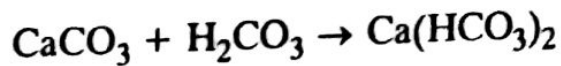


Of the above mentioned processes of physical weathering, unloading by erosion and crystal growth are especially significant. Other processes have minor roles in weathering overall, although their role in specific environments for some rocks should not be overlooked. Physical weathering contributes to chemical weathering of rocks by reducing particle size, thus increasing specific surface area for chemical reactivity. Sand is exclusively, and silt-sized particles are to large extent the products of physical weathering.

2.4.2 Chemical weathering

Chemical weathering involves processes that alter rocks and minerals that are stable at the temperatures and pressures at the surface of the earth. These processes are solution, hydrolysis, oxidation, reduction, carbonation, and hydration. The kinds of reactions and combination of reactions in soils depend on environmental factors such as temperature, water content, presence or absence of oxygen, and leaching intensity. Chemical weathering can be divided into congruent and incongruent dissolution. **Congruent dissolution** is when a mineral goes into solution completely with no precipitation of other substances. The soluble salt minerals halite and gypsum, and silica minerals are examples of congruent dissolution. In **incongruent dissolution**, all or some of the ions released by weathering precipitate to form new compounds.

Solution and carbonation. Water is the main solvent in rock-soil systems. The solution effect of water on rock minerals depends in part on the dipole nature of water, which readily allows the dissolution of ionic solids such as salts of Na, K, Mg (especially their chlorides and sulphates) to produce a stable ionic solution. Gypsum is less soluble, while CaCO_3 and SiO_2 are sparingly soluble. Solubility of some elements such as iron and manganese depends upon redox potential, while the solubility of silica is somewhat pH dependent (much higher at pH above 9). Water is never pure in a weathering system, and nearly all the substances are soluble to varying degrees. The solvent action of H_2O is increased by the presence of CO_2 , which reacts with water to form carbonic acid. The effect of carbonic acid is especially effective on limestones. The carbonic acid-containing water dissolves CaCO_3 readily in the reaction:

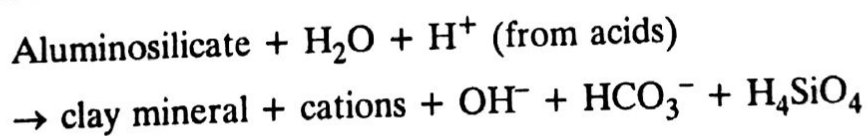


The effect of the partial CO_2 pressure of the atmosphere on the dissolution of limestone indicates that the solubility of CaCO_3 increases markedly (2–18 times) with increasing CO_2 content (up to 100%) of the atmosphere.

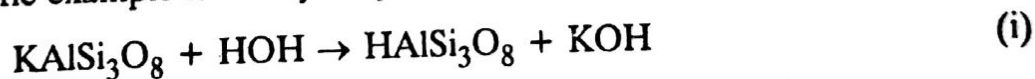
The solvent power of water is further increased by the presence of

traces of organic and mineral acids. It becomes then one of the most potent factors in the decomposition of rocks, provided the water is continuously renewed. Calculated for the entire globe, 37 tons of material per square km is removed in solution annually, consisting of 19, 8, 3, 3, 2, 1.5, and 0.5 tons of CaCO_3 , CaSO_4 , NaCl , SiO_2 , alkali carbonates and sulphates, MgCO_3 , and Fe_2O_3 respectively. Mineral contents of spring water, well water, and flowing rivers confirm the dissolving power of water whenever it comes in contact with solid material. Over geological time, the ocean water has become too saline (35 g l^{-1}) for drinking or irrigation purposes.

