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Soil

Soil particles

(From Hillel, pp. 61-62)

The main or principal groups of particles in soil are, in order of size, clay, silt and sand:

- clay
 - the colloidal particle fraction
 - clay has the largest surface area per unit mass and so is the most reactive physically and chemically
 - clay particles adsorb water, causing soil to expand on wetting and shrink on drying
 - clay particles are negatively charged and when they're hydrated they form a double layer with exchangeable ions in the soil solution around them
- silt
 - larger surface area per unit mass than sand and often coated with clay, so they may behave physically and chemically a little like clay
- sand

Silt and sand are relatively inert and make up the soil "skeleton". Clay is the "flesh" that supports a lot of the chemical, physical and biological activity in soil.

Soil organic matter

About 20% to 40% of what a plant produces through photosynthesis in a growing season is returned to the soil.

Plant cells are made up mostly of carbohydrates, proteins and fats.

Of the carbohydrates, sugars and starch are decomposed quickly, while cellulose is less easily decomposed.

Proteins are quickly decomposed ultimately into amino acids.

Some of the amino acids are used by micro-organisms for growth.

Whether there is any surplus amino-N that is mineralised for plants to use depends on the C:N ratio of the substrate material and the type of micro-organisms.

When the C:N > 25, there is no excess N and all N is immobilised by the micro-organisms.

When C:N < 25, some mineralisation (see glossary) of N is likely.

Lignin, a complex phenolic polymer, makes up 10% to 20% of cereal straw dry matter and 20% to 30% of wood dry matter. It is not easily decomposed. When it is decomposed, monocyclic phenols are formed and these are then used by soil organisms to make humic macro-molecules.

Soil organisms

One way of classifying soil organisms is by the method they use to make food:

- *heterotrophs* need C in the form of organic molecules; they include many species of bacteria and all fungi;
- *autotrophs* include remaining bacteria and most algae; can grow using C from CO₂, deriving energy from sunlight (i.e. photosynthetic bacteria and algae) or else deriving energy from oxidising inorganic compounds (i.e. chemoautotrophs).

Another way of classifying them is according to their need for molecular O₂:

- *aerobes* need O₂ as the terminal electron acceptor in respiration
- *facultative anaerobes* normally need O₂ but can survive in anoxic conditions by using NO₃⁻ and other inorganic compounds as electron acceptors in respiration
- *obligate anaerobes* grow only in oxygen-free environments because oxygen is toxic to them

Humus

Ageing plant material is invaded by micro-organisms that begin to decompose it. At the same time, biochemical changes occur in that ageing material, breaking down cell membranes. Plant material eventually falls to the ground, is invaded by many soil organisms and decomposition quickens, as shown by increasing CO₂ production. This leads to:

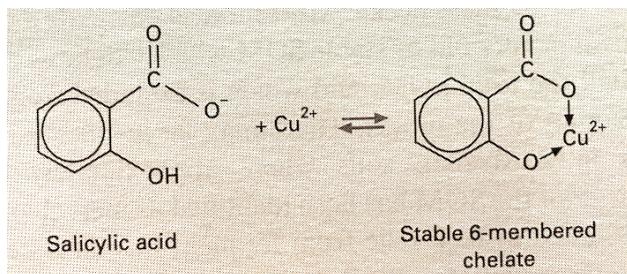
- immobilisation of elements by micro-organisms (i.e. micro-organisms use elements for growth)
- mineralisation of elements, making them available for plants
- synthesis of new compounds that form a dark brown to black shapeless material called *humus*

This process of breaking down litter, releasing mineral nutrients and synthesising new compounds is *humification*.

The biochemical changes that occur in organic matter in the soil during decomposition and humus formation are complex! White (pp. 48-49) mentions some.

Two important features of humus are:

- humification produces organic colloids that have a high CEC
 - the CEC of soil organic matter depends completely on pH
 - * the most important functional groups containing oxygen are those that dissociate to produce H⁺ ions and are the carboxylic and phenolic groups; carboxylic groups have a pK value between 3 and 5 and phenolic groups only release protons if pH > 7 (Note: For an acid, HA + H₂O ⇌ H₃O⁺ + A⁻, $K_a = [H_3O^+][A^-] / [HA]$ and pK = -log₁₀K; e.g. for acetic acid, CH₃COOH, $K_a = 1.8 \times 10^{-5}$ and pK = 4.74; for formic acid, HCOOH, $K_a = 1.8 \times 10^{-4}$ and pK = 3.74)
- humic compounds can form coordination complexes with metallic cations, producing a *chelate* compound; phenolic groups are involved in this (see figure below).



Peds and pores

Notes below are based on White, pp. 72-74; Young and Young, pp 62-63.

Bulk density = mass of oven-dry soil / total soil volume

Volumetric water content = volume of water / total soil volume

Air-filled porosity = volume of soil air / total soil volume

Field capacity is water content at a suction of 10 kPa (Australian definition). See below also.

Permanent wilting point is water content at a suction of 1,500 kPa.

Available water capacity is the nominal amount of soil water that plants can use. The upper limit is the water content at field capacity and the lower limit is the water content at which plants can no longer extract water from the soil, lose turgor and wilt - i.e. permanent wilting point (turgor is the normal rigidity of plant cells caused by the pressure of the cell contents against the cell wall). The plant-available water capacity for a particular planted area or crop is the difference between the volumetric water content at field capacity and that at permanent wilting point (summed through the root zone).

Note the above three values are a little arbitrary!

Pore space ratio = volume of pores / total soil volume

Note pore space ratio tells you nothing about the size distribution of the pores.

In a soil with reasonable structure, pores can be classed as *macropores* or *micropores*.

Macropores are the pores between soil aggregates. They allow water to infiltrate and drain through the soil. Water can drain into and through them under the influence of gravity. Air also enters and moves through the soil in them; they are responsible for soil aeration. When the macropores are drained, the soil is at field capacity.

Micropores are the pores inside soil aggregates. They are responsible for the storage of water and solutes. The water in these pores is held onto the soil particles by adhesion and surface tension, so a suction has to

be applied to remove it. The water in micropores can be removed by evaporation and can be extracted by plants but does not drain out under the influence of gravity.

With rain or irrigation, water infiltrates and wets the soil. The drainage rate often becomes very small 1 - 2 days after the rain or irrigation stops. The reason is that when most of the macropores have drained, there is a large drop in hydraulic conductivity. The water content at this point is usually taken as field capacity (although in Australia, field capacity is set at a suction of 10 kPa, which is around about this point).

