Chemical properties of soils

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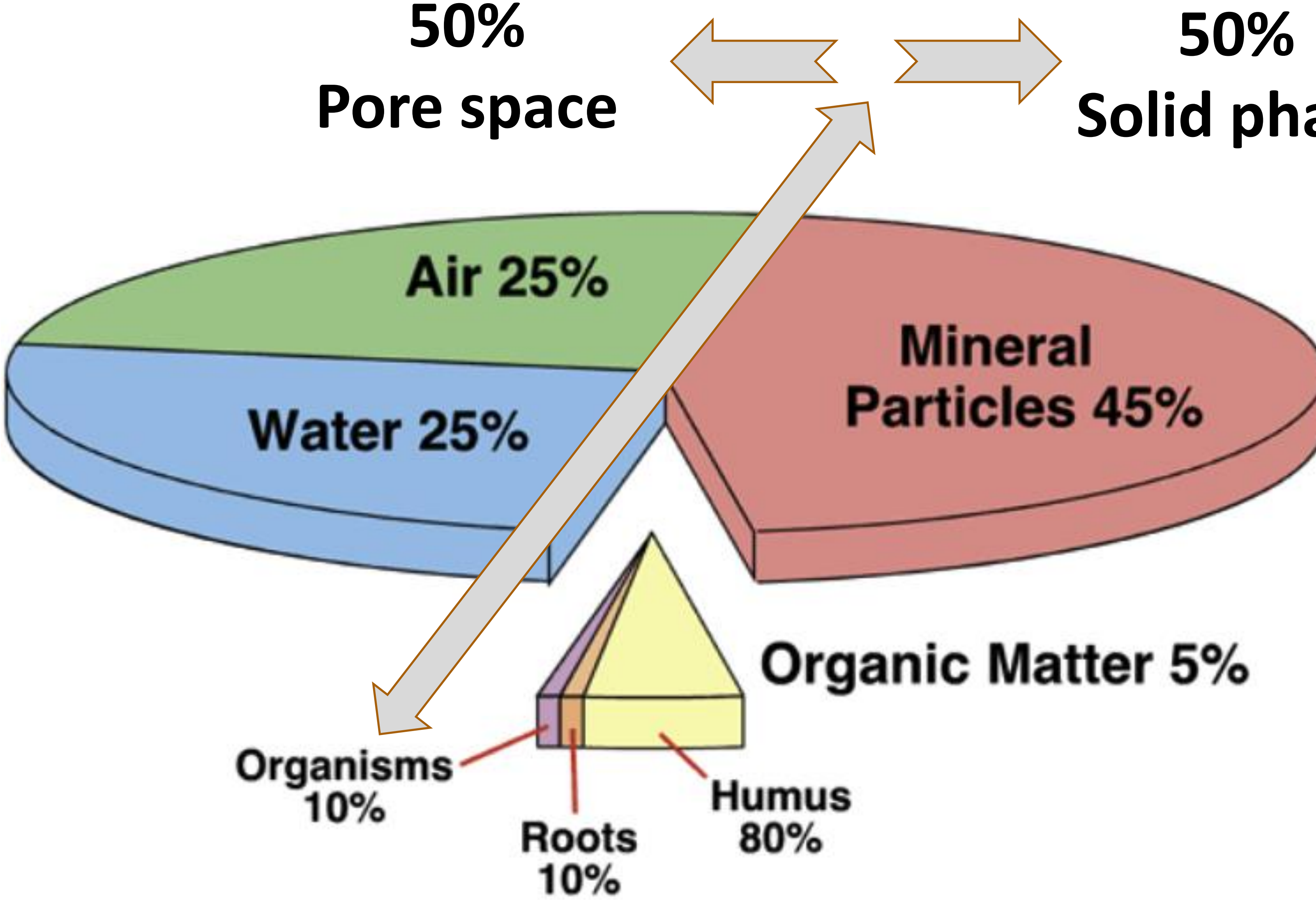
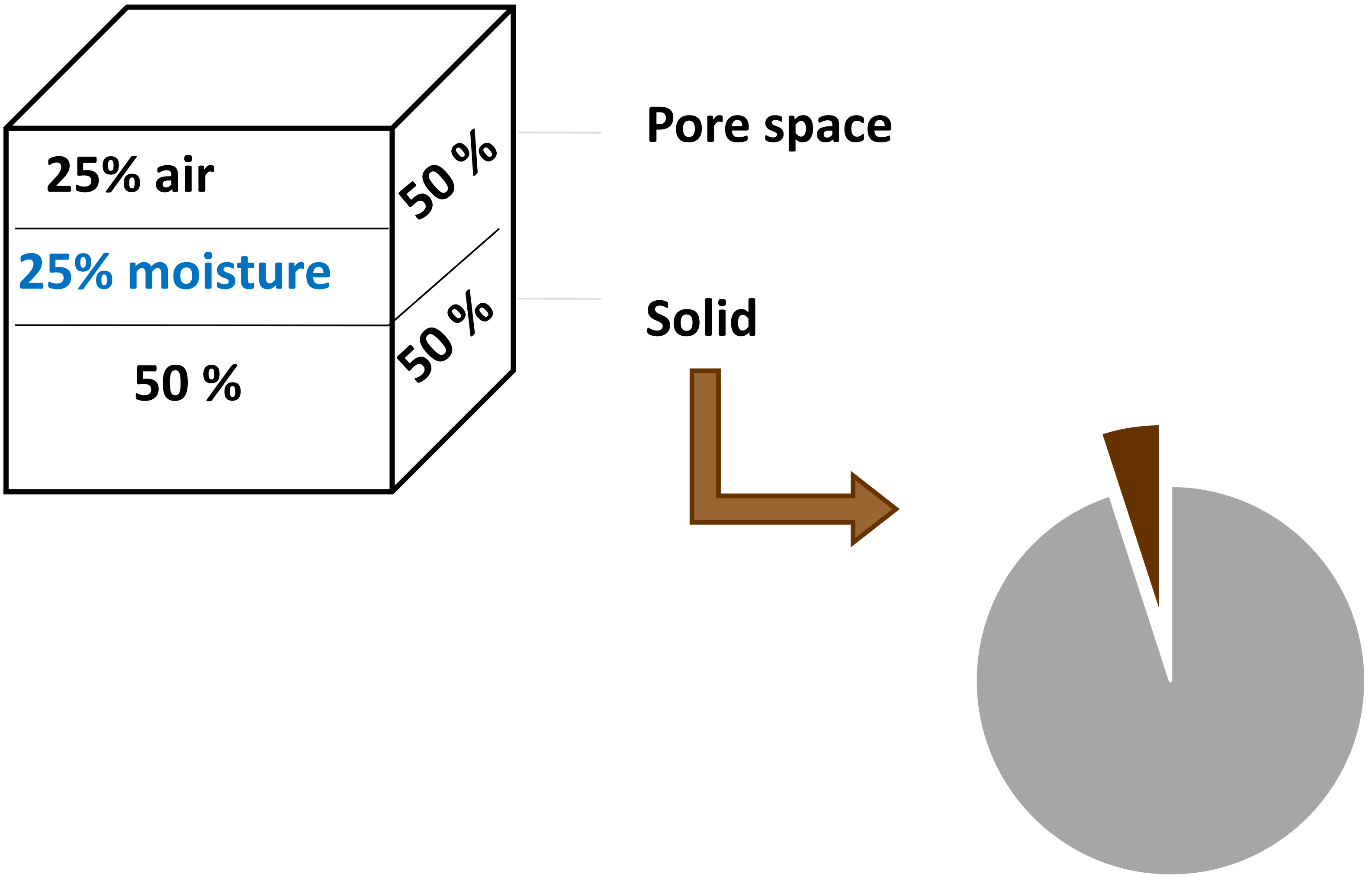
Soil composition

50%
Pore space

50%
Solid phase

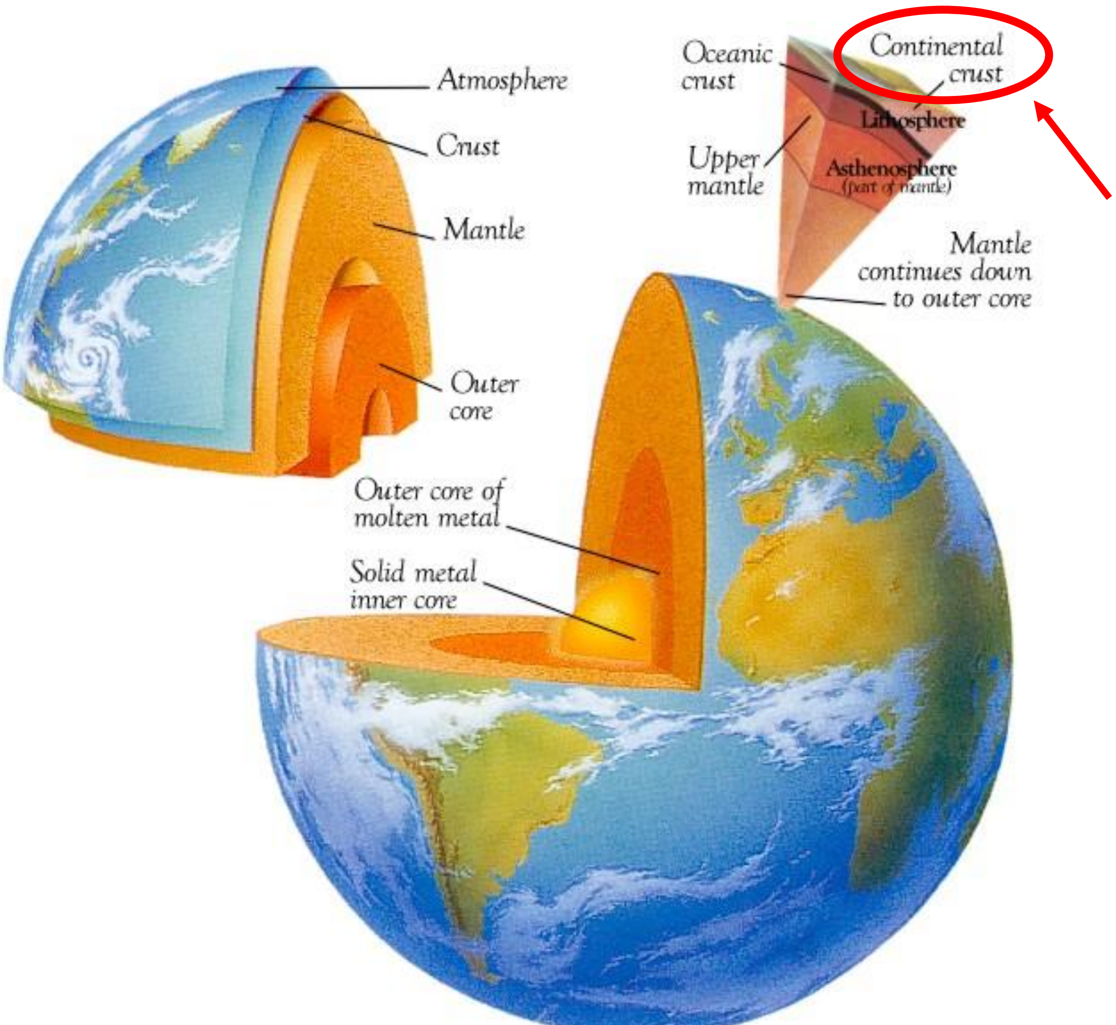




The soild phase of the soils consists of 95% mineral, 5% organic fractions.

The great importance of silicate minerals

The „sial”



In geology, the **sial** is the upper layer of the Earth's (continental) crust made of rocks rich in silicates and aluminium minerals.

Major elements of sial:

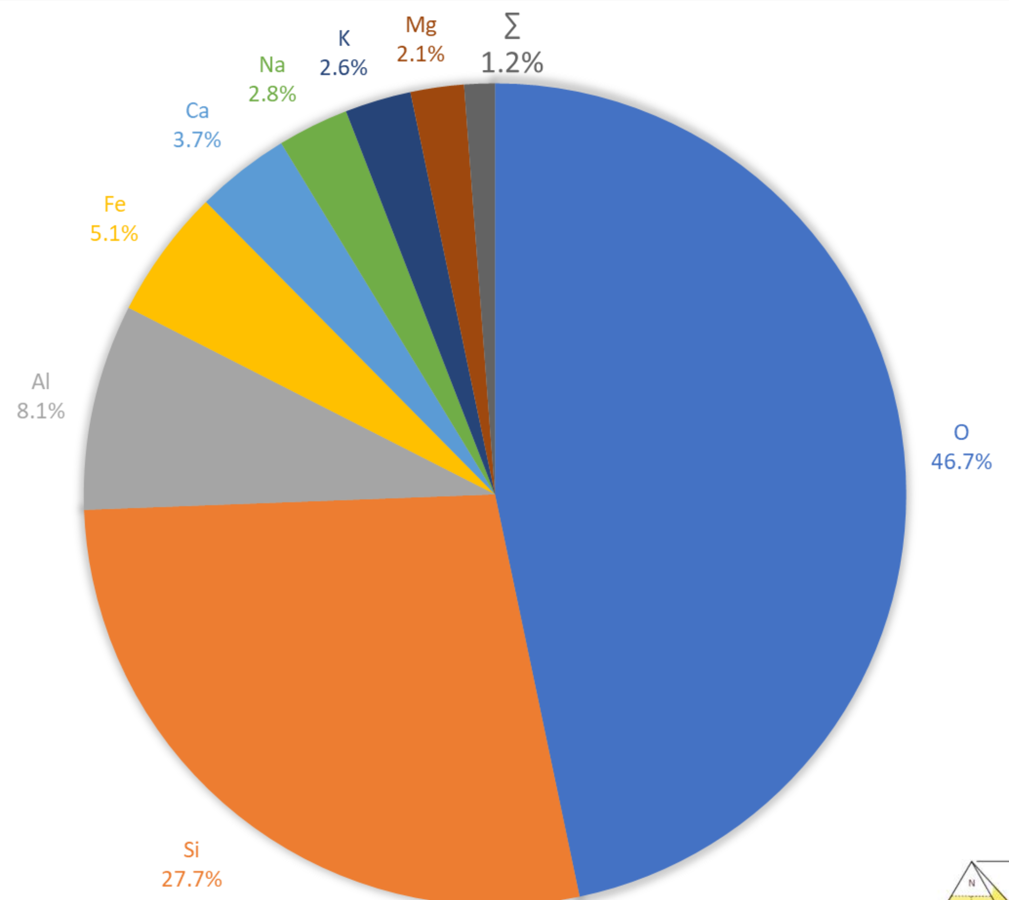
- Si, Al (> 90%)

