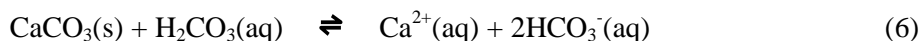
Carbonic acid dissociates in water to generate hydronium ions:



The hydronium ions react with calcium carbonate generating free calcium ions and hydrogen carbonate ions:

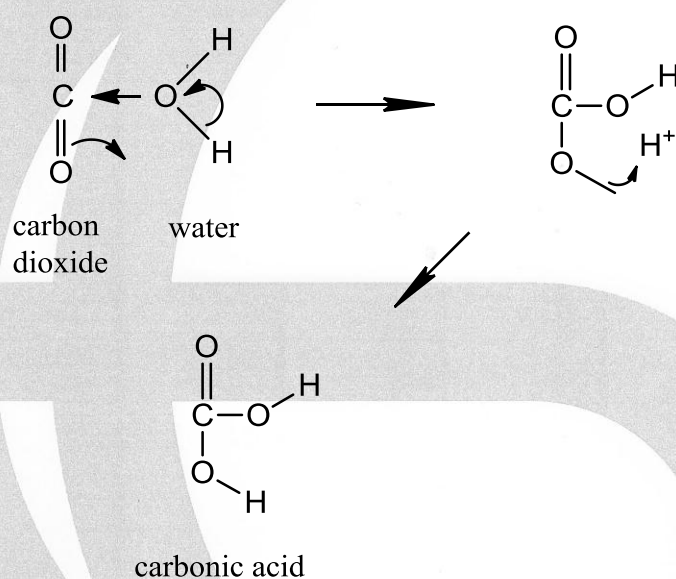


Adding equations 4 and 5 gives the overall reaction:



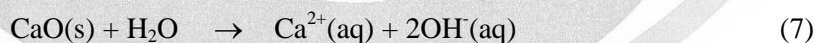
This is a common and rapid weathering process. Now, the calcium hydrogen carbonate formed in the reaction can only exist in solution. Any attempt to isolate it by evaporating off the water will cause it to decompose into calcium carbonate, carbon dioxide and water; in effect, the reverse reaction in equation 6. Thus, the caves and potholes formed in chalk and limestone areas are the result of the forward reaction in equation 6, stalactites and stalagmites are formed as waters rich in calcium hydrogen carbonate evaporate while dripping slowly from the ceiling to the floor of caves.

Hydrolysis: This type of reaction involves the splitting of water molecules and, as a consequence of this, any resulting solutions tend to be either acidic or alkaline. The reactions of silica and carbon dioxide with water are hydrolysis reactions and, as can be seen, the product in both cases is an acid. If we consider the carbon dioxide and water reaction, what happens is this:

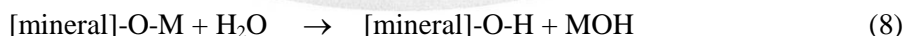


Scheme 1: The reaction carbon dioxide and water

Calcium oxide will hydrolyse water; this time the reaction generates an alkaline solution:



The hydrolytic weathering of silicate minerals is similar and often involves the breaking of metal-oxygen bonds:

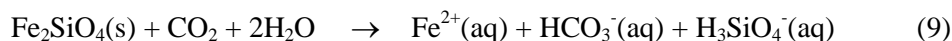


Much depends on the strength of the oxygen-metal (O-M) bond; the weaker the bond the more easily does weathering take place. For example, Ca-O and Mg-O bonds are weaker than Al-O bonds and so calcium and magnesium are displaced more easily from minerals than aluminium. Indeed, the aluminium-oxygen bond is so strong that aluminium oxide (bauxite) hardly weathers at all, and the same is true of iron(III) oxide (haematite).

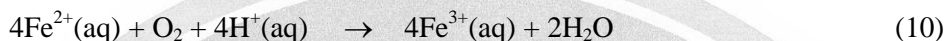
In dry, arid climates and in moist, temperate climates the end results of silicate weathering are clays. When the climate is dry and arid the clays formed are illite and montmorillonite. When the climate is

damp and temperate the clay formed is kaolinite (eg China clay). In the wet tropics, the results of silicate weathering are metal oxides such as bauxite and haematite.

Redox Reactions: These occur when the elements involved have more than one available oxidation state. For example, iron can exist as iron(II) [ferrous iron, Fe^{2+}] and as iron (III) [ferric iron, Fe^{3+}]. Consider the weathering of fayalite (a ferrous silicate, Fe_2SiO_4). This involves first a carbonation reaction in which the iron is converted into iron(II) hydrogen carbonate:

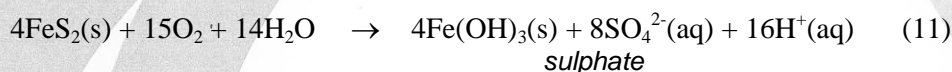


The iron(II) is now oxidised to iron(III) by oxygen in the atmosphere:



The iron(III) so formed then reacts with water in a hydrolysis reaction to form insoluble iron(III) hydroxide and iron(III) oxide. These products colour their environments red.

The minerals iron pyrites and marcasite contain iron(II) in the form FeS_2 . On exposure to the air both the iron and the sulphur are oxidised:



Note that in this reaction sulphuric acid, H_2SO_4 , is formed. Hence the acidity of many mine tailings (the water draining out of old mine workings).