Soil structure and aggregation

Soil with a reasonable amount of clay in it forms *aggregates*:

- *macroaggregates* or *peds* - visible, usually from a few millimetres to a few centimetres in diameter, and are made up of groupings of
- *microaggregates*, which are made up of groupings of the primary particles, clay, silt and sand; bundles of clay particles attach themselves to the larger silt and sand particles or sometimes even surround them; *the fundamental mechanism that gives microaggregates stability is clay particles binding together*

Roots contribute to soil structure:

- roots travel around and through aggregates, creating a three-dimensional “mesh” in the soil
- roots exert pressure on aggregates, compressing and separating them
- roots take up water from the soil, causing localised dryness, shrinkage and cracking of soil in the root zone
- roots and root hairs grow and die, promoting microbial activity and this results in “humic cements” being produced
- these cements are often broken down in turn by microbes, so organic matter has to be constantly supplied to the soil to maintain the stability of the aggregates

If the soil surface has no protective cover and is left exposed (e.g. after harvesting annual crops), the topsoil will dry out, resulting in desiccation:

- if it is then cultivated, the dried aggregates can be reduced to dust
- if it rains on the dry aggregates, they may slake

If the soil is cultivated when it is very wet, the churning effect of cultivation causes compaction.

Humus is accumulated best and soil aggregates stabilised most effectively under perennial vegetation.

Microbes contribute to soil structure:

- microbial activity varies over time as does the mix of microbes, which include protozoa (one-celled organisms with a true nucleus containing DNA - eukaryotes), bacteria (one-celled organisms without a true nucleus, where DNA is contained in the cytoplasm - prokaryotes), fungi and actinomycetes (bacteria that can break down more resistant carbon compounds like lignin)
- bacteria living in the rhizosphere are particularly important
- fungi are also particularly important, as they produce extensive networks of hyphae (or mycelia)

- soil microbes bind aggregates by adsorption, physical entangling the particles and excreting viscous material that acts like a glue
- microbial excretions (organic polymers):
 - can be adsorbed onto clay surfaces
 - can penetrate between individual clay particles
 - can form a protective coating around soil aggregates
 - can dissolve in the soil solution, penetrate aggregates and then precipitate in the aggregate forming an internal cement

Some inorganic substances can also act like a cement:

- calcium carbonate and iron and aluminium oxides can contribute a lot to aggregate stability (in soils without much organic matter - e.g. tropical soils - these substances can provide considerable stability)

Stability

Slaking

Putting a ped into water results in the water infiltrating the ped. The infiltrating water will increase the pressure of the air in the pores in the ped. If the air bubbles out and the ped remains intact, it is stable. If the ped breaks up, it has “slaked”. This means it does not have enough material to hold it together strongly enough to withstand the increased air pressure.

Dispersion

If the ped, after putting it into water, produces cloudiness in the water, it has “dispersed”. This is the result of the clay particles in the ped becoming separated from one another (deflocculation). It shows that the clay layers in the particles were initially bound together by sodium ions. Sodium ions are large ions with a single charge, Na^+ , and are in the clay interlayer spaces. Water molecules can move into the interlayer spaces, attracted by the sodium ions, and hydrate those ions. This increases the space between the clay layers to such an extent that the layers separate and the clay particle disintegrates. This causes the cloudiness around the ped. Such a soil is “sodic”.

Calcium ions, Ca^{2+} , are smaller and hold the clay layers together more strongly than sodium. Water cannot move into the interlayer space if calcium ions are binding the layers together. Water molecules can only move to the edge of the particles under any attraction by the calcium ions but do not break the calcium-clay bonds.

Organic matter, iron and aluminium sesquioxides and cations, especially calcium and magnesium, encourage flocculation (i.e. bind clay layers together).

Much of the material on mineralogy below comes from: Essington, M. 2004. *Soil and Water Chemistry: An Integrative Approach*, CRC Press, Chapter 2.

Climate

Moisture

In moist or humid climates, water moves downwards, on balance, for most of the year. This leads to leaching of soluble minerals and translocation downwards of clay particles.

In arid climates, water moves upwards, on balance, over the year. This leads to salts being brought up the soil profile and closer to the surface.

Temperature

Temperature affects the rate of mineral weathering and formation and biological processes, such as growth and decomposition.

Parent material

Rocks are classified as igneous, sedimentary or metamorphic.

Notes below are based on: <https://australian.museum/learn/minerals/shaping-earth/classification-of-igneous-rocks/>

Igneous rocks

- these are formed by the solidification of molten magma in the Earth's crust or on the surface of the Earth's crust
- they are divided into classes based on grain size and silica content:
 - grain size
 - * volcanic rocks - they solidify close to the Earth's surface and so cool quickly; they have finer grains
 - * plutonic rocks - they solidify deep in the Earth's crust and cool slowly; they have coarse grains
 - silica content
 - * *acidic* - rocks with more than 63% silica (mostly light-coloured K/Na feldspars and quartz); mainly *intrusive* (i.e. forming within the crust) - e.g. granite
 - * *basic* - rocks with 45% to 55% quartz but high in dark-coloured ferromagnesian minerals (i.e. Fe and Mg) and Ca feldspars; mainly *extrusive* (i.e. forming on Earth's surface from lava) - e.g. basalt

Metamorphic rocks

Igneous and sedimentary rocks that are subjected to high temperature and pressure have their mineral composition and structure changed and are transformed into metamorphic rocks.

Under high temperature and pressure, existing minerals break down and form new minerals. Particular pressure/temperature conditions cause particular *index minerals* to form and these minerals can be used as one classifying feature of metamorphic rocks.

Apart from index minerals, other classifying features are grain size and degree of foliation.

Texture:

- foliated (leaf-like layers) - newly formed minerals align themselves perpendicular to the direction of stress; metamorphic rocks break easily along foliation planes
- non-foliated, massive or granular - a granular texture develops if a rock's chemical composition is similar to that of a particular mineral (e.g. marble - see below)

As the grade of metamorphism increases (i.e. higher pressure and temperature), crystal size increases and foliation becomes coarser (e.g. in limestone, calcite recrystallises into larger crystals and forms marble).

	Grain size	
Foliation	Fine	Coarse
Poor	Hornfels	Marble, quartzite
Good	Slate	Gneiss

Sedimentary rocks

These are composed of the products of the weathering of igneous and metamorphic rocks and are formed when these products are deposited by wind or water. As more and more sediment layers are laid down, they exert weight on deeper sediments, which harden and form rock.

Some sedimentary rocks form by precipitation of minerals, such as limestone.

Soil mineralogy - introductory ideas

Minerals in soils can be

- crystalline - these are naturally occurring inorganic compounds with atoms in a 3-D structure that repeats
- amorphous - these are naturally occurring inorganic compounds with no repeating structure

The O^{2-} anion is the dominant anion in soil minerals (47% by weight).

The *coordination number* is the number of anions that can be packed around a cation with no overlap. The bigger the cation, the more anions that can fit around it.