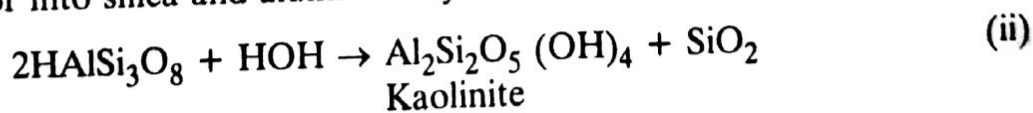
Hydrolysis. Hydrolysis is an important process in the chemical weathering of the aluminosilicates, common rock-forming minerals. Hydrolysis is a chemical reaction between a mineral and H_2O , that is, between the H^+ or OH^- ions of water. Actually hydrolysis is the attack of an acid in water on a mineral. Common acids are carbonic acid and other acid byproducts of the decay of organic matter. In hydrolysis, cations that are part of the crystal lattice of aluminosilicate minerals are replaced by H^+ (H_3O^+) with resulting distortion and disintegration of the mineral structure. Simultaneously H_2O dissociates into H^+ and OH^- ions which then combine with Al, Si, O, and OH on the mineral surface, breaking the Si-O and Al-O bonds. Common byproducts are H_4SiO_4 , HCO_3^- , OH^- , and cations along with clay minerals if conditions are favourable. The silicic acids formed are partly leached, recombined with Al, or further decomposed. A general reaction is:



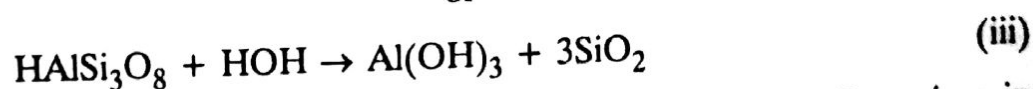
A specific example is the hydrolysis of orthoclase.



The formation of KOH can be recognized by the fact that an aqueous suspension of orthoclase powder reacts alkaline. The aluminosilicate formed is unstable, and hydrolysed further, changes either into a clay mineral (kaolinite) or into silica and aluminum hydroxide as given below.



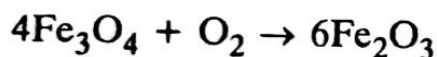
or



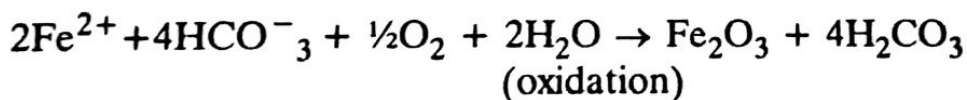
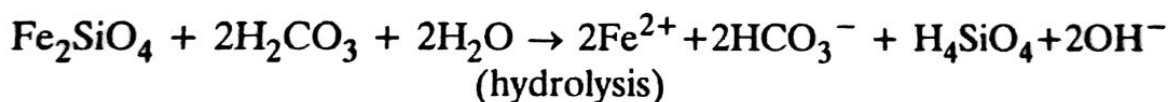
The crystal lattice of orthoclase is completely decomposed. Potassium in mica is gradually displaced by H, and after complete removal of K, mica decomposes, however very slowly.

The alteration of ferromagnesium minerals most commonly occurs by simultaneously occurring hydrolysis and oxidation.

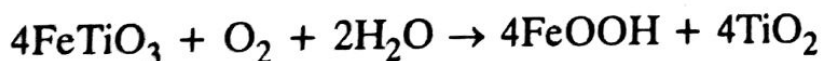
Oxidation. From the point of view of simple weathering, the term oxidation means a reaction with oxygen to form oxides. If water is also incorporated the reaction is hydrolysis. In a strict sense, oxidation means the loss of electrons. Oxidation affects specially the Fe (II) and Mn (II) containing minerals, mainly ferromagnesium ones. The oxidation of iron alters the structure of such minerals, causing disintegrative weathering. Oxidation of Fe^{2+} to Fe^{3+} disrupts the electrostatic neutrality of the crystal, so that other cations leave the crystal lattice to maintain neutrality. The vacancies make the mineral susceptible to attack by other weathering processes. The alteration of biotite to vermiculite is one example of weathering due primarily to oxidation. Pure oxidation is represented by the transformation of magnetite into hematite, when exposed to air.