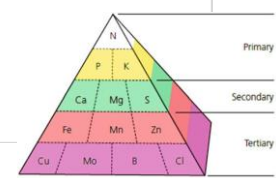
Other elements of sial:

- Fe, Ca, Na, K, Mg (~2-5%)

Structure of the Earth: ttp://mediatheek.thinkquest.nl/~ll125/en/struct.htm

The mineral composition of soils





Elements are released through weathering

Elements might be leached, bound to colloids or form new (secondary) minerals

Mineral groups of high importance in soils

Soil minerals are only a part of the many minerals found in nature. The important mineral classes of soils:

I. Chlorides
II. Sulfides
III. Sulfates
IV. Nitrates
V. Phosphates
VI. Borates

(I.–VI.) Nutrients

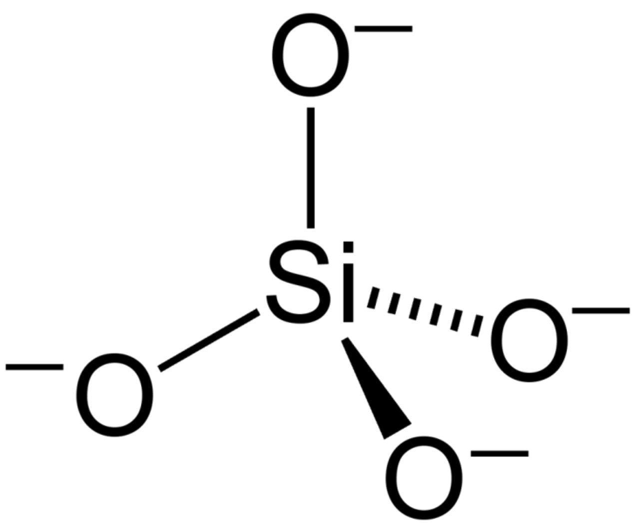
VII. Carbonates → pH, puffing capacity, soil structure
VIII. Oxides and hydroxides → soil structure, colour
IX. Silicates → major soil functions

→ **silicate clay** → the main mineral soil constituents determining soil properties & functions

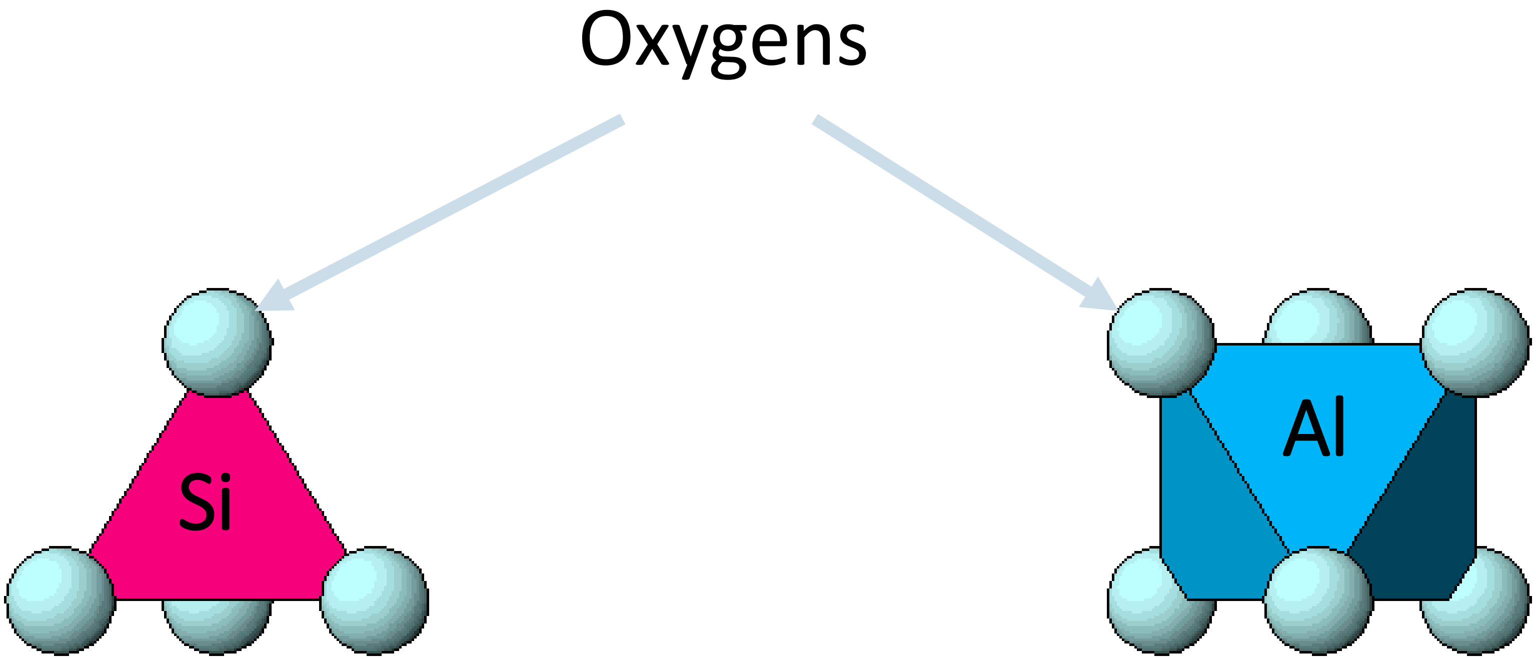
Silicates

The **silicate minerals** make up the largest and most important class of rock-forming minerals, constituting more than 90% of the crust of the Earth.

The great diversity of silicate minerals are due to the **-Si-O-Si-** bound



Silicate Mineral Structural Units



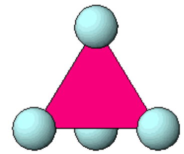
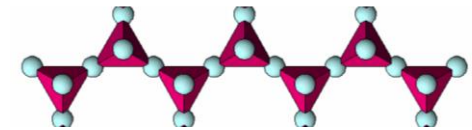
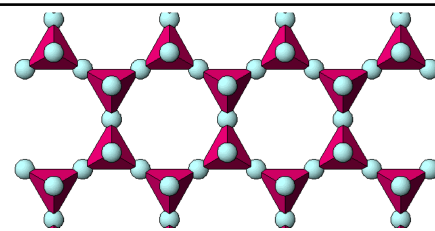
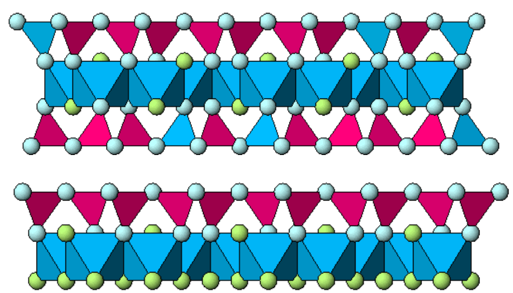
Silicon Tetrahedron

(4 sided)

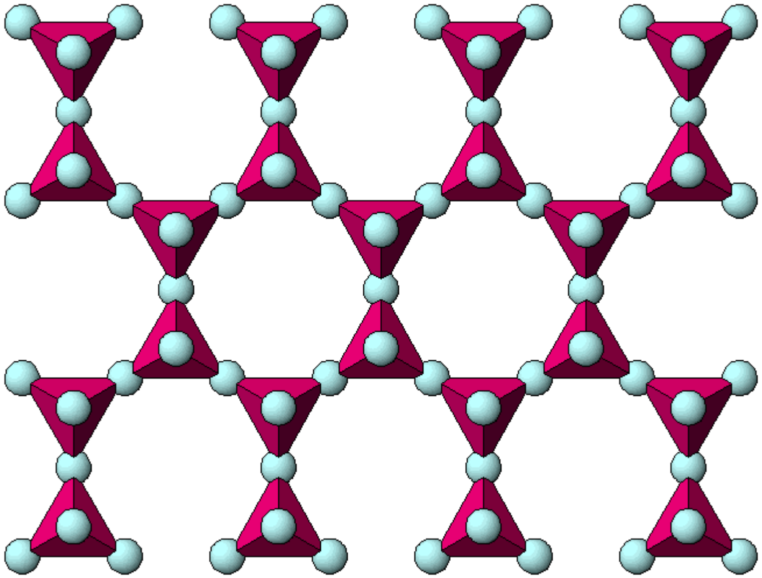
Aluminum Octahedron

(8 sided)

Classification of silicates

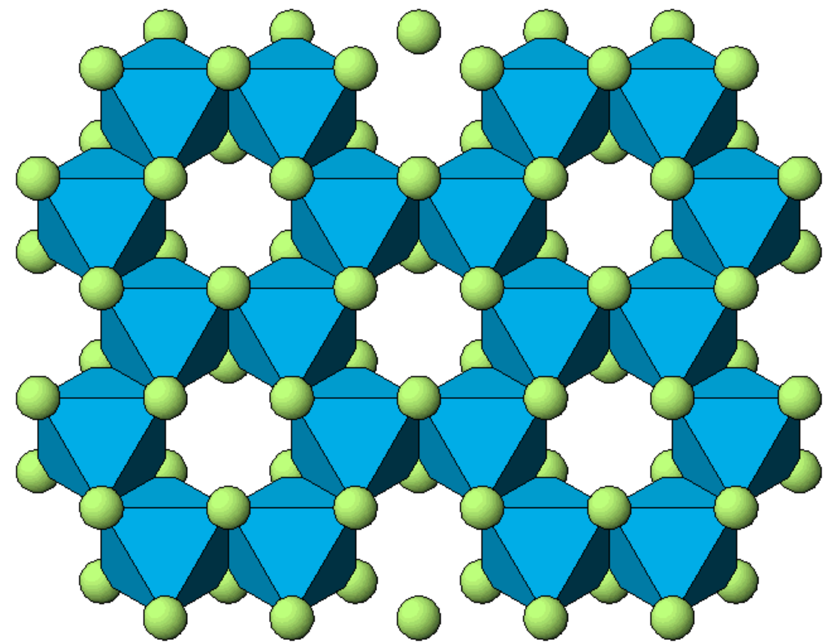
Neosilicates or orthosilicates		i.e. olivine, zirkon
Inosilicates or single chain silicates		i.e. pyroxene group
Double chain inosilicates		i.e. amphibole group
Phyllosilicates or sheet silicates		**i.e. clay mineral group**
Tectosilicates, or framework silicates	**have a three-dimensional framework**	**i.e. feldspars**

Phyllosilicates or sheet silicates

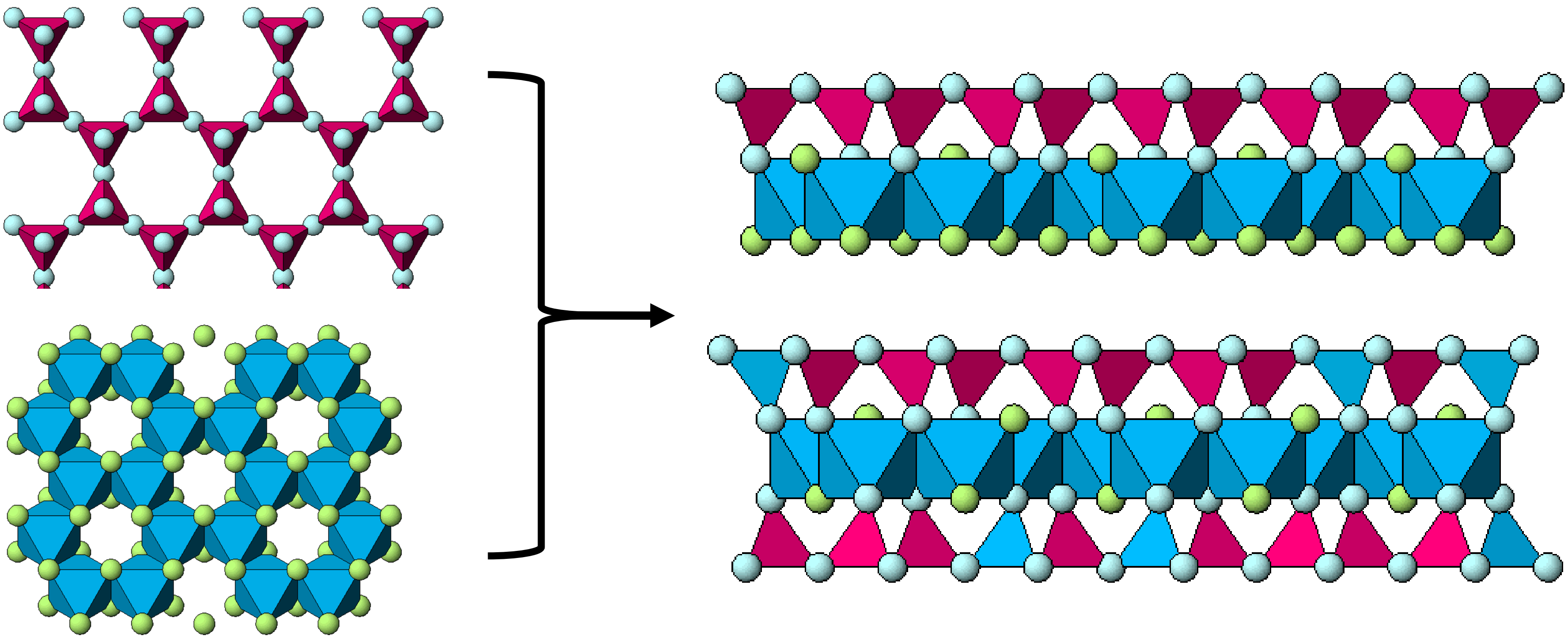


Tetrahedral sheet
(share 1 oxigen)

Oktahedral sheet
(share 2 oxigens)