The figure below from Essington shows how charges of bonds are counted.

First, a definition: bond strength = cation valence / coordination number.

On the left are silicon tetrahedra, with the Si^{4+} ions in tetrahedral coordination, each surrounded by four O^{2-} ions. The strength of each Si-O bond is $+4 / 4 = +1$. The tetrahedra are bonded through a shared basal corner O^{2-} ion. The -2 charge on the O ion is exactly balanced by the 1+ charge on each of the two Si ions it's bonded to.

On the right hand side are Al^{3+} ions in octahedral coordination, each surrounded by six OH^- ions. The strength of each Al-OH bond is $+3 / 6 = +1/2$. Consequently, each OH^- ion can only be bonded by two Al^{3+} ions. The -2 charge on each O^{2-} ion is exactly balanced by its bond with two Al^{3+} ions and one H^+ ion.

A *unit cell* of a crystal is the smallest three-dimensional repeating unit of atoms.

The most commonly occurring minerals in soil are the silicates. One class of silicates, the phyllosilicates or clay minerals, has a substantial effect on the physical and chemical properties of soil.

The *primary silicate minerals* formed as liquid magma cooled and make up the bulk of the sand- and silt-sized fractions of soil.

The *secondary silicate minerals*, formed from the weathering of the primary silicates or from precipitation of soluble mineral material, are found mainly in the clay fraction of soil and are responsible for many chemical reactions in soils.

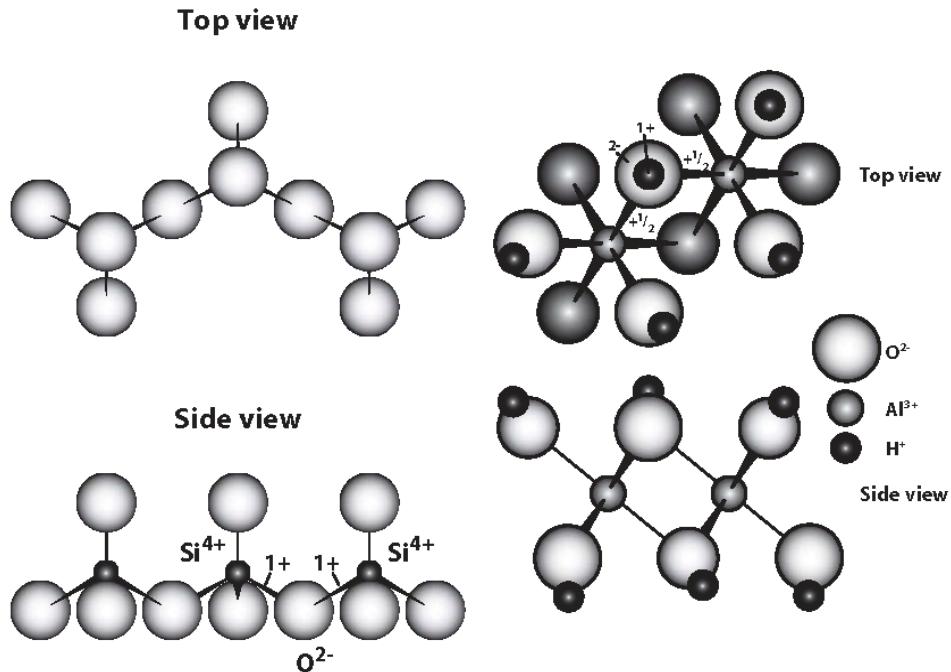


Figure 1: Essington, Fig. 2.5, p. 41

Silicate minerals

Silicate minerals make up more than 90 % of the Earth's crust. As soil is derived from minerals in the Earth's crust, the mineral makeup of soil is similar.

The tetrahedron is the basic structural unit of silicate minerals. It has strong Si - O bonds. Oxygens are shared between tetrahedra in different ways, resulting in six different structural configurations. Some of these configurations are:

- nesosilicates - independent tetrahedra are held together by cations, such as Fe^{2+} and Mg^{2+} (e.g. olivines)
- inosilicates - tetrahedra are linked to form single chains by sharing two oxygen atoms (e.g. pyroxenes) or double chains by alternately sharing two and three oxygen atoms (e.g. amphiboles)
- phyllosilicates - formed by linking all three basal oxygen atoms to form a sheet (e.g. muscovite and biotite micas)
- tectosilicates - all four oxygen atoms of each tetrahedron are linked with neighbouring tetrahedra to form a three-dimensional network; this creates very strong bonds and these minerals are very stable; about two-thirds of the Earth's crust is made up of tectosilicates, which include quartz (SiO_2) and feldspars

Primary silicate minerals are the most common minerals in soils. Probably the most important chemical weathering processes - but not the only ones - in soils are the ones that involve primary silicate minerals and their weathering products, namely, secondary silicates and accessory minerals¹.

The Earth's crust is composed of the following main primary minerals²:

¹Essington, ch. 3

²Sparks & Singh, pp., 51-53

- feldspars 50 % (39 % plagioclase feldspars, 12 % K-feldspars)
 - *An aside:*
 - * the chemical composition of feldspars is very variable
 - * the range of their composition can be represented on a ternary diagram (a triangle) with the three most important feldspar minerals at the vertices: orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$)
 - * at high temperatures, there is complete solid solution between orthoclase and albite, with K and Na substituting for each other - feldspars in this range are *alkali feldspars*
 - * similarly, there is complete solid solution between albite and anorthite at high temperatures, with a coupled substitution occurring to maintain charge - Na^+ substitutes for Ca^{2+} and Si^{4+} substitutes for Al^{3+} ($Na^+ + Si^{4+} \rightleftharpoons Ca^{2+} + Al^{3+}$) - feldspars in this range are *plagioclase feldspars*
 - * there is no solid solution between orthoclase and anorthite due to the large difference in size between K^+ and Ca^{2+}
 - 25 % to 50 % of the Si^{4+} is substituted with Al^{3+} and the charge is balanced with K^+ , Na^+ and Ca^{2+}
 - the most common weathering product is kaolinite, but you also get smectite, mica and gibbsite
- quartz 12 %
- amphiboles 11 % and pyroxenes 5 %
 - these weather to secondary clay minerals, including chlorite, vermiculite, smectite and Fe oxides
- micas 5 %
 - micas are phyllosilicates
 - muscovite and biotite are the most important two
 - micas have K^+ in the interlayer space and weather to release K^+
 - weathering produces secondary phyllosilicates, including vermiculite, smectite, kaolinite

The most important secondary minerals are phyllosilicates and various oxides of Fe, Al and Mn (i.e. oxides, hydroxides and oxyhydroxides)

Clay mineralogy

Clay minerals or clay material is made up of:

- phyllosilicates, of which there are three types, based on the ratio of tetrahedral to octahedral sheets
 - 1:1
 - 2:1
 - interlayered 1:1, 2:1 and octahedra
- accessory minerals - i.e. metal oxides, hydroxides and oxyhydroxides and organic matter.