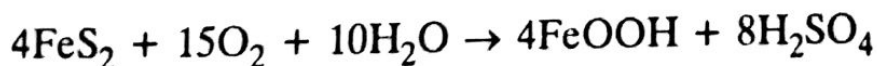
Hydrolysis results in the weathering of Fe^{2+} -containing minerals and the release of soluble Fe^{2+} , along with other byproducts. Then, in the presence of oxygen, Fe^{2+} is converted into Fe^{3+} ; thus oxidation follows the hydrolysis process, as in the oxidation of olivine.



Similarly ilmenite weathers into goethite and rutile.



Pyrite, frequently present in acid rocks, is oxidized into goethite and sulphuric acid.

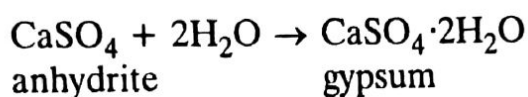


Reduction. Reduction, the gain of electrons, is the opposite of oxidation and takes place in geochemical environments where the material remains saturated with water, and oxygen supply is low and biological oxygen demand is high. Where seasonal wetting and drying are the climatic pattern, soils often undergo many oxidation–reduction cycles during formation; in waterlogged conditions, on the other hand, they remain in a permanently reduced anaerobic state.

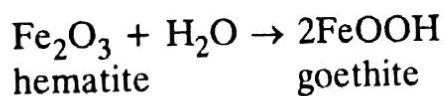
Iron and polyvalent elements are reduced to more soluble and mobile forms which either react to form sulphides or are likely to be lost by leaching. Reduction of Fe^{3+} to Fe^{2+} imparts the characteristic green and blue-

green colours to many reduced soil materials. Much reduction is done by bacteria; for example, organic matter is reduced by fermenting bacteria, and sulphates are reduced by bacteria to sulphide. Many silicate minerals contain cations ($\text{Fe}^{2+}/\text{Fe}^{3+}$ or $\text{Mn}^{2+}/\text{Mn}^{4+}$) that are easily converted into another oxidation state. A change of the redox potential (Eh) may cause oxidation or reduction of these cations. To maintain the electrostatic neutrality of the crystal structure, some other ions must enter or leave the lattice. This causes the lattice to become unstable and more susceptible to other weathering reactions such as hydrolysis or to alteration to other minerals.

Hydration. Hydration is the association of water with a mineral, without actual decomposition or modification of the mineral itself. Sorption of water molecules mainly occurs on mineral surfaces and at the broken edges of silicate minerals. Dehydration, the removal of water, is the reverse of hydration. An example of hydration–dehydration is the formation of gypsum and anhydrite by adding or removing water, respectively.



Another example is the conversion of hematite to goethite



Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is a hydrated mineral of Al_2O_3 . Muscovite easily converts into hydromuscovite.

Hydration is an exothermic reaction, and also involves a considerable volume change (average 50%) which may be important in physical weathering. The sorbed water in silicate minerals allows entry of hydronium (H_3O^+) ions to attack the structure. Thus hydration prepares the mineral surface for the oxidation and hydrolysis processes.

2.4.3 Biotic weathering

Biotic weathering can be defined as physical and chemical weathering by biological agents. The breakdown of rocks and minerals is accelerated by plants, animals, and microorganisms. Physical effects are produced especially by plant roots, which penetrate into the crevices and cracks of rocks. Pressure exerted by roots as they grow is sometimes able to rupture the rock, or widen cracks to force blocks apart. Lichen (symbiotic association of algae and fungi) growing on rock surfaces also contributes to physical weathering. Loose mineral and rock fragments become attached to the underside of the lichens and are pulled free of the surface when the lichens contract during a dry spell. Large plants covering the surface of a rock change the microclimate by stabilizing the surface and controlling temperature and soil erosion.