The basic building blocks of clay minerals are:

- silicon atoms surrounded by four oxygen atoms (tetrahedra), and
- aluminium atoms surrounded by six hydroxide groups (dioctahedra), or
- magnesium atoms surrounded by six hydroxide groups (trioctahedra).
Negative Surfaces of Clays

These groups of atoms are **arranged in sheets.**

The atoms in these sheets are tightly bound and **are not exchangeable** with other ions in the soil solution.

When the single tetrahedra and octahedra join to form sheets, the positive (Si$^{4+}$, Al$^{3+}$, Mg$^{2+}$) and negative charges (O$^{2-}$, OH$^{-}$) are balanced.
Negative Surfaces of Clays

However, oxygen atoms that are exposed on the surface of the clay are not wholly balanced by positively charged atoms.

A net negative charge results.

The total negative charge—is the soil's cation exchange capacity, CEC.

The negative surfaces of clays can attract and hold cations.
The negative charge on the surface of clay particles attracts positive ions (cations).

This is important because it allows us to alter soil structural characteristics chemically by changing the cations that are adsorbed on the clay surface.
Elements having an electrical charge are called ions.

Positively-charged ions are cations;

Negatively-charged ions are anions.
Why do soils have a CEC?

Soils have a CEC primarily because clay particles and organic matter in the soil tends to be negatively charged.

Silicate clay minerals: clay minerals that contain silica.

Each silicate clay particle is made up of individual layers or “sheets”.
If the mineral was pure silica and oxygen (silica oxide more commonly referred to as quartz), the particle would not have any charge.
However, clay minerals commonly, contain aluminum as well as silica. They have a net negative charge because of the substitution of silica (Si\(^{4+}\)) by aluminum (Al\(^{3+}\)) in the mineral structure of the clay.

This replacement of silica by aluminum in the clay mineral’s structure is called isomorphous substitution, and the result is clays with negative surface charge.
Substitution of silica by aluminum in soil clay particles causes clays to have a negative charge. Because of this negative charge, the soil can hold on to positively charged cations such as calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$) and potassium (K$^+$).
The most common soil **cations** (including their chemical symbol and charge) are: calcium (Ca++), magnesium (Mg++), potassium (K+), ammonium (NH4+), hydrogen (H+) and sodium (Na+).

**Common soil anions** (with their symbol and charge) include: chlorine (Cl-), nitrate (NO3-), sulfate (SO4=) and phosphate (PO43-).

**Note also** that anions can have more than one negative charge and may be combinations of elements with oxygen.
Cations are positively charged ions such as:

calcium (Ca$^{2+}$),  
magnesium (Mg$^{2+}$),  
potassium (K$^+$),  
sodium (Na$^+$)  
hydrogen (H$^+$),  
aluminum (Al$^{3+}$),  
iron (Fe$^{2+}$),  
Manganese (Mn$^{2+}$),  
zinc (Zn$^{2+}$) and  
copper (Cu$^{2+}$).
These cations are held by the negatively charged clay and organic matter particles in the soil through electrostatic forces.

**Electrostatic forces:** negative soil particles attract the positive cations.
Cations held on the clay and organic matter particles in soils can be replaced by other cations; thus, they are exchangeable.

For instance, potassium can be replaced by cations such as calcium or hydrogen, and vice versa.
The total number of cations a soil can hold--or its total negative charge--is the soil's cation exchange capacity.

The higher the CEC,
the higher the negative charge and
the more cations
that can be held.
The ability of clay minerals to hold cations is called the ‘cation exchange capacity’ (CEC).

**Smectite** has a much greater ability than kaolinite to hold cations.
The CECs of kaolinite, smectite and illite are approximately 9, 100 and 25 cmol(+) /kg or (meq/100g) respectively.

*Organic matter* also contributes to CEC and has a CEC of approximately 250 cmol(+) /kg or (meq/100g) at pH 8.5.
Charge Development on Clays

Two main sources of charge in clay minerals are:

- Isomorphous substitution and
- pH-dependent charges.

Charge development of silicate clays is mainly due to isomorphous substitution.

It takes place during crystallization and is not subject to change afterwards.
In *tetrahedral* coordination, $\text{Al}^{3+}$

for $\text{Si}^{4+}$ and

in *octahedral* coordination

$\text{Mg}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}$

for $\text{Al}^{3+}$.