1:1 phyllosilicates

Dioctahedral: kaolinite group

- Kaolinite is probably the most common aluminosilicate mineral in soil.
- Its 1:1 layers are held together quite tightly by hydrogen bonding. It has low CEC (it has a little isomorphous substitution and also has some edge charge due to protonation and deprotonation).

Trioctahedral: serpentine group

2:1 phyllosilicates

These minerals are can be grouped according to layer charge.

The *mica* group, which consists of primary minerals, has a layer charge of about 0.6 to 2, due to isomorphous substitution (note that vermiculite is a secondary mineral derived from mica).

The *smectite* group has a layer charge of up to about 0.6 and includes both dioctahedral and trioctahedral minerals.

- As the layer charge of smectites is fairly low, water molecules and hydrated cations can get between the 2:1 layers.
- The hydrated cations in the interlayer space that satisfy the charge can be displaced and are exchangeable.

The *vermiculite* group has a charge between about 0.6 and 0.9.

- Even though the layer charge is higher than the smectites, water and hydrated cations can still get between the 2:1 layers.

Interlayered 1:1, 2:1 and octahedra

This group includes, for example, the chlorite group, which is interlayered octahedral.

Accessory minerals

Accessory minerals are hydrous and anhydrous oxides, hydroxides and oxyhydroxides of metals, such as Fe^{III}, Al, Mn and Si. They are often closely associated with primary and secondary aluminosilicates, from which they are produced by chemical weathering. Some examples are gibbsite Al(OH)₃, haematite Fe₂O₃ and goethite FeOOH³.

They are amphoteric - i.e. they can carry positive or negative charge depending on the characteristics of the soil solution.

Gibbsite, Al(OH)₃, is a ubiquitous metal hydroxide, occurring particularly in highly weathered soils.

Compounds of iron are also very common, with goethite, FeOOH, the most common hydrous iron oxide.

Iron oxides accumulate in highly weathered soils, especially those that form from the weathering of *basic* rocks. All the iron oxides form by precipitation.

Haematite, an Fe^{III} oxide, Fe₂O₃, often occurs with goethite.

Chain silicates

In the figure below, silicon tetrahedra are shown linked into single chains (top) and double chains (bottom).

Pyroxenes are made up of single chains of silicon tetrahedra linked through basal oxygen atoms. The basic unit is SiO₃²⁻. How do you get this unit formula? Each Si-O bond has a strength of +4 / 4 = +1. The four O atoms in a single tetrahedron in focus are numbered. O no. 1 is shared with the neighbouring Si atom, so only half of it "belongs to" the tetrahedron in question. O nos. 2 and 3 both belong wholly to the focal tetrahedron. Like O no. 1, only half of O no. 4 is counted. So, there are one Si atom and three O atoms in the basic pyroxene unit, giving SiO₃²⁻.

³Essington, pp. 80-81

Amphiboles are made up of double chains of silicon tetrahedra linked through basal oxygen atoms. The basic unit is $\text{Si}_4\text{O}_{11}^{2-}$. How so? The Si atoms are numbered 1 to 4. The set of tetrahedra with these Si atoms constitutes the basic repeating unit of the chains. Some of the oxygen atoms in this unit are marked in groups (with A, B and C), while the other six O atoms in the repeating unit are unmarked. Again, each Si-O bond has a strength of +1.

- The six unmarked O atoms in the unit belong wholly to the unit and contribute their full value. Contribution here is 6.
- O atoms marked A are shared with Si atoms in neighbouring tetrahedra, so each contributes half to the basic unit. Contribution here is 2.
- One of the O atoms marked B is shared between Si atoms 1 and 2 (i.e. half with each Si atom), both of which are in the basic unit, so that O atom contributes its full worth. The other O atom marked B is shared in the same way with Si atoms 3 and 4 and also contributes its full worth. Contribution here is 2.
- Oxygen atom C is shared in a similar way to the Bs, so also contributes its full worth. Contribution here is 1.
- Total oxygen “value” is 11.

This gives the basic unit of $\text{Si}_4\text{O}_{11}^{2-}$.

Phyllosilicates

Phyllosilicates are sheet silicates or layer silicates. The basic unit is $\text{Si}_2\text{O}_5^{2-}$. Each individual tetrahedron shares three basal O atoms, as shown below. The result is a sheet structure.

An example of primary phyllosilicate minerals is the micas. They are 2:1 layer silicates - i.e. two silicate tetrahedral sheets sandwiching an octahedral sheet.

The basic unit of the octahedral sheets is three octahedra. If two out of the three positions available in the octahedra for cations are occupied by cations, the sheet is dioctahedral. If all three positions are occupied, the sheet is trioctahedral.

Isomorphous substitution occurs when an atom replaces another atom which has a similar size - e.g. Al^{3+} can replace Si^{4+} in a tetrahedral sheet and Fe^{2+} , Fe^{3+} or Mg^{2+} can replace Al^{3+} in octahedral sheets.

If Al^{3+} substitutes for Si^{4+} in a tetrahedral layer in a dioctahedral mica, there will be a charge deficit of -1. This is balanced by K^+ ions in the interlayer space.

In trioctahedral micas, the three octahedral spaces are occupied by divalent cations (e.g. Mg^{2+}) to maintain the charge balance. If Al^{3+} substitutes for Si^{4+} in a tetrahedral layer in a trioctahedral mica, there will be a charge deficit of -1. This is balanced by K^+ ions in the interlayer space, as in the dioctahedral case.

Weathering processes of primary minerals

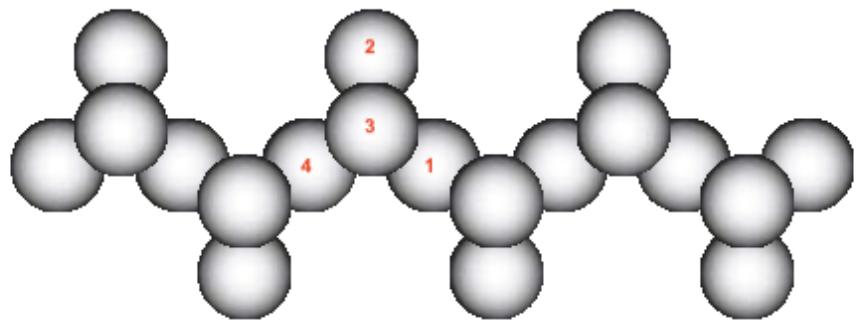
See Sparks & Singh, p. 53

Weathering of primary minerals produces secondary minerals, which include many plant nutrients (K, Ca, Mg, Fe, Mn, Na, Si) and some toxic elements (As, Co, Cr, Ni, Pb).