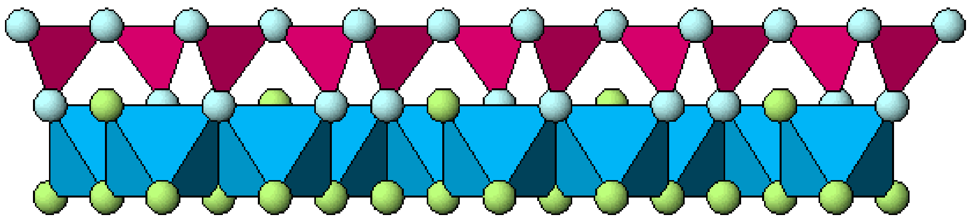
Phyllosilicates or sheet silicates



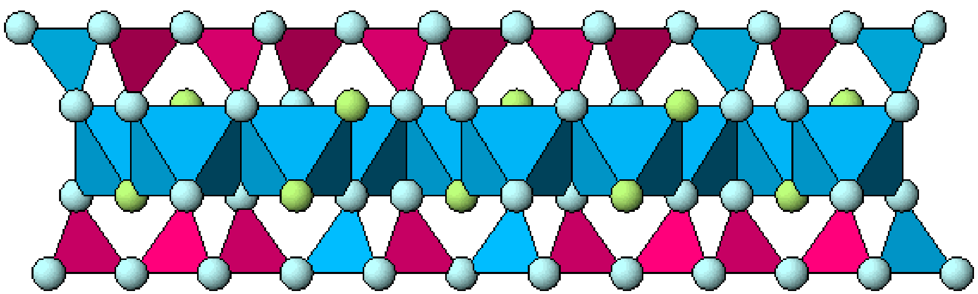
- Micas – i.e. muscovite, biotite
- Clays – the dominant inorganic **colloids** in most all soils

Silicate clay colloids in soils

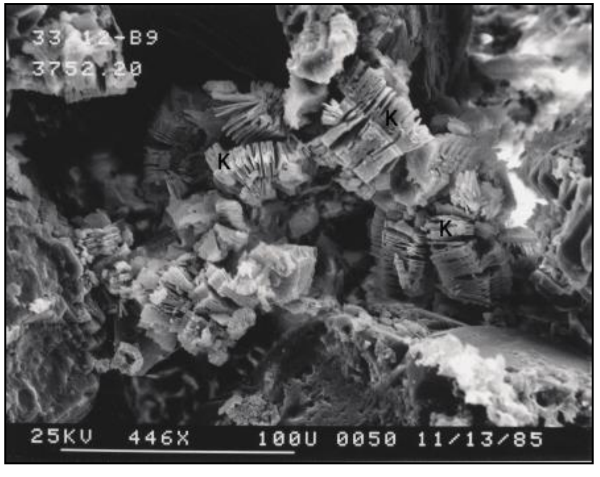
Phyllosilicates → layerlike, crystalline stucture