Charges developed as a result of isomorphous substitution are permanent and not pH-dependent.
The negative charge of the clay particles is balanced by the positive charge of the cations in the soil.

The negative charges associated with isomorphous substitution are considered permanent, that is, the charges do not change with pH changes.
● **Permanent Negative Charge:**

Due to imperfections in the chemical structure of clay crystals, almost all common clays contain a negative charge (referred to as the *permanent* negative charge due to isomorphie substitution).

● **pH-dependent charge**

Soils also have a *pH-dependent charge* on their surface, which means that there are more cation exchange sites on clay and organic matter as the pH increases and fewer as the pH declines.
pH-dependent charges

Organic matter can have a 4 to 50 times higher CEC per given weight than clay.

The source of negative charge in organic matter is different from that of clay minerals;

The dissociation (separation into smaller units) of organic acids causes a net negative charge in soil organic matter, and again this negative charge is balanced by cations in the soil.
Self-ionization of water

The self-ionization of water is the chemical reaction in which a proton is transferred from one water molecule to another, in pure water or an aqueous solution, to create the two ions, hydronium, $\text{H}_3\text{O}^+$ and hydroxide, $\text{OH}^-$. 
Cation exchange capacities also vary with the pH (index of acidity or alkalinity) of the medium, which greatly affects dissociation of the hydroxyls.

Clay particles have hydroxyls (OH)$^-$ exposed on their surfaces and edges. The tendency for the hydroxyls to dissociate (separate) in water is strongly influenced by the pH.

$$\text{SiOH} \rightarrow \text{SiO}^- + \text{H}^+$$
Clay minerals also have pH-dependent charges, which result from the ionization of hydrogen ions from SiOH groups around the edges of the crystals and perhaps for other reasons.
The higher the pH,
the greater the tendency for
the H\textsuperscript{+} to go into solution,
and
the greater the effective
negative charge of the particle.
pH

$$pH = -\log_{10} H^+ \text{ concentration}$$

- pH < 7 is acid. → High H\(^+\) concentration
- pH > 7 is basic. → Low H\(^+\) concentration
The pH scale is a measure of the acidity or basicity of a solution. It is defined as the negative logarithm of the hydrogen ion concentration ($[H^+]$) in moles per liter (M):

$$\text{pH} = -\log([H^+])$$

The pH scale ranges from 0 to 14, with 7 being neutral. Values below 7 indicate acidity, and values above 7 indicate basicity. The scale is logarithmic, meaning each whole number increase in pH represents a tenfold decrease in hydrogen ion concentration.

- **Acidic** solutions have a pH less than 7 and increase in concentration of hydrogen ions ($H^+$).
- **Basic** solutions have a pH greater than 7 and increase in concentration of hydroxide ions ($OH^-$).

Common pH values and their corresponding concentrations are:

- pH 0 to 1: $10^{-1}$ to $10^{-12}$
- pH 1 to 6: $10^{-6}$ to $10^{-12}$
- pH 6 to 7: $10^{-7}$
- pH 7 to 14: $10^{-12}$ to $10^{-14}$

The pH scale is crucial in many fields, including chemistry, biology, and environmental science, as it helps in understanding the behavior of substances in aqueous solutions.
The higher the pH, the greater the negative charge of the particle

<table>
<thead>
<tr>
<th>H⁺</th>
<th>pH</th>
<th>as H⁺ ↑ pH ↓</th>
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</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
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</tbody>
</table>
As pH is increased above 6, the pH-dependent charge increases progressively, reaching a maximum at a pH of around 10.

Such charges do not develop below a pH of about 6, and do not contribute to the effective cation-exchange capacity of acid soils.
The negative charge, or effective cation-exchange capacity, of clays and organic matter varies with pH. Those of kaolinite (curve 1) and montmorillonite (curve 2) are constant below pH 6 but increase at more alkaline reactions. The negative charge of humus (curve 3) increases linearly with pH.
Because organic acid dissociation depends on the soil pH, the CEC associated with soil organic matter is called pH-dependent CEC.

This means that the actual CEC of the soil will depend on the pH of the soil.

Given the same amount and type of organic matter, a neutral soil (pH ~7) will have a higher CEC than a soil with e.g. pH 5,

or in other words,

the CEC of a soil with pH-dependent charge will increase with an increase in pH.