Physical weathering leads to rocks disintegrating.

Chemical weathering causes rocks to decompose. The rate of chemical weathering is affected by:

Pyroxene



Amphibole

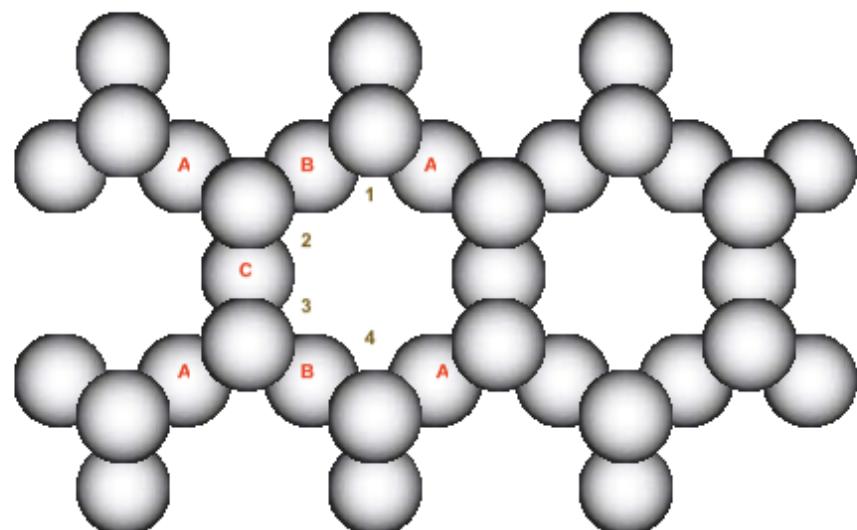


Figure 2: Essington, Fig. 2.10, p. 49

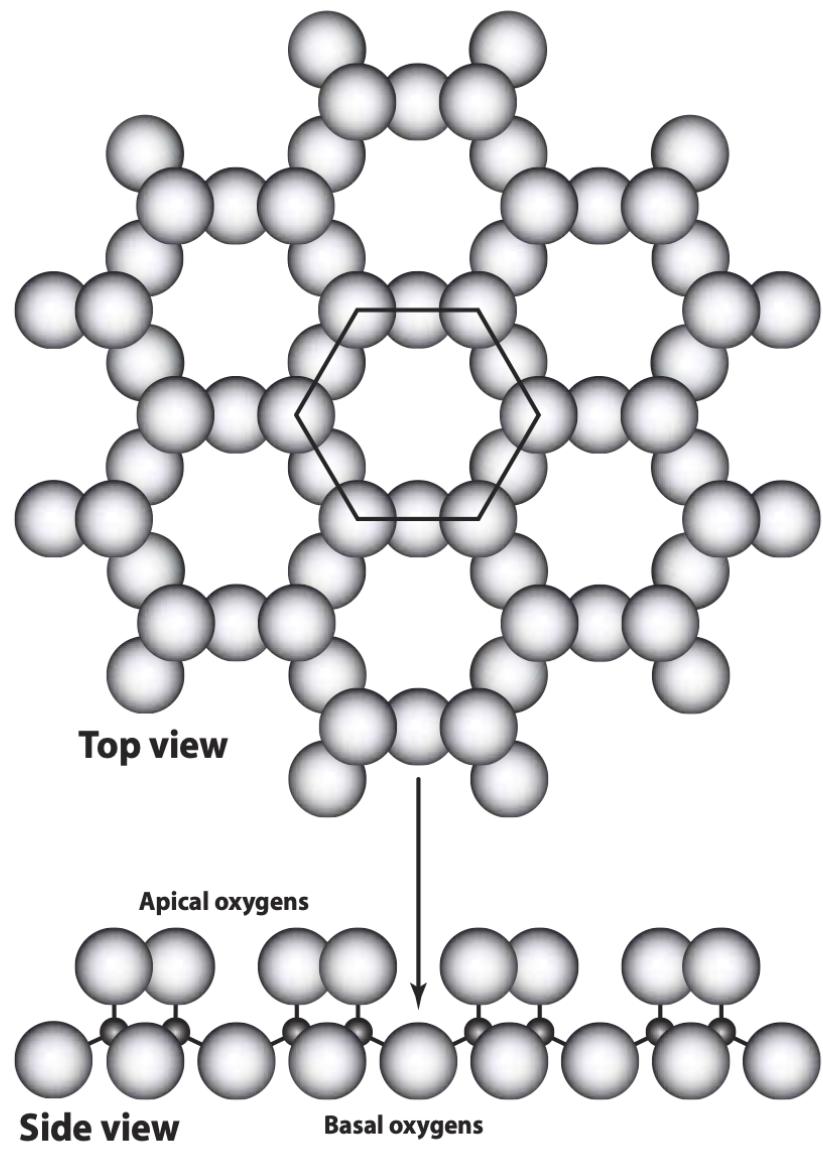


Figure 3: Essington, Fig. 2.11, p. 50

- structure and composition of minerals
- specific surface area
- availability of water
- temperature

Water, with oxygen and acids, drives chemical weathering through these processes:

1. hydration

- absorption of water by minerals - this is reversible (e.g. haematite absorbs water to form goethite: $\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{FeOOH}$)

2. carbonation

- CO_2 dissolved in rainwater produces carbonic acid ($\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$), a weak acid that can cause chemical weathering
- limestone dissolving in acidic water is classic carbonation ($\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$)
- the concentration of CO_2 in soil is much higher than in air due to microbes and plant roots respiring
- acidity from this dissolved CO_2 drives hydrolysis of primary minerals, the most important weathering process of primary silicates

3. oxidation

- iron in primary minerals is predominantly Fe^{2+}
- when this iron is exposed to air and water, it oxidises to Fe^{3+}
- the oxidation of Fe^{2+} in ferromagnesian silicates often starts the chemical weathering of these minerals

4. hydrolysis

- a water molecule breaks chemical bonds in the structure of a primary mineral

Surface charge - and CEC

Cations (and anions) are adsorbed onto the surfaces of clay minerals and oxides owing to:

- permanent negative charge on clay minerals due to isomorphous substitution
- the amphoteric properties (i.e. can be negatively or positively charged) of the edges of kaolinite and the oxides and oxyhydroxides of Fe and Al.

The cation (or anion) charge adsorbed gives the *cation exchange capacity* (or CEC) of the mineral. Analogously, there is also the anion exchange capacity (AEC).