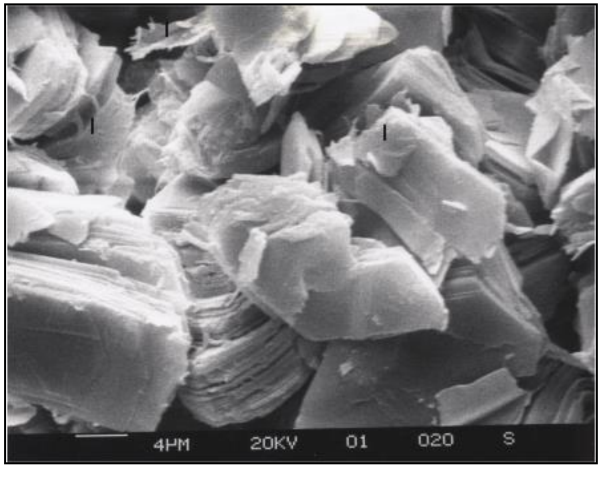


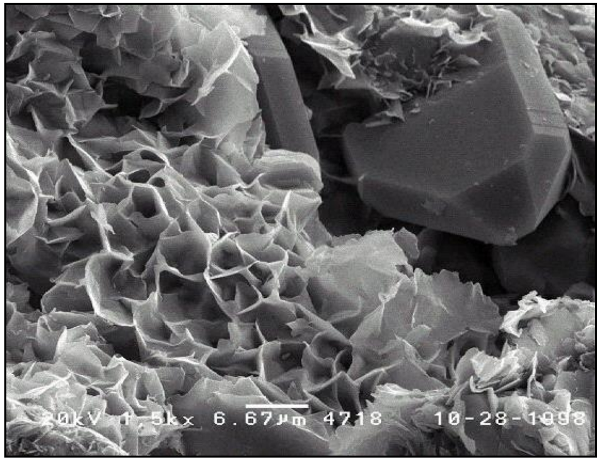
1:1 type clays



2:1 type clays

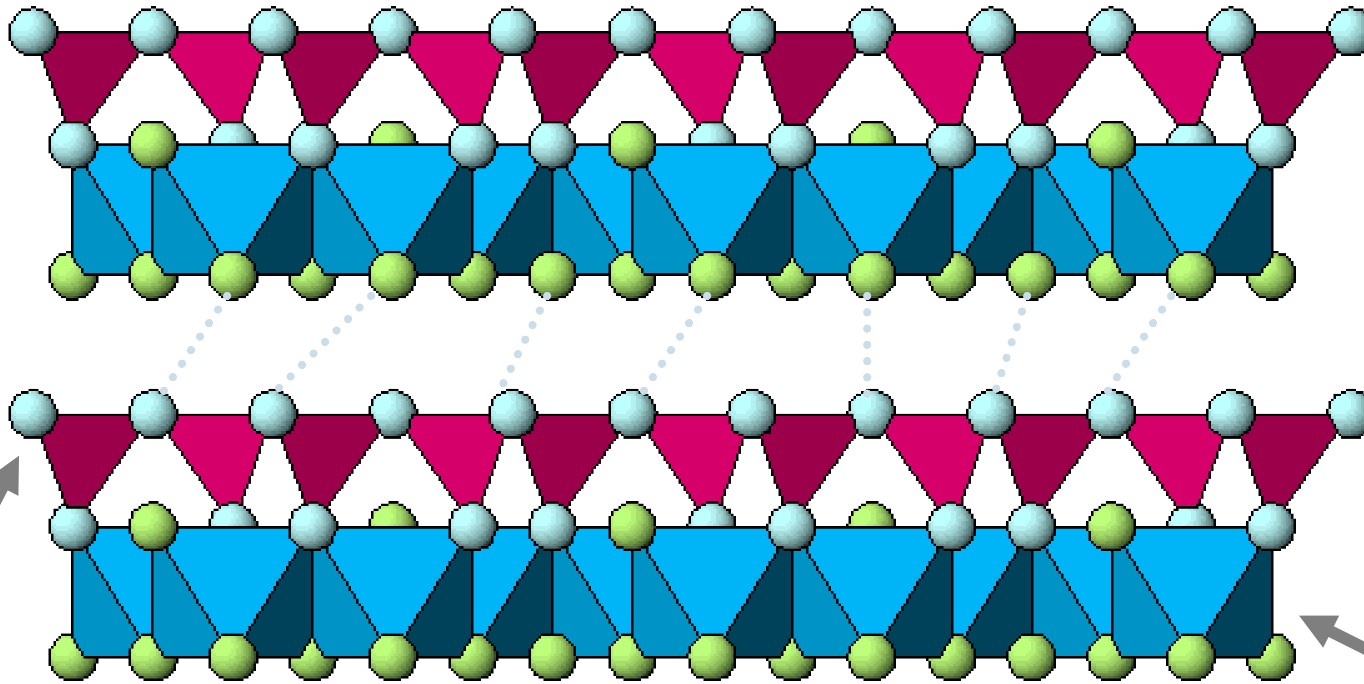






Kaolinite

Non-Expanding **10 cmol(+)/kg**



Aluminum Octahedral Sheet

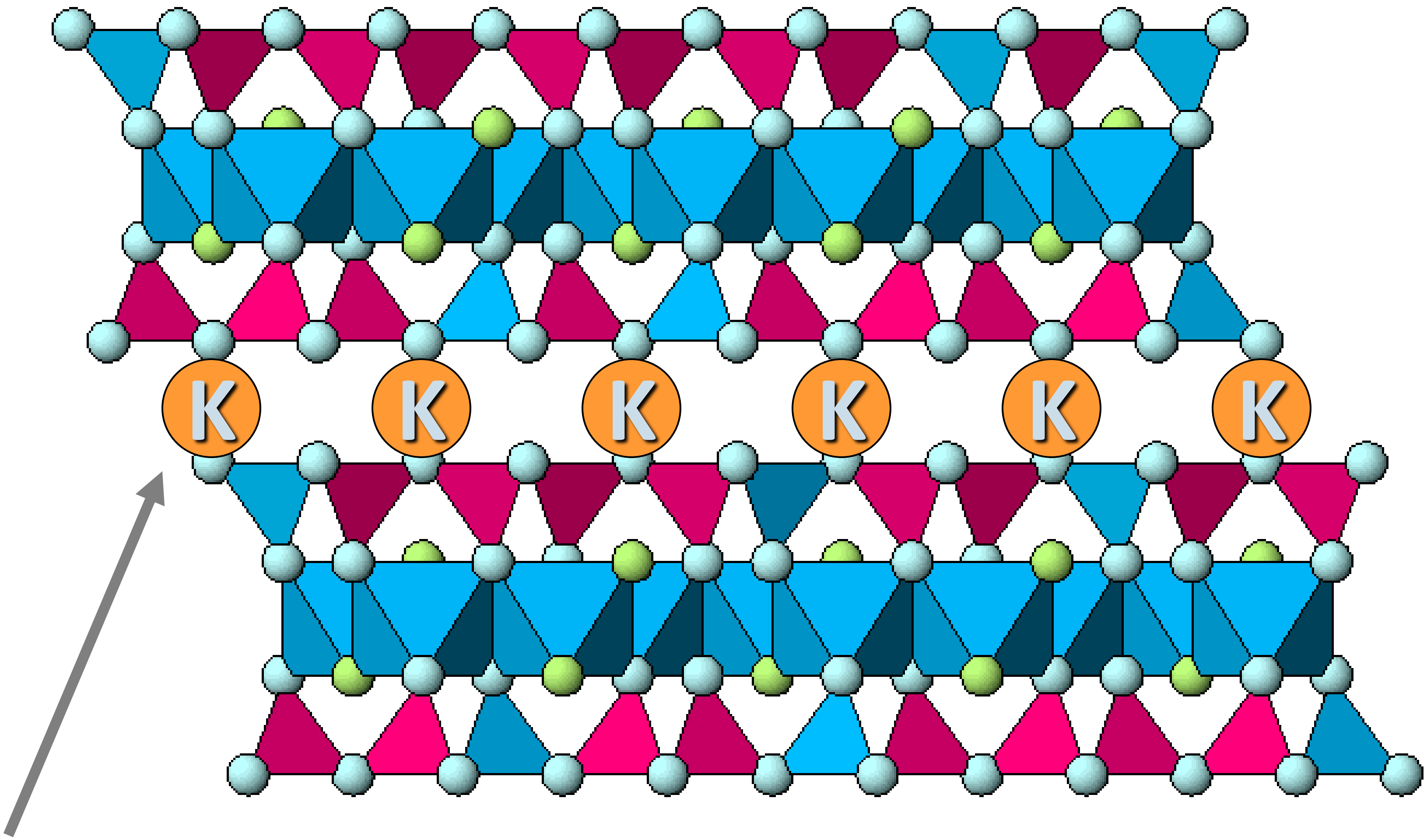
Silica Tetrahedral Sheet

1:1 Clay

40 cmol(+)/kg

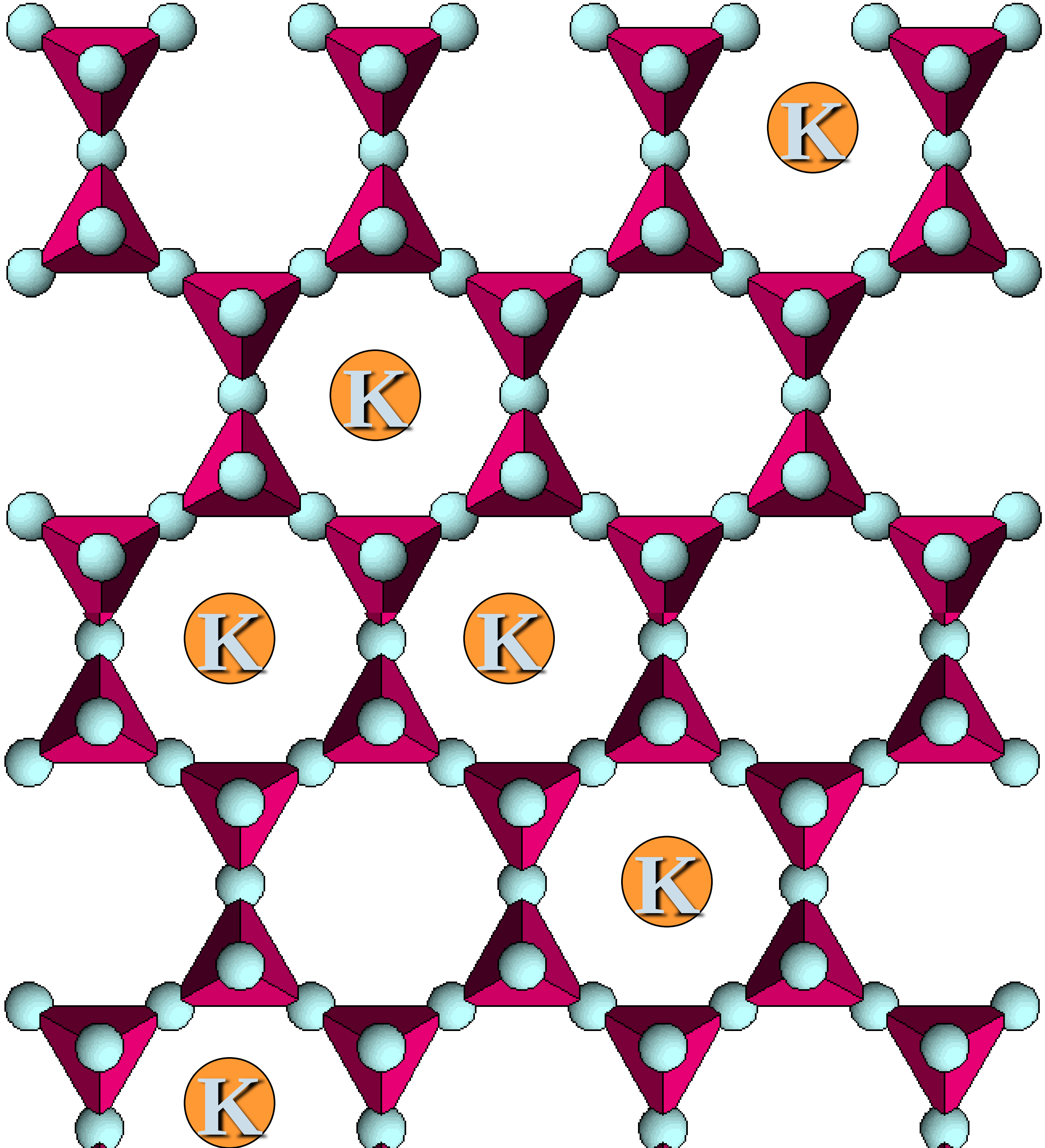
Illite

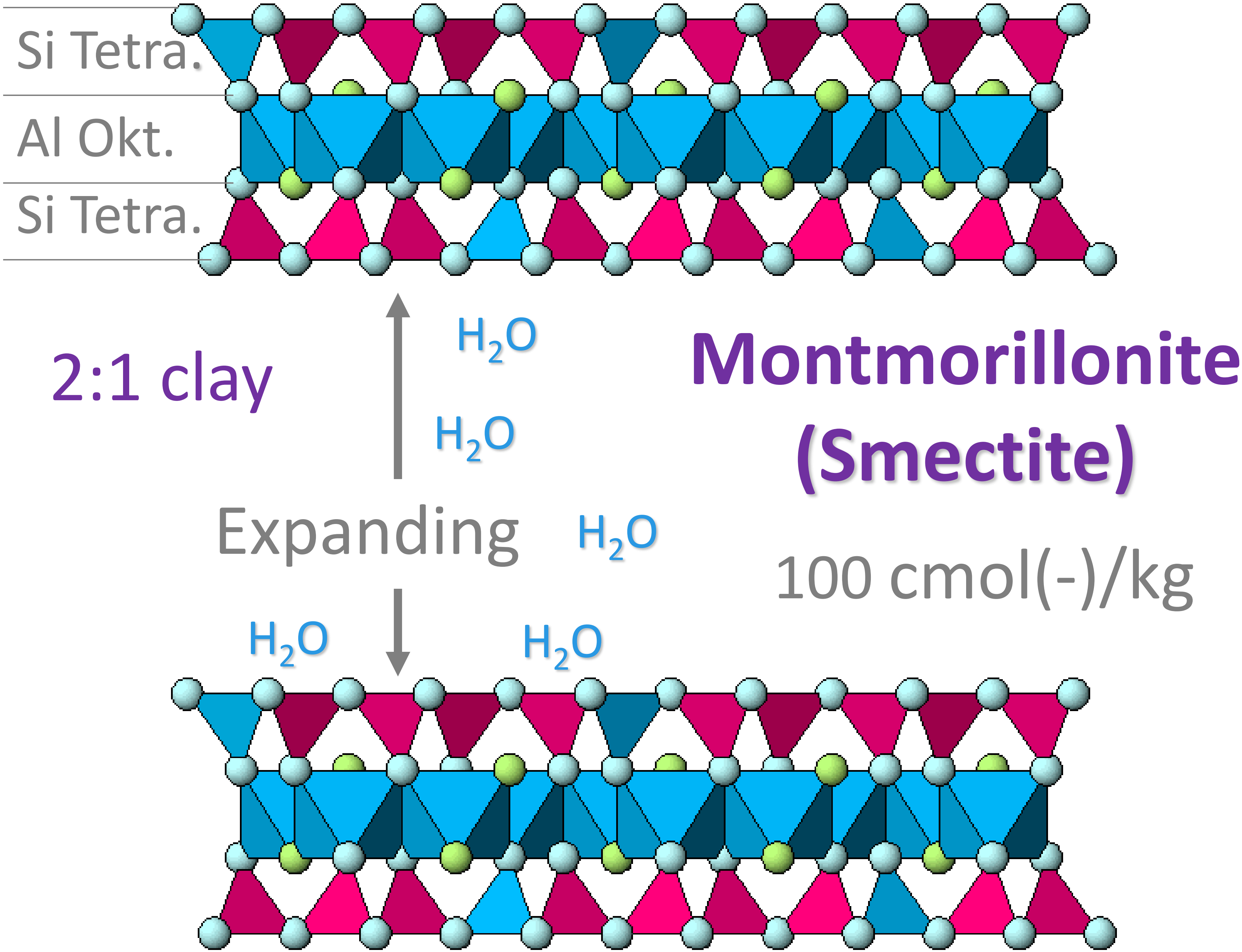
2:1 Clay



Interlayer K^+

Non-expanding


K
K
K
K
K
K



Si Tetra.
Al Okt.
Si Tetra.
2:1 clay
H_2O
H_2O
Expanding
H_2O
H_2O
H_2O
Montmorillonite
(Smectite)
100 cmol(-)/kg

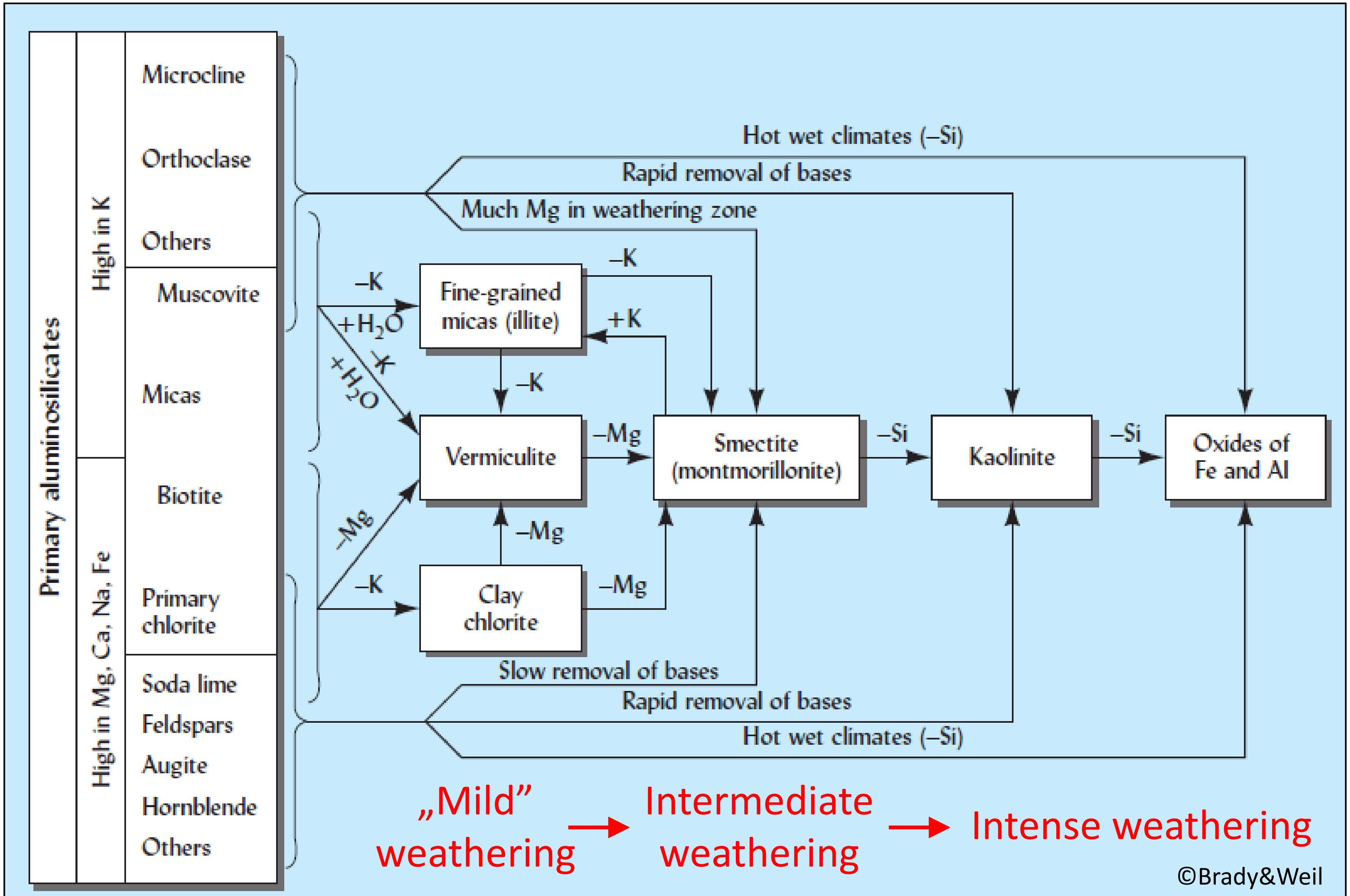
Origin of clay minearls in soils

1. Deposition prior to soil formation
2. Weathering

   → Secondray minerals

   - *Alteration* of primary phyllosilicates (structure is inherited)
   - Modification of other complex silicates (e.g. feldspars, amphiboles, pyroxenes) by *neoformation* (decomposition and recrystallization) ↔ much more intesive weathering

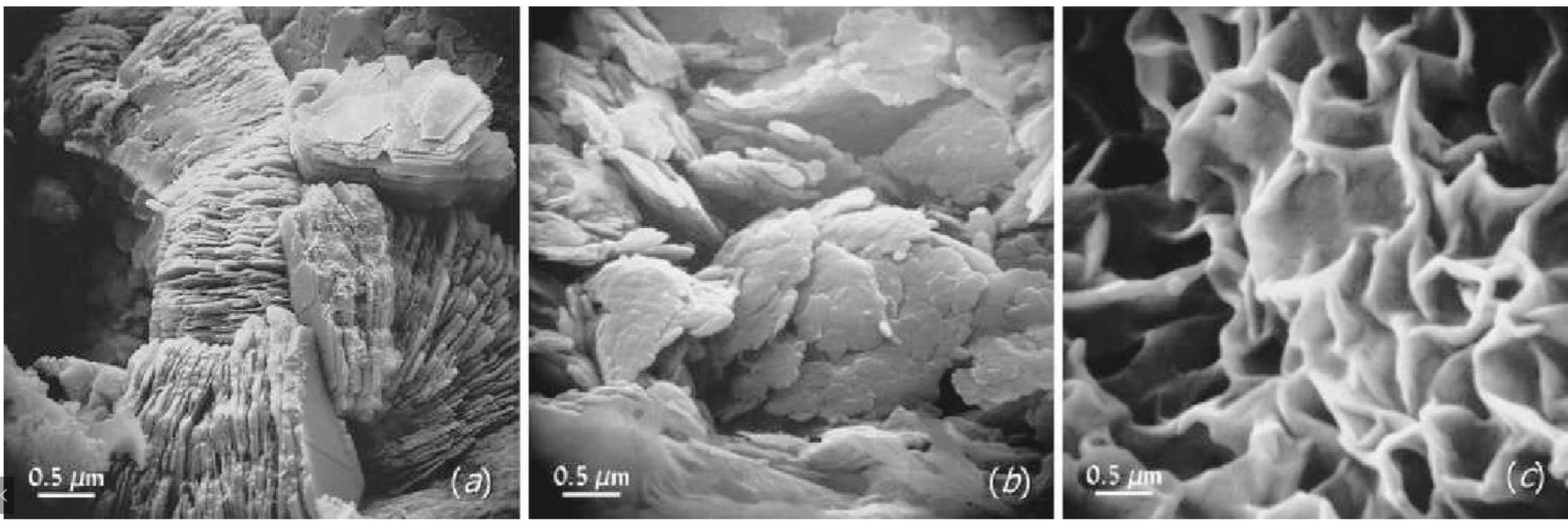
General conditions for the formation of layer silicate clays, and oxides of Fe &Al



Clay minerals

Clays are the most active mineral constituent of soils.

Clays are mineral **soil colloids**.



(a) kaolinite (b) illite (c) montmorillonite

Bohor, B. F., and R. E. Hughes, 1971, Scanning electron microscopy of clays.

Soil colloids

General properties of soil colloids:

- Size < 2 µm
- Large surface area (m^2/g)
- Surface charge – negative charges predominate!
- Adsorption of cations and water

Types of soil colloids:

- **Crystalline silicate clays**
- Noncrystalline silicate clays (allophane, imogolite)
- Iron and aluminum oxides (goethite, hematite, gibbsite)
- Organic soil colloids: **humus**

Sources of Charges in Soils

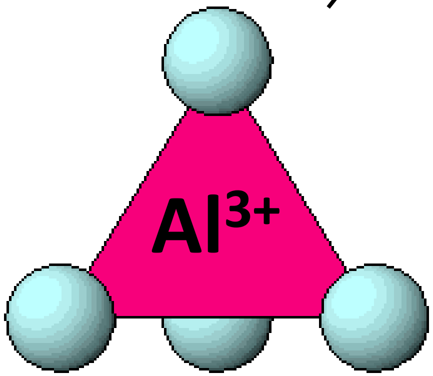
- Clay Minerals (Mineral colloids)
  - Isomorphic Substitution → permanent charge
  - pH dependent charge

- Organic colloids (Humic Materials), noncrystalline silicate clays, Fe&Al oxides
  - pH dependent charge

Examples of Isomorphic Substitution

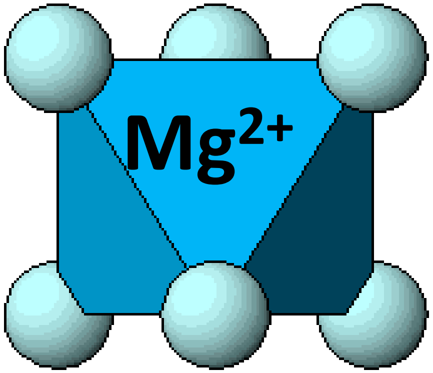
- Occurs in clay minerals when they form
- One element substitutes for another of similar size:

Al^{3+} for Si^{4+}



Silicon
Tetrahedron

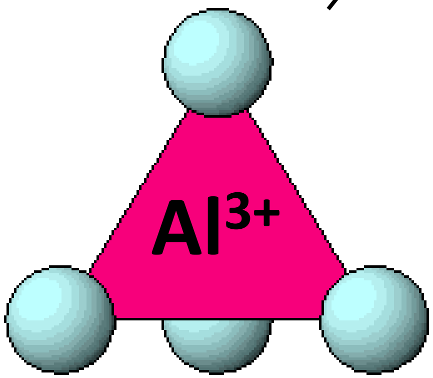
Mg^{2+} or Fe^{2+} for Al^{3+}



Aluminum
Octahedron

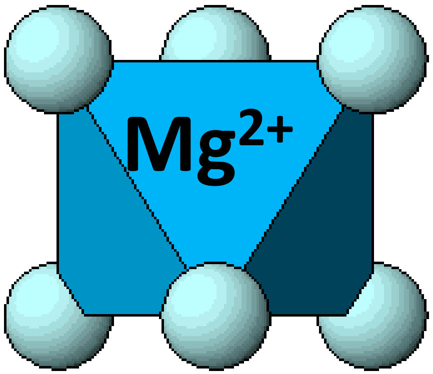
Examples of Isomorphic Substitution

Al^{3+} for ~~Si^{4+}~~



Silicon
Tetrahedron

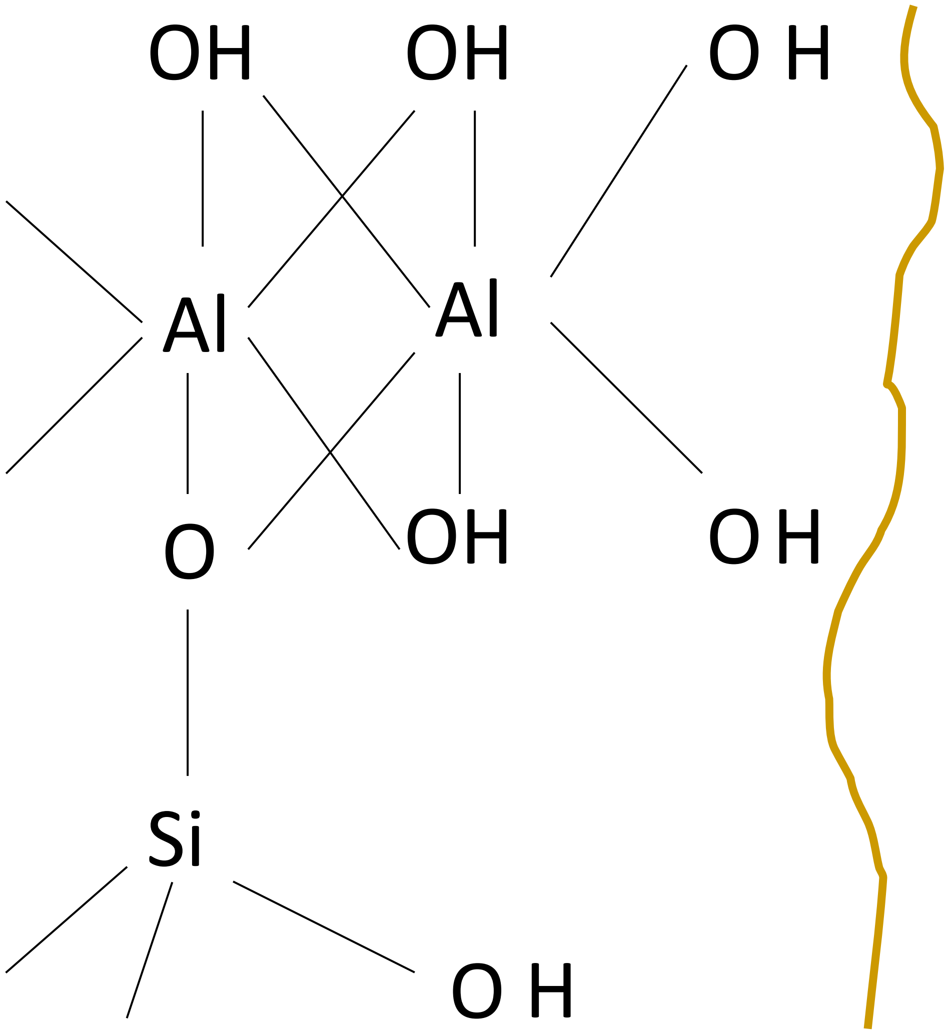
Mg^{2+} or Fe^{2+} for ~~Al^{3+}~~



Aluminum
Octahedron

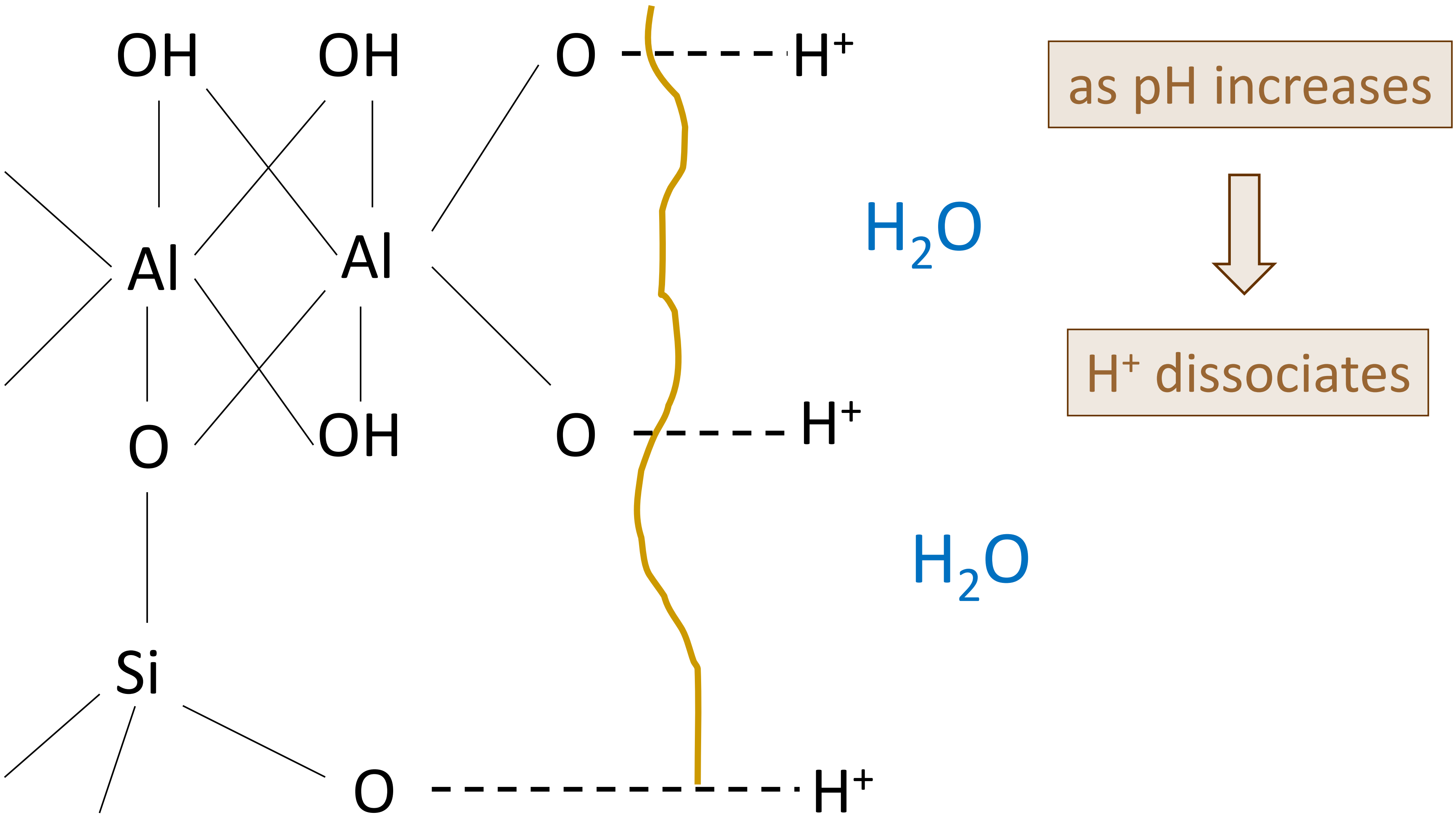
Produces a **Net Negative Charge**
based on the structure of the crysal→**permanent**

Example of pH dependent charge in clays

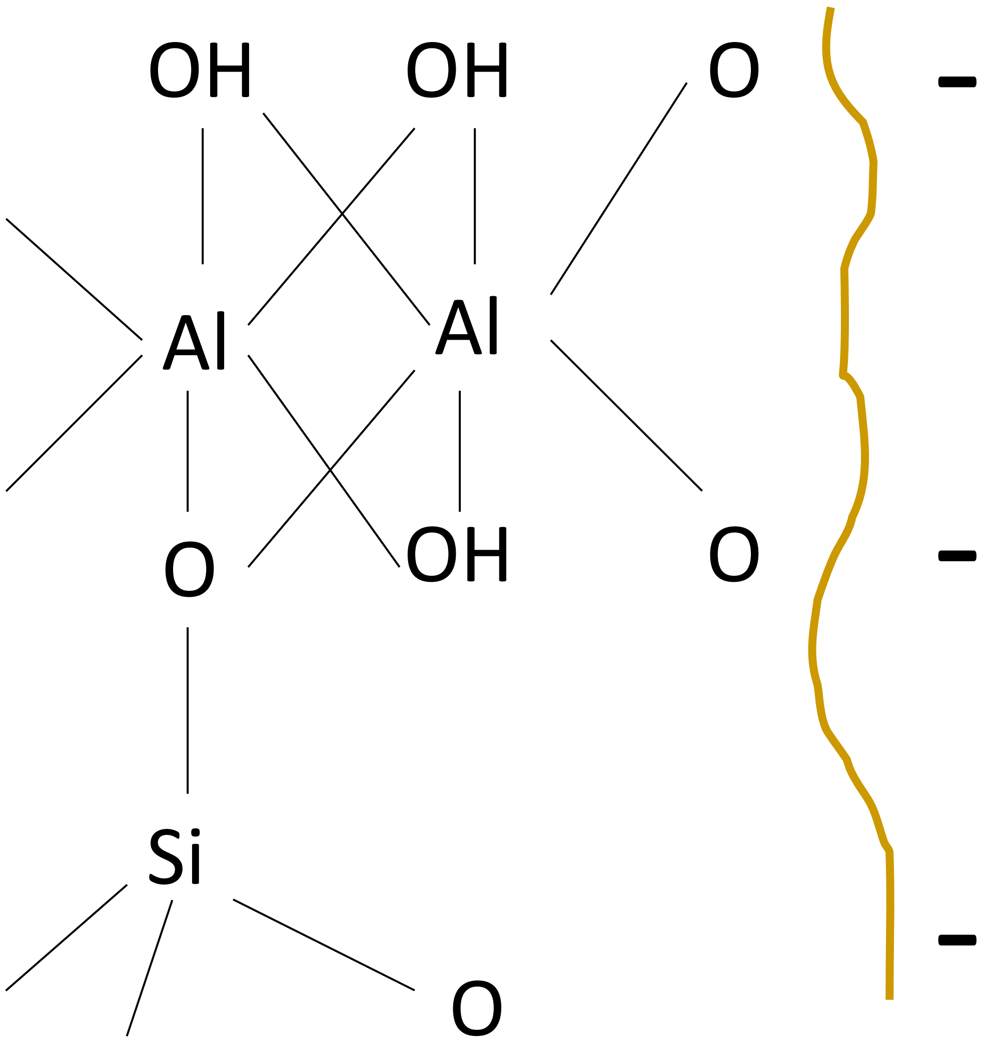


- develops on the exposed edges and surfaces of the clay crystals
- associated mainly with OH groups