- For crystalline 1:1 and 2:1 phyllosilicates, permanent negative charge and so CEC is more important. Note CEC varies quite a lot within mineral groups.
 - In 2:1 clays, illites, for example, have a low CEC, as a lot of the charge is neutralised by interlayer K^+ , which is non-exchangeable. In vermiculites, however, the interlayer Ca^{2+} and Mg^{2+} are exchangeable and so the CEC is high.
- In sesquioxides, the charge *depends on pH*. Sesquioxides are positively charged up to a pH of 8 and so contribute nothing to CEC.

Soil acidity and pH

Overview and story - Essington

Material below is from Essington, sect. 10.1 and 10.2

Proton activity controls many chemical reactions, so pH is a “master” variable.

pH measures the true activity of protons in solution, not the (negative log of the) molar concentration of protons. It is an *indicator* of soil acidity.

Soils with a pH of less than 5 present environmental and agronomic problems:

- the availability of macronutrients is reduced
- microbial activity is reduced
- levels of soluble Al and Mn are toxic to plants
- the solubility and so availability of potentially harmful trace elements is high

While human activities can increase soil acidity, soil acidification is a natural part of weathering.

- during weathering, carbonic acid and organic acids are involved in the hydrolysis of soil minerals;
- in areas where rainfall exceeds evapotranspiration, base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) and silica become soluble and are leached from the soil
- other products of weathering, such as Al^{3+} and Fe^{3+} , hydrolyse and release protons in the hydrolysis reactions, as well as accessory minerals (e.g. gibbsite (Al(OH)_3) and goethite ($\alpha\text{-FeOOH}$))
 - the hydrolysis products of Al^{3+} are mainly AlOH^{2+} and Al(OH)_2^+
 - the hydrolysis products of Fe^{3+} are Fe(OH)_2^+ ($\text{pH} < 7.4$), Fe(OH)_3 ($7.4 < \text{pH} < 8.5$) and Fe(OH)_4^- ($\text{pH} > 8.5$) (See Lindsay & Schwab 1982 - paper in Soil folder)⁴

There are three important processes that increase soil acidity:

- the hydrolysis reactions just described
- the removal of base cations from exchange sites by Al^{3+} , AlOH^{2+} and Al(OH)_2^+
- the subsequent leaching of the basic cations, which do not hydrolyze to produce protons

However, the *fundamental cause of soil acidity* is Al species, which are labile (i.e. reactive, unstable) and can undergo hydrolysis and so produce protons, occupying exchange sites

Physical processes affect soil acidity:

- the processes that transport acidic and alkaline substances into, out of and throughout the soil profile
- substances that cause acidity enter the soil via precipitation (rain or snow) - such substances include carbonic acid and (hydrated) protons from industrial emissions (e.g. sulphuric acid from SO_2 produced by coal-burning electric power stations)
- precipitation also supplies the water that leaches base cations through the soil profile
- various dry particles fall onto the soil surface (e.g. N and P fertilisers)

Most of the stuff below comes from Sparks, *Environmental Soil Chemistry*, chapter 9.

Soil acidity affects:

- nutrients

⁴Lindsay & Schwab, 1982, The chemistry of iron, <https://doi.org/10.1080/01904168209363012>

- macronutrients are more available above a pH of about 5.5
- micronutrients are more available below a pH of about 6
- bacteria and actinomycetes - they like a pH above about 5.5
- fungi - they don't really care about pH, as long as it's not extreme - they're pretty happy in the range, $4 < \text{pH} < 9$

In most soils, soil acidity is related to H and Al. The latter is more important except when $\text{pH} < 4$.

As pH drops below about 5, Al, Fe and Mn - and other transition metals - become more soluble and can be toxic to plants. As pH increases, they become less soluble, start to precipitate and so become unavailable to plants.

Buffering

Carbonic acid in soil, produced by microbes oxidising organic matter and from CO_2 in soil air, could produce an acidic soil solution, if it were the only substance controlling pH. However, there are many other acid-base reactions involving organic functional groups that buffer soil pH. Soil organic matter contains many functional groups that are weak acids (e.g. carboxyl ($-\text{COOH}$), phenolic (aromatic hydrocarbon group— OH) and amino ($-\text{NH}_2$) groups)⁵.

Generally, primary mineral weathering consumes protons (for example, hydrolysis); secondary mineral precipitation produces protons⁶.

Most reduction reactions consume protons; most oxidation reactions produce protons⁷.

Al and soil acidity

Al hydrolyses in an aqueous solution - this reaction is reversible. (Hydrolysis is a reaction where a substance is split or decomposed by water.)

There's a series of reactions “starting” with $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and “ending” with $[\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2]^{1-}$. The product of each hydrolysis reaction is a monomeric Al ion and H_3O^+ . At each “step”, one molecule of water is deprotonated.

The reaction equations and a plot showing the distribution of the Al species relative to the pH are below.

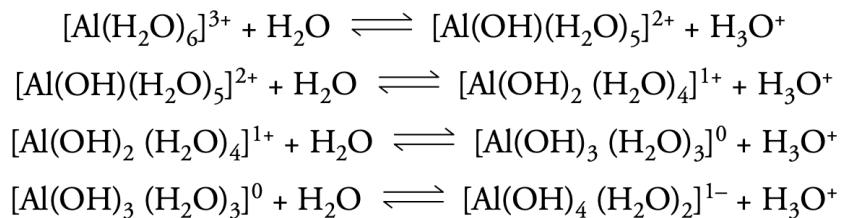


Figure 4: Sparks 2003, p. 271.

Some points to notice in the above plot are noted below and others as a table (Sparks et al. 2024, p. 394):

- the relative concentrations of the various monomeric Al ions depend on the pH of the soil solution:
- if $\text{pH} < 5$ or $\text{pH} > 7.5$, the concentration of Al^{3+} quickly increases
- the amount the pH drops owing to the production of protons as these reactions occur depends on the concentration of Al in the soil solution

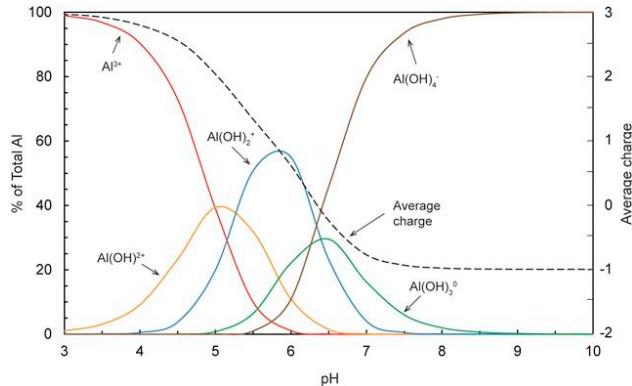


FIGURE 9.8 Relationship between pH and the distribution and average charge of soluble aluminum species. The data for various Al species were obtained using Visual MINTEQ with a total Al concentration of 1×10^{-4} M.

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Figure 5: Sparks et al. 2024, Fig. 9.8, p. 395. Note: This diagram differs slightly in different books depending on how it was derived.

pH range	Dominant Al species
pH < 5.0	$\text{Al}^{\sim 3+}$
5.0 < pH < 5.25	$\text{Al}(\text{OH})^{\sim 2+}$
5.25 < pH < 6.5	$\text{Al}(\text{OH})^{\sim 2\sim}$
pH = ~6.4	$\text{Al}(\text{OH})^{\sim 2\sim}$, $\text{Al}(\text{OH})^{\sim 3\sim}$ and $\text{Al}(\text{OH})^{\sim 4\sim}$ in equal proportions
pH > 6.5	$\text{Al}(\text{OH})^{\sim 4\sim}$
5.0 < pH < 7.5	Solubility of Al is low and Al precipitates as $\text{Al}(\text{OH})^{\sim 3\sim}$

The soil exchange complex accepts Al^{3+} and $\text{Al}(\text{OH})_2^+$ in preference to base cations, which are easily displaced by the Al species.

If the base cations are not leached, the acid neutralisation capacity of the soil is increased. However, water percolating through the soil will mobilise the displaced base cations rather than adsorbed Al species and, as a result, acid neutralisation capacity of the soil will decrease and soil acidity will increase.

Free Al^{3+} might only account for a small proportion of Al in the soil solution. There may be quite a lot bound to fluoride or sulphate ions, humic material or organic acids.

As pH increases above about 5, the proportion of Al^{3+} decreases and various monomeric (one Al atom) and polymeric (more than one Al atom) hydroxy-Al species become more common. These latter species can occur in the interlayers of smectite and vermiculite, in organic complexes and oxyhydroxide coatings on clay particles.

These hydroxy-Al species are non-exchangeable (because they cannot be replaced or extracted by a salt like KCl).

The polymers are large and positive and are more likely to be in interlayer spaces than monomeric species.

If these polymeric species are arranged around the edge of the interlayer space, they can block other ions reaching exchange sites further into the interlayer space.

If they are arranged throughout the interlayer space, they act as props, keeping the interlayer space open, and increase ion exchange.

Soil acidity - some more detail

The main forms of acidity in mineral soils relate to Al; the two main forms are exchangeable (or *extractable*, since the technique used can affect the result) and nonexchangeable.

Exchangeable acidity is the amount of total CEC due to H^+ , which contributes the smaller component, and Al^{3+} , the larger component, combined.

The amount of exchangeable acidity depends on the soil type, and so the amount of CEC due to exchangeable bases (i.e. Ca^{2+} , Mg^{2+} , K^+ and Na^+), which varies with soil type.

For the minerals below, the proportion of exchangeable acidity out of total acidity decreases in this order:

- montmorillonite - it has mostly constant charge sites
- dioctahedral vermiculites - a substantial amount of their acidity is nonexchangeable and made up of polymeric hydroxy-Al material in the interlayer space and depends on pH
- kaolin minerals - it has low CEC and variable charge

Al and Fe coatings on clay particles reduce the amount of exchangeable acidity that can be extracted and so reduce the proportion of exchangeable acidity in the total acidity.

Acidity and weathering

Essington, pp. 473ff

Soil acidification is a natural result of weathering.

- During weathering, carbonic and organic acids hydrolyse soil minerals.

⁵Essington, p. 480

⁶Essington, p. 480

⁷Essington, p. 482

- Base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) and silica become soluble (are “solubilised”).
- Other products of weathering, such as soluble Al^{3+} and Fe^{3+} , hydrolyse, producing protons in the process and also, on the Al side, mainly AlOH^{2+} and $\text{Al}(\text{OH})_2^+$.
- Al species (Al^{3+} , AlOH^{2+} and $\text{Al}(\text{OH})_2^+$) then displace base cations from the exchange complex.
- In areas where rainfall exceeds evapotranspiration, base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), which do not hydrolyse to produce protons, are leached from the soil.
- *The fundamental cause of soil acidity is Al species occupying the exchange complex. These Al species are labile (i.e. they can be removed from the exchange complex easily and hydrolysed, producing protons).*

Many soils across the world, such as soils in the humid tropics and in forests in temperate zones, are acidic.

Acidity and biological processes

See Essington, *Soil and Water Chemistry*, chapter 10.

{p. 482}

Most oxidation reactions produce protons. Most reduction reactions consume protons. Curious!

Systems with lots of electrons are reduced (here hydrogen will be more stable relative to water) and those depleted of electrons are oxidised (here, oxygen will be more stable relative to water) (Essington, pp. 445 & 447).

You need to look at the whole redox reaction to see what's happening - oxidation or reduction half-reactions on their own don't show the full picture.

Example

Oxidising ammonium can potentially lead to acidification through nitrification:



Nitrification will only lead to acidification if the nitrate and base cations are leached from the soil.

If this leaching happens, the protons produced by nitrification will stay in the soil. They will occupy organic exchange sites and also take part in mineral weathering.

The Al dissolved in this weathering will hydrolyse, producing more acidity and also displace base cations from exchange sites.

If the nitrate is not leached, acidification may not occur. This is because, when plants absorb a nutrient anion, they release OH^- and HCO_3^- , generating alkalinity:

$$[\text{equivalents anions absorbed}] - [\text{equivalents cations absorbed}] = [\text{equivalents hydroxide and hydrogen carbonate released}]$$

Similarly, when plant roots absorb cations, acidity is generated:

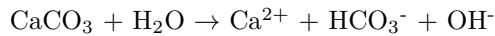
$$[\text{equivalents cations absorbed}] - [\text{equivalents anions absorbed}] = [\text{equivalents protons released}]$$

Plants usually absorb more cations than anions, so, on the whole, more protons are released than hydroxide and hydrogen carbonate. The pH of the rhizosphere can be up to two units lower than the soil solution.

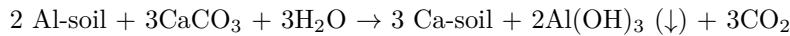
Neutralising soil acidity, liming ...

Sparks, pp. 281-282

To neutralise soil acidity, apply lime. The general reaction is:



The hydroxide reacts with existing H^+ or H^+ formed by hydrolysing Al^{3+} :



The products are Ca^{2+} , which can move onto exchange sites, and Al(OH)_3 , which precipitates, removing Al from exchange sites and the soil solution.

Essington, s. 10.3 & 10.4, pp. 483ff.