Example of pH dependent charge in clays



Example of pH dependent charge in clays

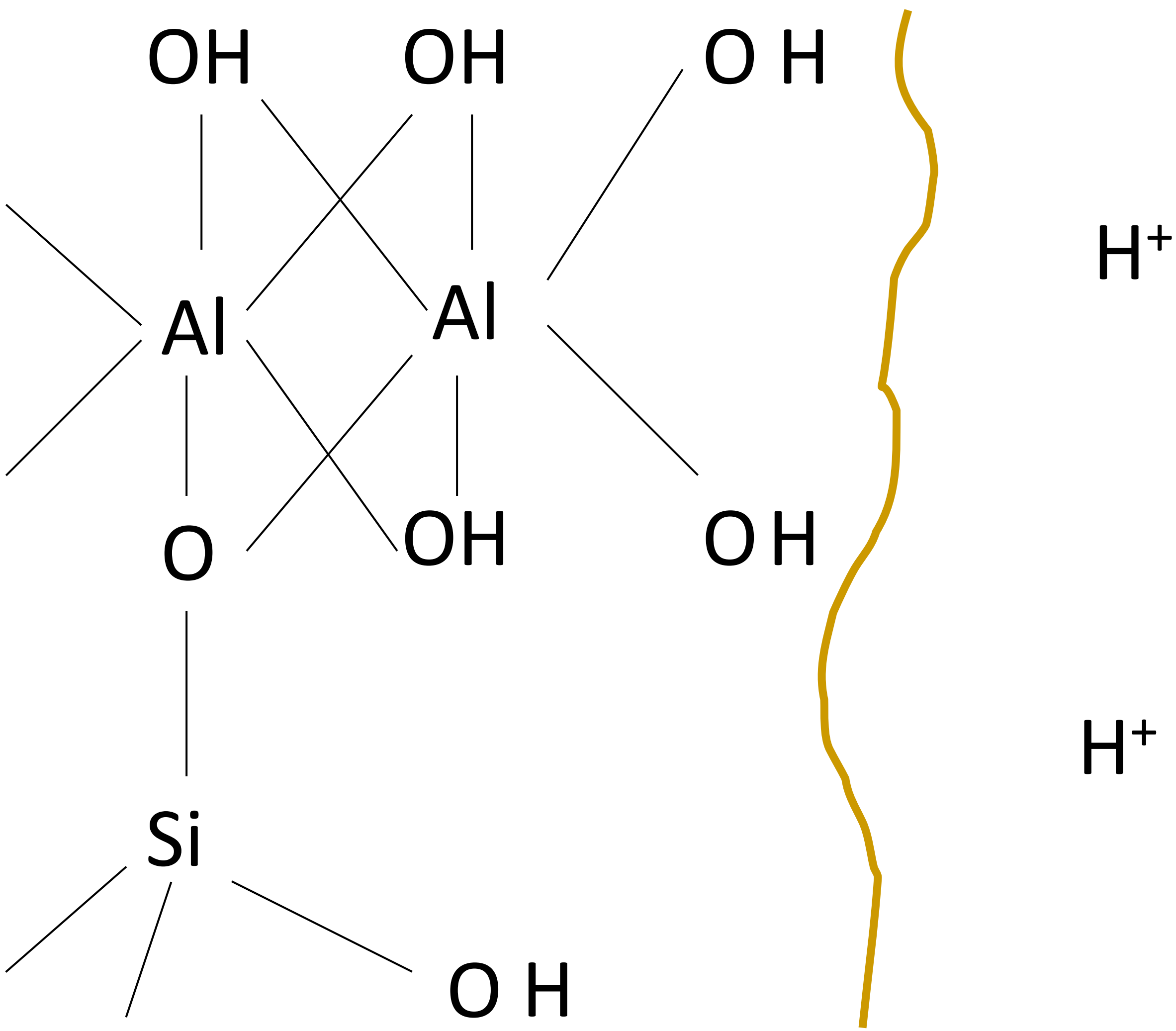


as pH increases

H^+ dissociates

Negative charges result

Example of pH dependent charge in clays

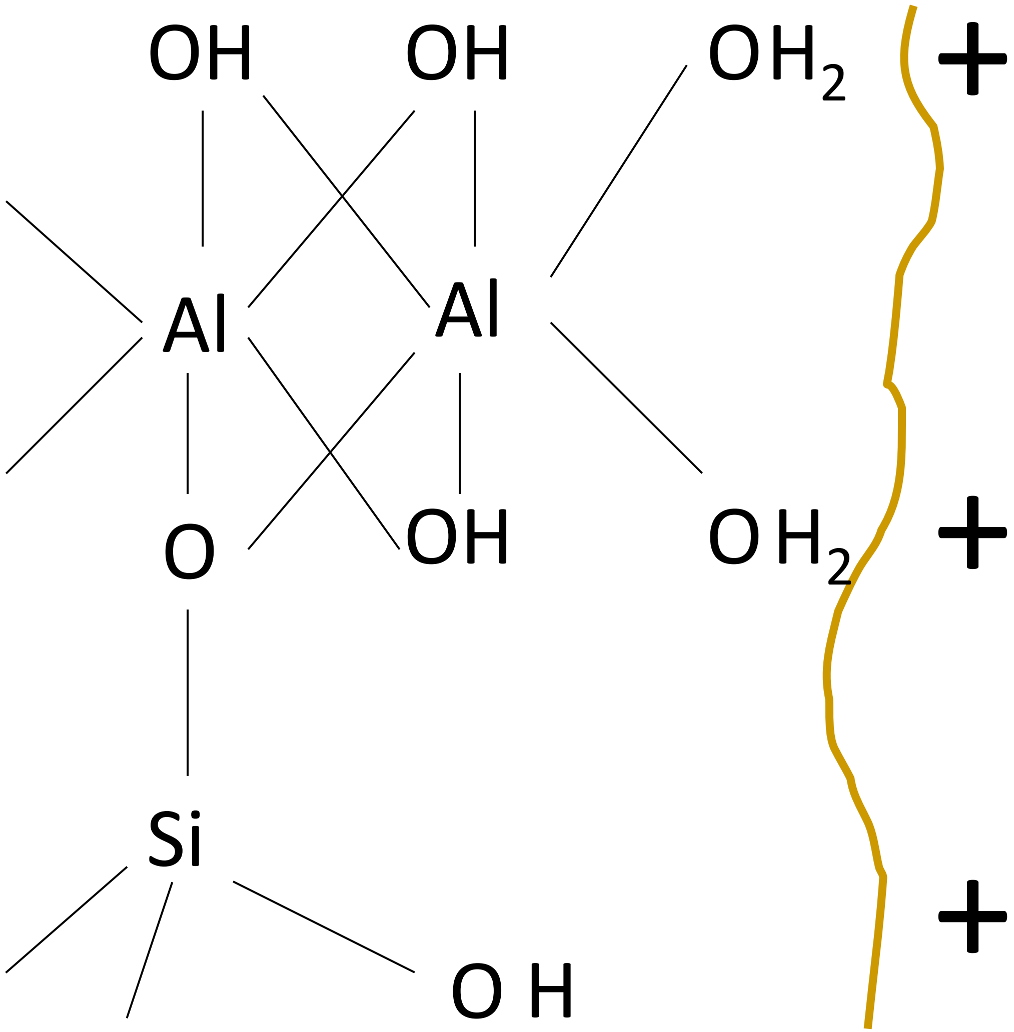


Moderate to extreme acid soil conditions

↓

Protonation

Example of pH dependent charge in clays



Moderate to extreme acid soil conditions

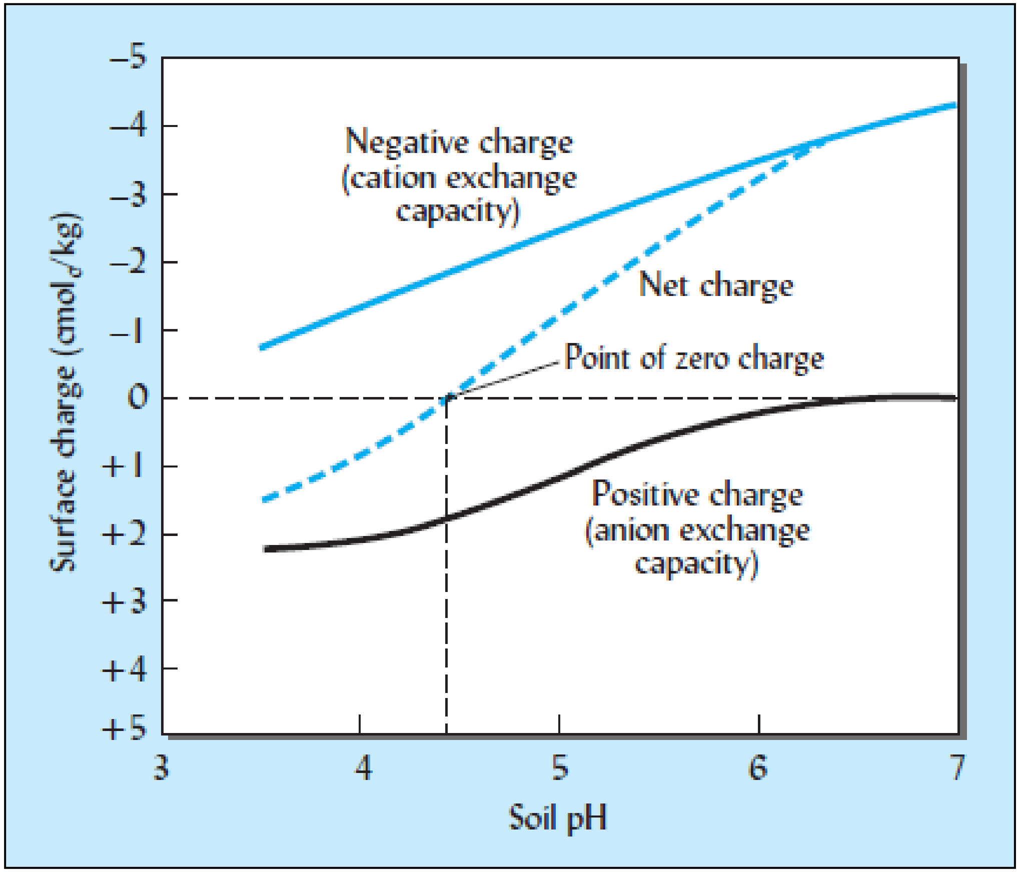
↓

Protonation

↓

Positive charges result

Relationship between soil pH & negative and positive charges



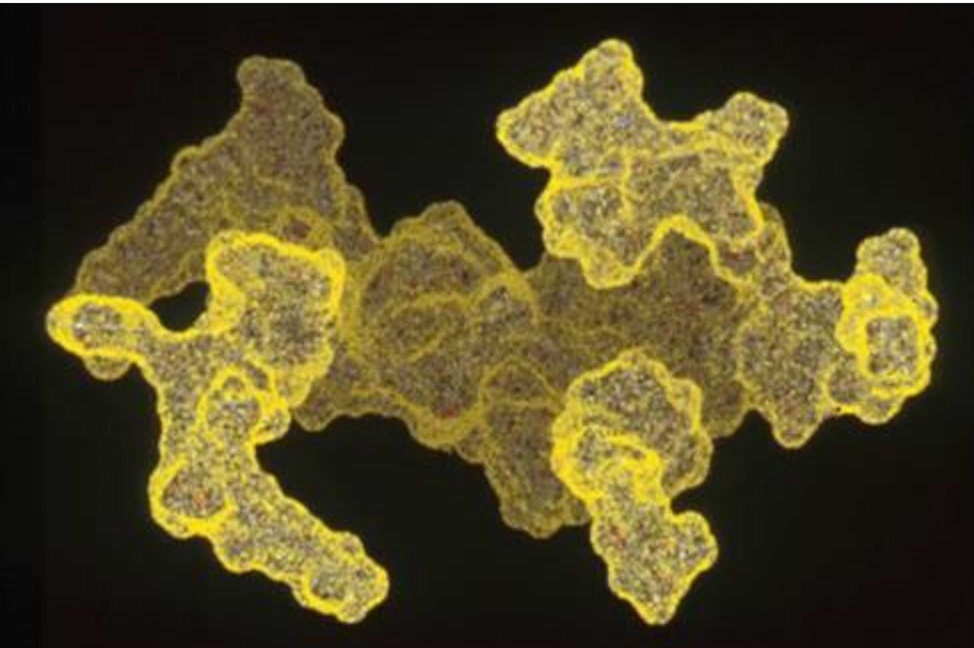
The „-” charges increase and the „+” charges decrease with increasing soil pH.

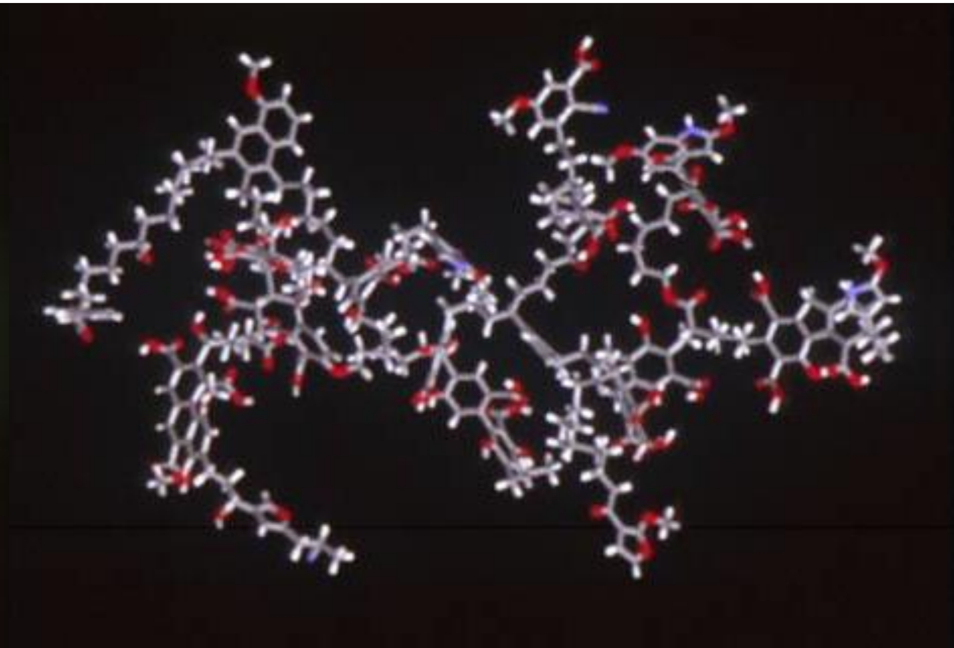
The point of zero charge is about pH 4.4

Soil organic matter - humus

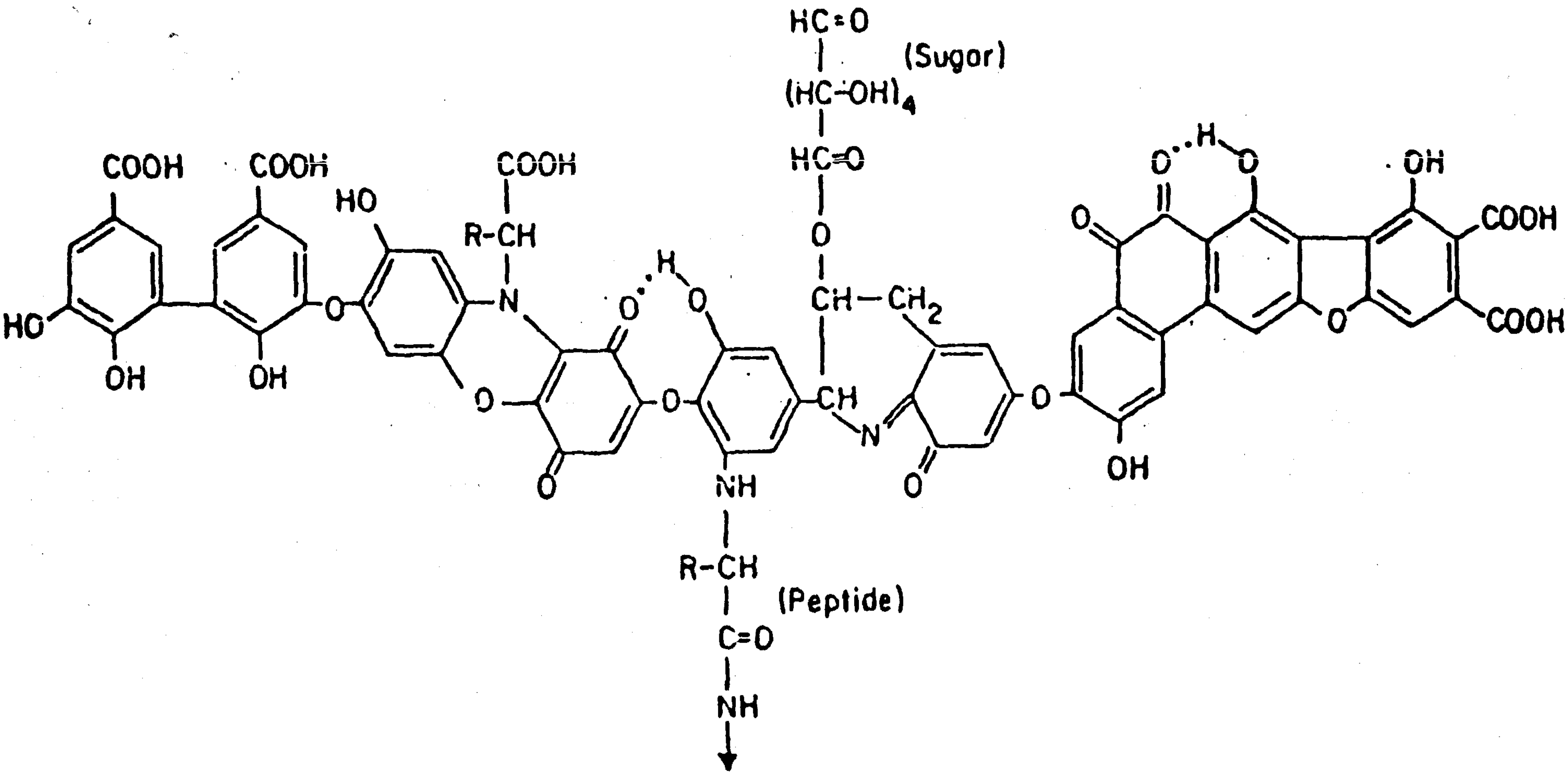
Dark coloured, amorf **colloids** with large molecular weight