Revisiting soil acidity. If less H^+ is neutralised than is produced by acid-forming processes, soil becomes acidic. Some of these neutralising processes are:

- mineral weathering
- plants taking up anions
- anions or surface functional groups being protonated
- base cations being retained on exchange sites
- reduction reactions

Definitions

Acid-neutralisation capacity of the soil solid phase (ANC)

- When K-feldspar, for example, is weathered by hydrolysis (i.e. dissolved), protons are consumed. This reduces the ANC of the soil solids by using up minerals (i.e. K-feldspar) that can neutralise protons.
- When Al^{3+} is hydrolysed, gibbsite (Al(OH)_3) is precipitated and protons are produced. This increases the ANC of the soil solids by producing a mineral that can neutralise protons (i.e. the reaction could go the other way, if conditions were right).
- The soil exchange complex responds quickly to any change in the soil solution.
- The ANC of the soil solids exchange complex (soil exchange phase ANC) is the amount of surface charge on the exchange complex that equals the charge of the exchangeable bases adsorbed on the complex. These exchangeable bases are the metals that do not hydrolyse at usual soil pH (Ca^{2+} , Mg^{2+} , K^+ , Na^+).
- The ANC of the soil exchange phase is also called “base saturation”.

So, ...

Total acidity

- Total acidity of a soil = CEC - ANC (i.e. the part of the CEC not occupied by exchangeable base cations)
- Actual total acidity is also called exchangeable acidity. (There is also non-exchangeable acidity. This is made up of Al species and protons that are bound onto surfaces but that cannot be displaced. This is not part of total acidity.)
- It's mainly made up of
 - Al^{3+} and Al(OH)_2^+ on clay exchange sites
 - Al species and protons that are in complexes with organic functional groups

Back to neutralising soil acidity ...

The point at which soil acidity needs to be reduced for optimal plant growth is not based on pH but on total acidity. Well, ...!

When total acidity reaches more than about 15 % of CEC, soil acidity needs to be reduced.

To reduce acidity to an appropriate level, base cations need to be added to remove acidic species from the exchange complex. Usually, Ca^{2+} or Mg^{2+} is added.

The lime requirement is based on the amount of these base cations needed to reduce total acidity and is not based on the pH.

Tests used to work out how much base cation is needed are built on buffer tests incorporating measured changes in pH values and give approximate values.

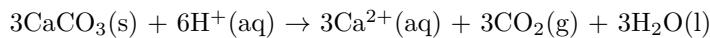
The liming materials usually used are limestone (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$).

Adding CaCO_3 initially consumes protons but the overall soil neutralisation reaction *conserves* protons.

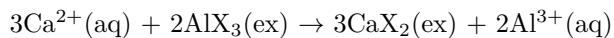
The aims of liming are to:

- displacing Al species from the exchange phase by base cations
- precipitate the Al that has been displaced

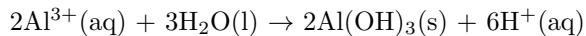
The reactions go like this:



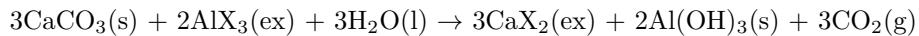
This first reaction quickly increases the pH of the soil solution. This increased pH promotes Ca^{2+} moving onto exchange sites:



The raised pH also promotes Al precipitating:



Adding the three equations above together gives the overall reaction equation:

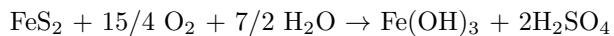


Note that there is no net decrease in H^+ ions.

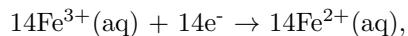
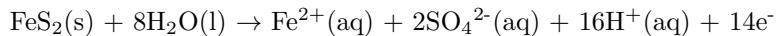
Acid sulphate soils - a little aside

Acid sulphate soils occur on marine floodplains in temperate and tropical climates. When these floodplains are drained, pyrite in the soil is oxidised and high levels of acidity produced. Disulphide (S_2^{2-}) is oxidised by ferric iron (Fe^{3+}) to produce sulphate (SO_4^{2-}), ferrous iron (Fe^{2+}) and protons.

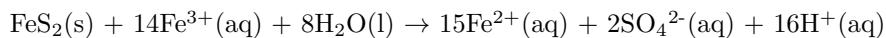
This is Sparks' equation (p. 270):



Essington gives his version, including the half reactions (p. 446):



with the overall reaction



Here, Fe^{3+} is the oxidant and S^{2-} is the reductant.

(*Another aside*: The pyrite structure also occurs in other MX_2 compounds, where M is a transition metal and X is a member of the oxygen group (O, S, Se and Te).)

Soil acidity - more of a storyline

Summary points below from Charman and Murphy, pp. 224ff

Natural factors affecting soil acidity:

- weathering of parent material
 - nature of parent material
 - climate - rainfall, temperature
- age of soil - younger soils have had less time to develop acidity
- season - soil pH fluctuates throughout the seasons

Factors influencing soil acidity due to human activities:

- agriculturally induced factors
 - applying fertilisers, especially ammonium fertilisers
 - allowing nitrate to leach from the soil
 - applying organic matter or allowing it to build up in the soil
 - removing produce
 - liming

Following on from Charman and Murphy's points....

See also White pp. 50, sect. 7.2, p. 133, p. 234, p. 172 (leaching)

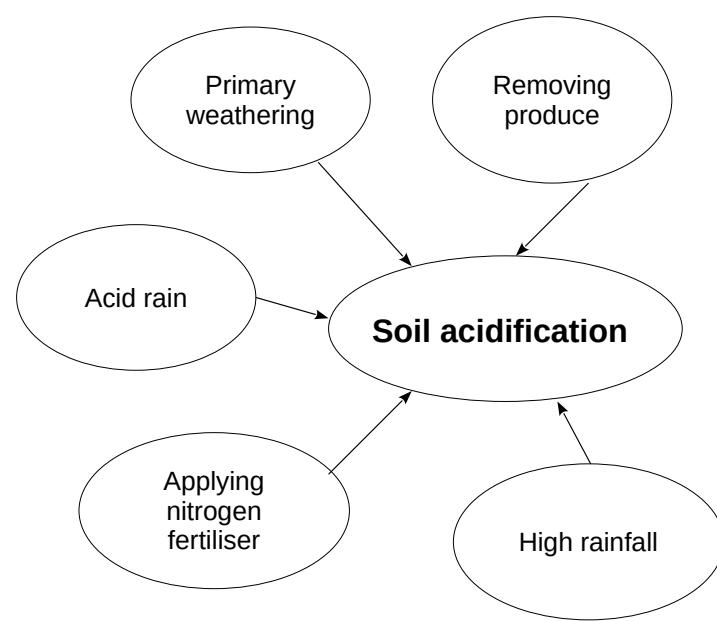


Figure 6: Factors contributing to soil acidification