Chemically not defined structure (humic acids, fulvic acids, humin)





Structure of Humic Acid

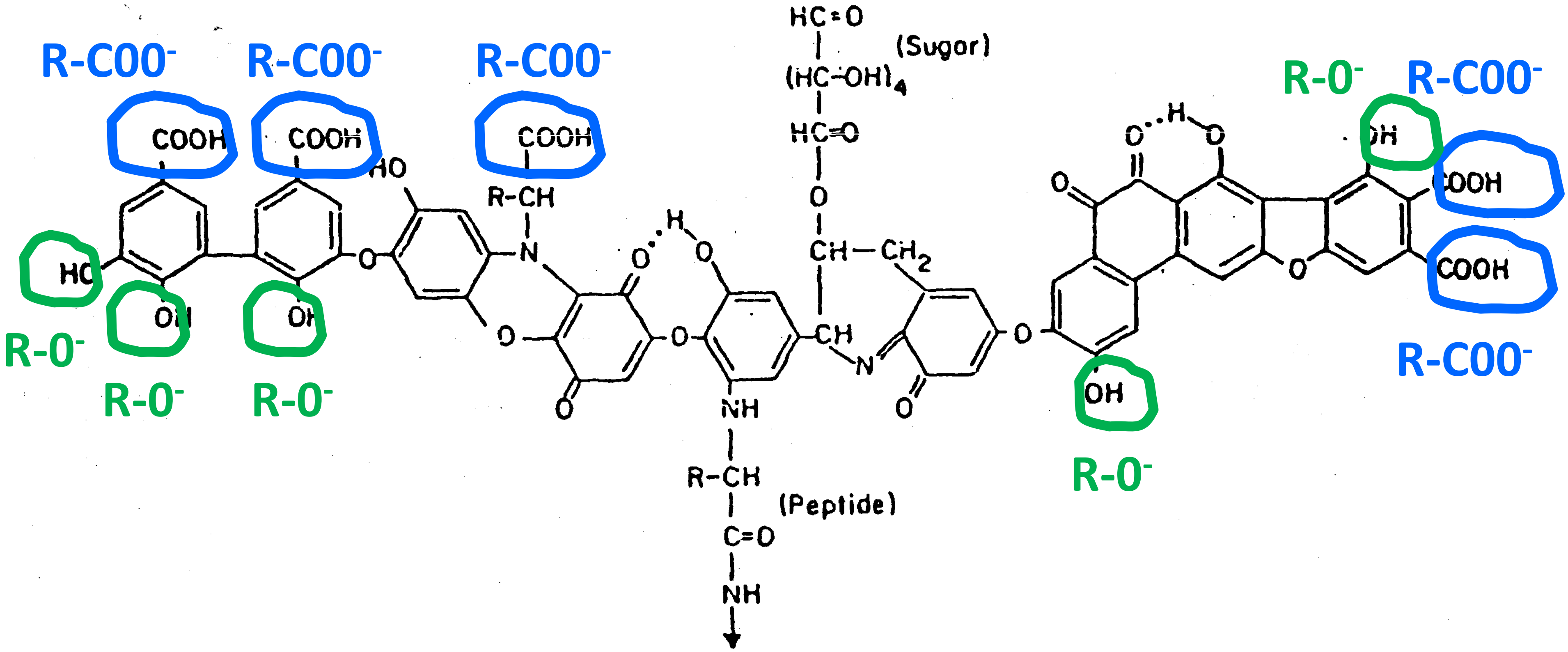


Aromatic rings

N containing carbonchains

Functional groups

pH dependent, variable charges of humic acid



As pH increases, H^+ dissociates from colloid functional groups

Contributes to high CEC → **200** – 1400 cmol(+)/kg

Net negative charge of selected colloids

Colloid	Charge cmol(-)/kg
Montmorillonite	100
Illite	40
Kaolinite	10
Humus	200

Source of charges on soil colloids

1. **Isomorphic substitution** is the process of replacing one structural cation for another of similar size but differing in charge in some clay crystal structures

   Result: **Permanent net negative charge**

   In: Layer silicate **clays**

2. Functional groups on surfaces of colloids releasing or accepting H^+ ions can provide either negative or positive charges

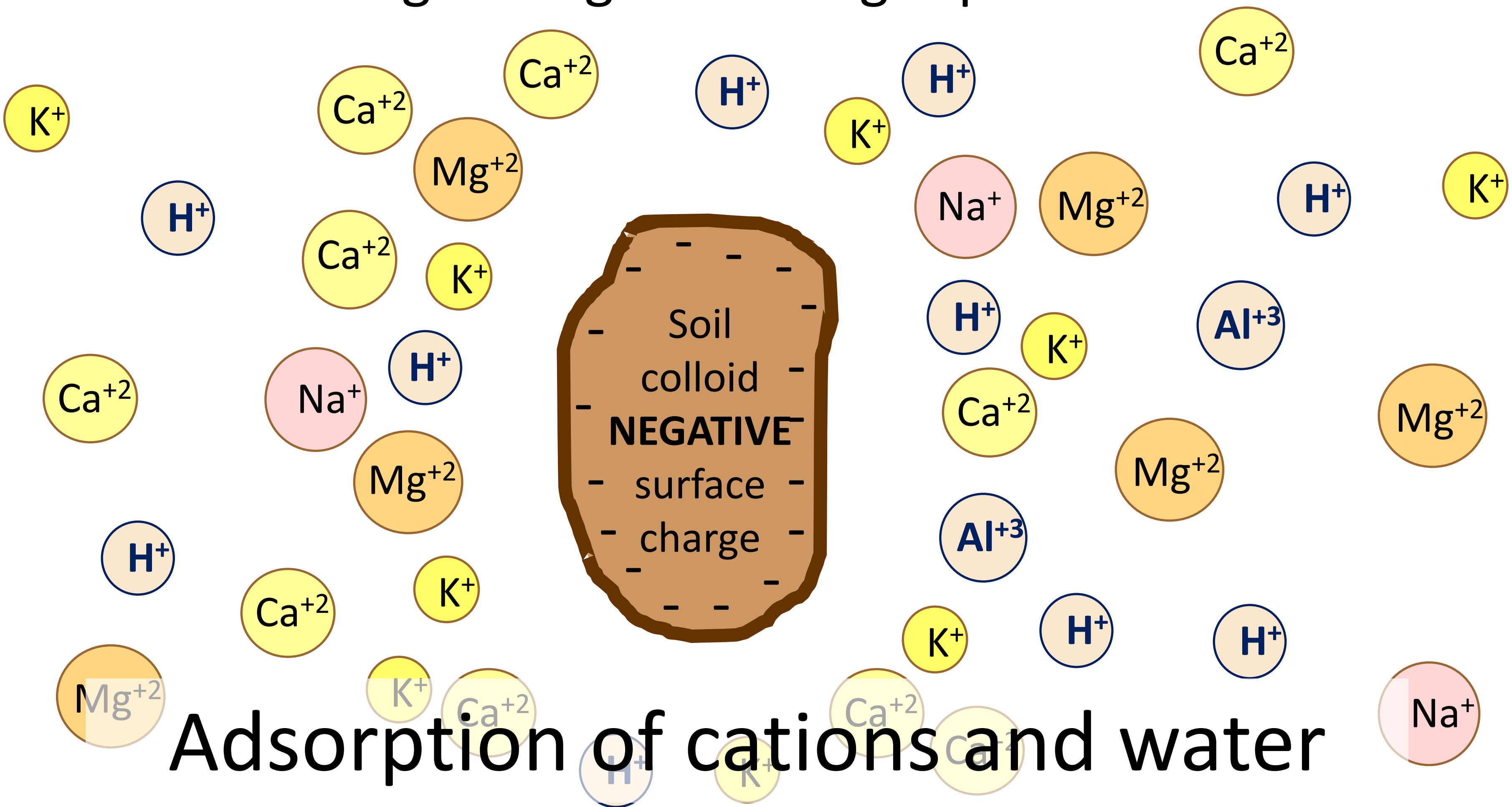
   In: pH dependent, or **variable charge**

   Layer silicate **clays** AND **humus**

   Noncrystalline silicate clays, Fe&Al oxides

The importance of soil colloids

- Small size < 2 µm
- Large surface area (m^2/g)
- Surface charge – negative charges predominate!



Adsorption of cations and water

The importance of soil colloids

Selected cations and anions commonly adsorbed to soil colloids:

Cation	*Formula*	*Comments*	*Anion*	*Formula*	*Comments*
Ammonium	NH_4^+	Plant nutrient	Arsenate	AsO_4^{3-}	Toxic to animals
Aluminum	Al^{3+} etc.[a]	Toxic to many plants	Borate	$B(OH)_4^-$	Plant nutrient, can be toxic
Calcium*	Ca^{2+}	Plant nutrient	Bicarbonate	HCO_3^-	Toxic in high-pH soils
Cadmium	Cd^{2+}	Toxic pollutant	Carbonate*	CO_3^{2-}	Forms weak acid
Cesium	Cs^+	Radioactive contaminant	Chromate	CrO_4^{2-}	Toxic pollutant
Copper	Cu^{2+}	Plant nutrient, toxic pollutant	Chloride*	Cl^-	Plant nutrient, toxic in large amounts
Hydrogen*	H^+	Causes acidity	Fluoride	Fl^-	Toxic, natural and pollutant
Iron	Fe^{2+}	Plant nutrient	Hydroxyl*	OH^-	Alkalinity factor
Lead	Pb^{2+}	Toxic to animals, plants	Nitrate*	NO_3^-	Plant nutrient, pollutant in water
Magnesium*	Mg^{2+}	Plant nutrient	Molybdate	MoO_4^{2-}	Plant nutrient, can be toxic
Manganese	Mn^{2+}	Plant nutrient	Phosphate	HPO_4^{2-}	Plant nutrient, water pollutant
Nickel	Ni^{2+}	Plant nutrient, toxic pollutant	Selenate	SeO_4^{2-}	Animal nutrient and toxic pollutant
Potassium*	K^+	Plant nutrient	Selenite	SeO_3^{2-}	Animal nutrient and toxic pollutant
Sodium*	Na^+	Used by animals, some plants, can damage soil	Silicate*	SiO_4^{4-}	Mineral weathering product, used by plants
Strontium	Sr^{2+}	Radioactive contaminant	Sulfate*	SO_4^{2-}	Plant nutrient
Zinc	Zn^{2+}	Plant nutrient, toxic pollutant	Sulfide	S^{2-}	In anaerobic soils, forms acid on oxidation

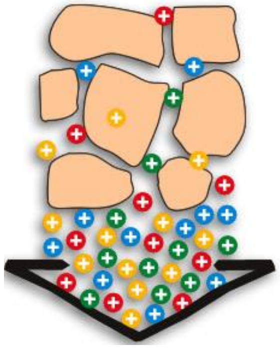
Soils are **storing**, **filtering** and **transforming** nutrients, substances and water!

The importance of soil colloids

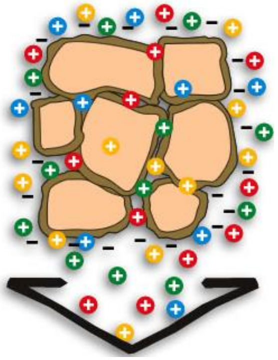
- Small size < 2 µm
- Large surface area (m^2/g)
- Surface charge – negative charges predominate!
  - → adsorption of nutrients
  - → adsorption of pollutants
  - → buffering capacity
  - → pH, soil acidity
  - → redox features
  - → soil structure formation → water & air management
  - → soil biological activity

FERTILITY & SOIL HEALTH

„macaw clay lick”



Cation exchange capacity (CEC)



The ability of a soil to attract and exchange cations → positively charged ions are attracted to negatively charged soil particles (colloids)

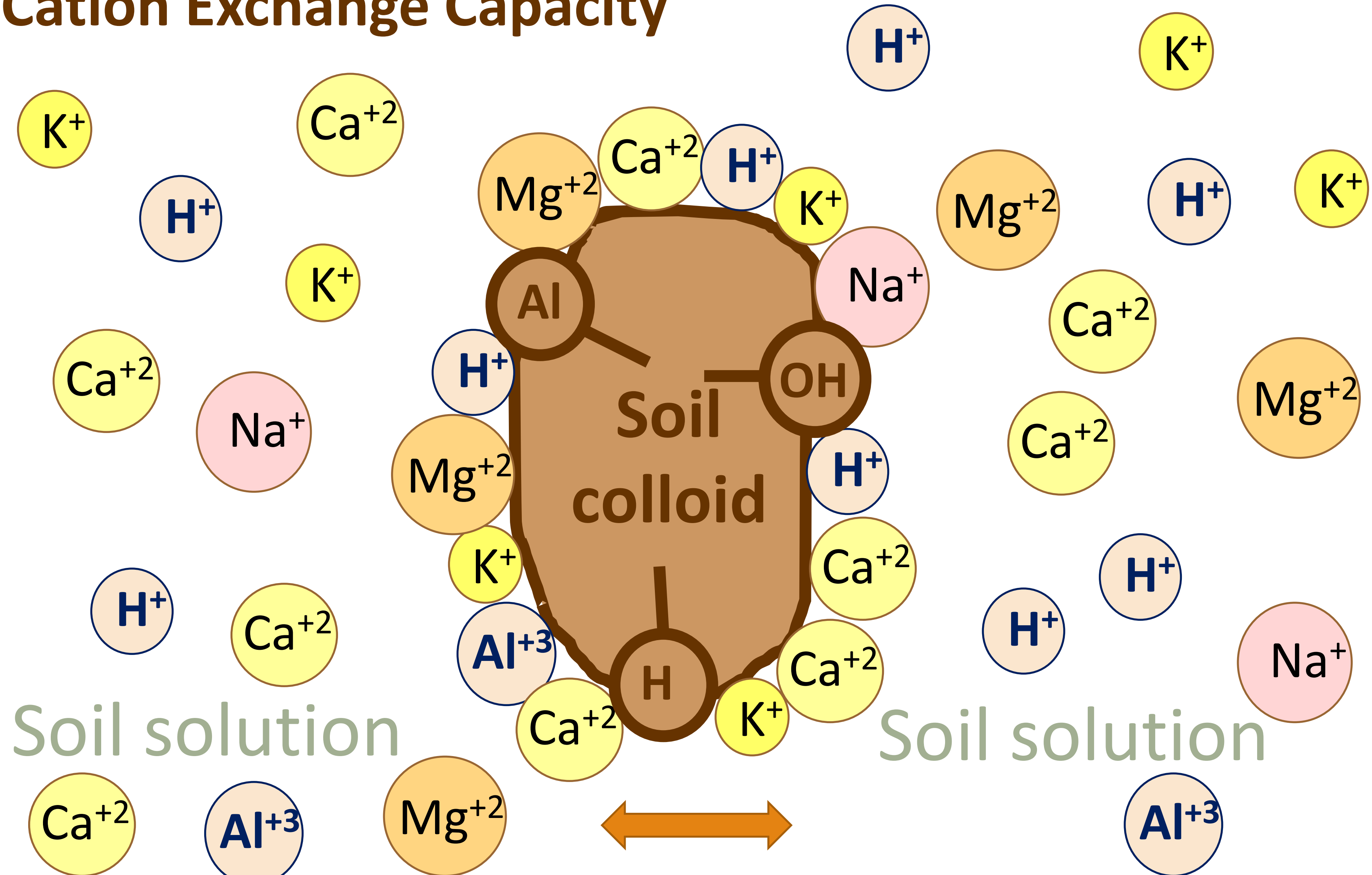
CEC is the mass of exchangeable cations that a given soil can retain (adsorb) per unit weight.

→ The amount of exchangeable cations adsorbed (attached) onto colloid surfaces

→ Is the quantity of negative charges

Expressed in units of **cmol(+)/kg**

Cation Exchange Capacity



Equilibrium between adsorbed ions and ions in the soil solution

cations indicate neutrality and alkalinity

- Calcium Ca^{++}
- Magnesium Mg^{++}
- Potassium K^{+}
- Sodium Na^{+}

Basic cations

cations indicate acidity

- Hydrogen H^{+}
- Aluminum Al^{+++}
- Silicon Si^{++++}
- Iron Fe^{++}/ Fe^{+++}

anions

- Carbonate CO_3^{--}
- Nitrate NO_3^{-}
- Hydroxide OH^{-}
- Sulfate SO_4^{--}
- Phosphate HPO_4^{--} $H_2PO_4^{-}$

Clay & Organic Matter act as anions

Base Saturation

Basic cation saturation of the soil.

Example:

$CEC = (\sum H^+, K^+, Al^{3+}, Ca^{2+}, Si^{4+}, Mg^{2+}, Fe^{2+}, Na^+) = 20$ cmol (+)/kg

Basic cations $= (\sum K^+, Ca^{2+}, Mg^{2+}, Na^+) = 10$ cmol (+)/kg

$$\textbf{Base saturation} = \frac{\textbf{Basic cations}}{\textbf{CEC}} \times 100$$

$$\text{Base saturation} = \frac{10 \text{ cmol } (+)/\text{kg}}{20 \text{ cmol } (+)/\text{kg}} \times 100 = \mathbf{50\%}$$

Calculate the CEC of the Ap horizon of this soil:

	cmol (+) / kg of soil
Calcium	6.0
Magnesium	2.5
Potassium	0.5
Hydrogen	2.0
Aluminum	1.0
	12.0

What is the CEC of the A horizon of this soil (assuming only one type of clay present)?

Silt loam soil with 6% SOM and 20% illite clay

CEC of SOM is 200 cmol(+)/kg

CEC of Illite is 40 cmol(+)/kg

SOM: 0.06 X 200 cmol (+)/kg = 12

Clay: 0.20 X 40 cmol (+)/kg = 8

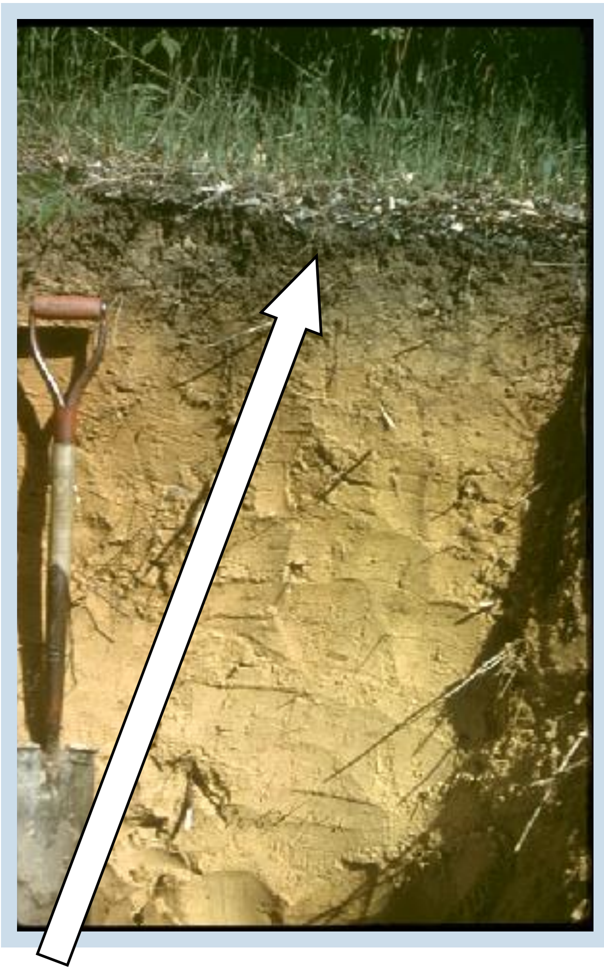
Thus, the CEC = **20 cmol/kg**

Normal Range of CEC Values for Common Color/Texture Soil Groups

Soil texture	**CEC (cmol/kg)**
Sands (light-colored)	3-5
Sands (dark-colored)	10-20
Loams	10-15
Silt loams	15-25
Clay and clay loams	20-50
Organic soils	50-100

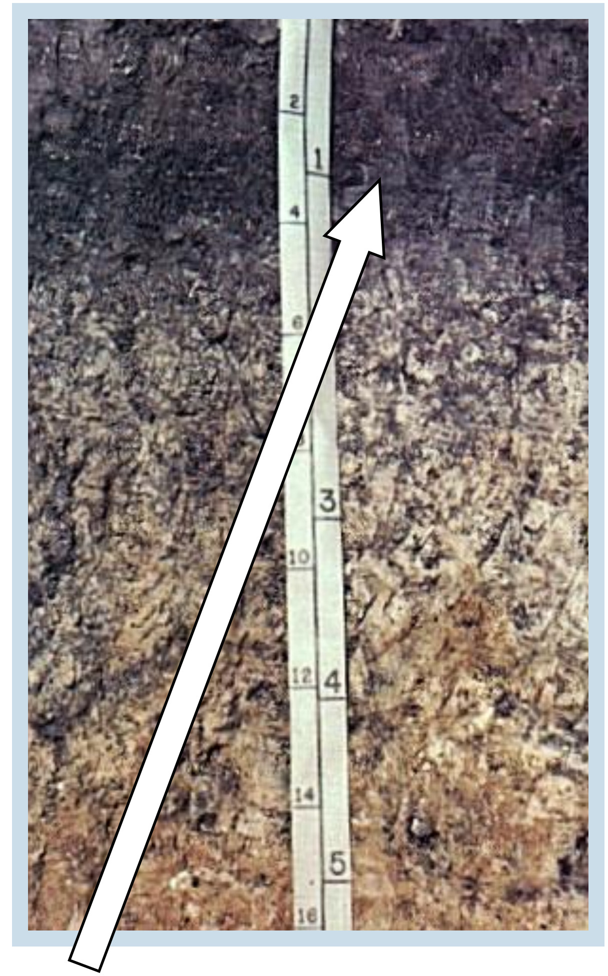
The higher the CEC the more clay or organic matter present in the soil.

Examples of Soil CEC Values

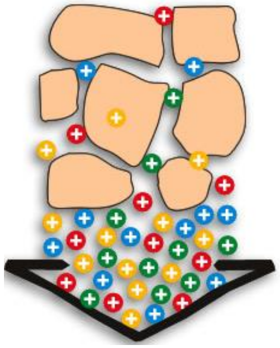


5 cmol + / kg

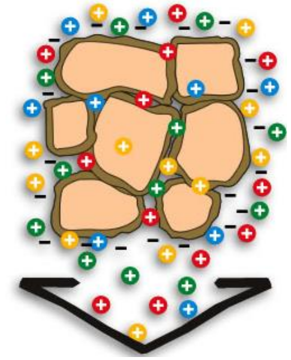
12 cmol + / kg



24 cmol + / kg



Importance of **cation exchange capacity** (CEC)



- Allows the soil to hold nutrient cations and water for plant growth → vital to biomass production
- Aids in filtering out impurities and potential contaminates to ground water
- Buffers the soil against rapid changes in pH
- Contribute to soil structure development (→ improve water & air management → soil biological activity)

Calculate the Cation Exchange Capacity (CEC) and Base Saturation (B%) for soils A and B!

The adsorbed cations of the two different soils (Soil „A" and Soil „B") in cmol(+)/kg soil are:

„A"	Al =7	Fe = 3	K = 4	Ca = 12	H = 10	Na = 2	Mg = 2

„B"	Mg = 2	Na = 2	H = 6	Ca = 9	K = 2	Fe = 4	Al =5

CEC soil "A": **40 cmol/kg**

B% soil "A": **50%**

Basic cations: 20 cmol/kg

CEC soil "B": **30 cmol/kg**

B% soil "B": **50%**

Basic cations: 15 cmol/kg

$$\text{Base saturation} = \frac{\text{Basic cations}}{\text{CEC}} \times 100$$

Soil pH

pH is defined as the negative logarithm (base 10) of the activity of hydrogen ions (H^+) in a solution.

$$pH = -\log [H^+] \text{ mol/liter}$$

		pH	$[H^+]$
alkaline	→	8	10^{-8}
neutral	→	7	10^{-7}
acidic	{	6	10^{-6}
		5	10^{-5}
		4	10^{-4}
		3	10^{-3}

Soil pH

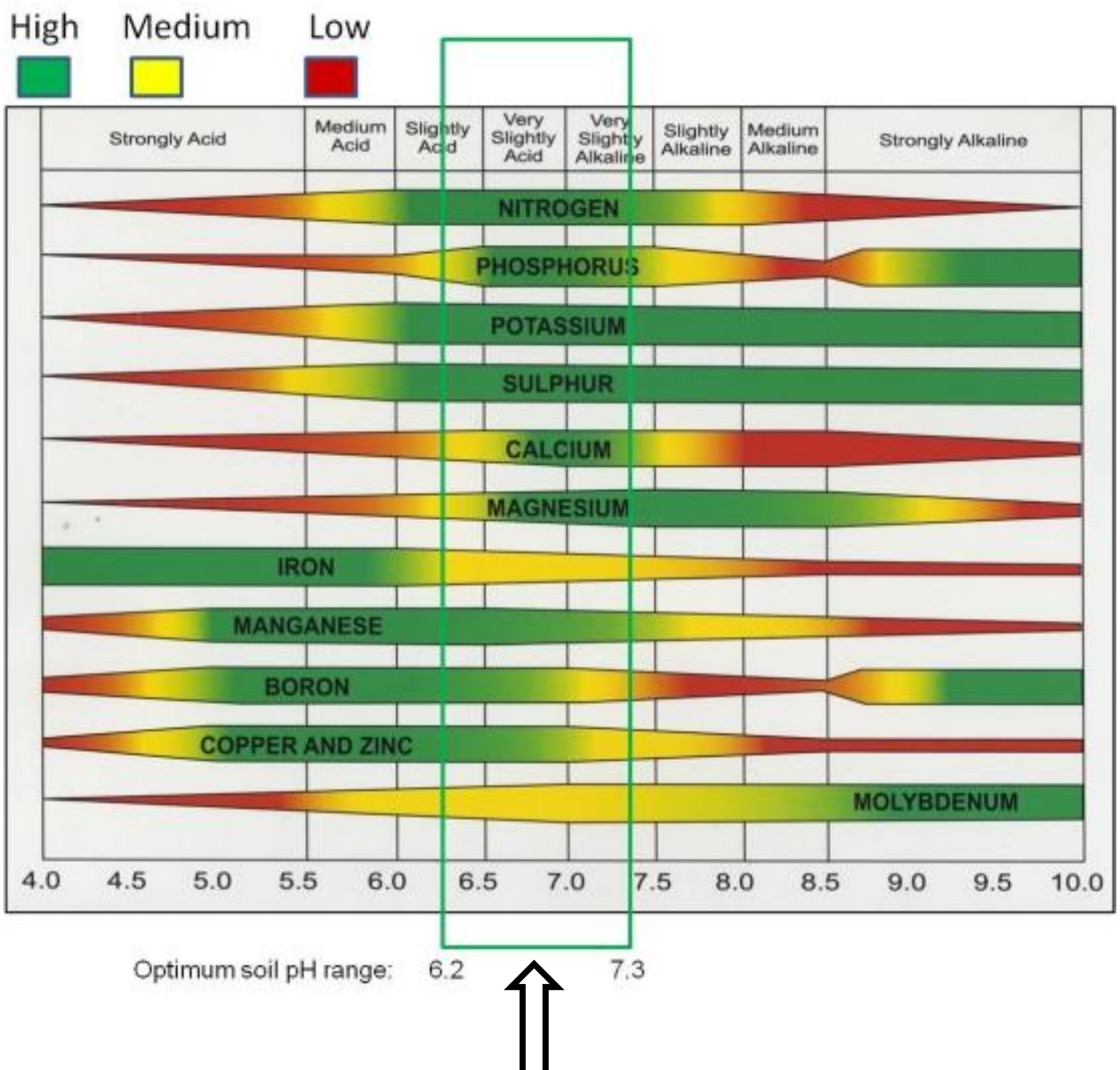
Classification of soil pH ranges (USDA NRCS):

ACIDIC

ALKALINE

Ultra acidic	< 3.5
Extremely acidic	3.5–4.4
Very strongly acidic	4.5–5.0
Strongly acidic	5.1–5.5
Moderately acidic	5.6–6.0
Slightly acidic	6.1–6.5
Neutral	**6.6–7.3**
Slightly alkaline	7.4–7.8
Moderately alkaline	7.9–8.4
Strongly alkaline	8.5–9.0
Very strongly alkaline	> 9.0

Soil pH – Nutrient availability



Optimal pH range

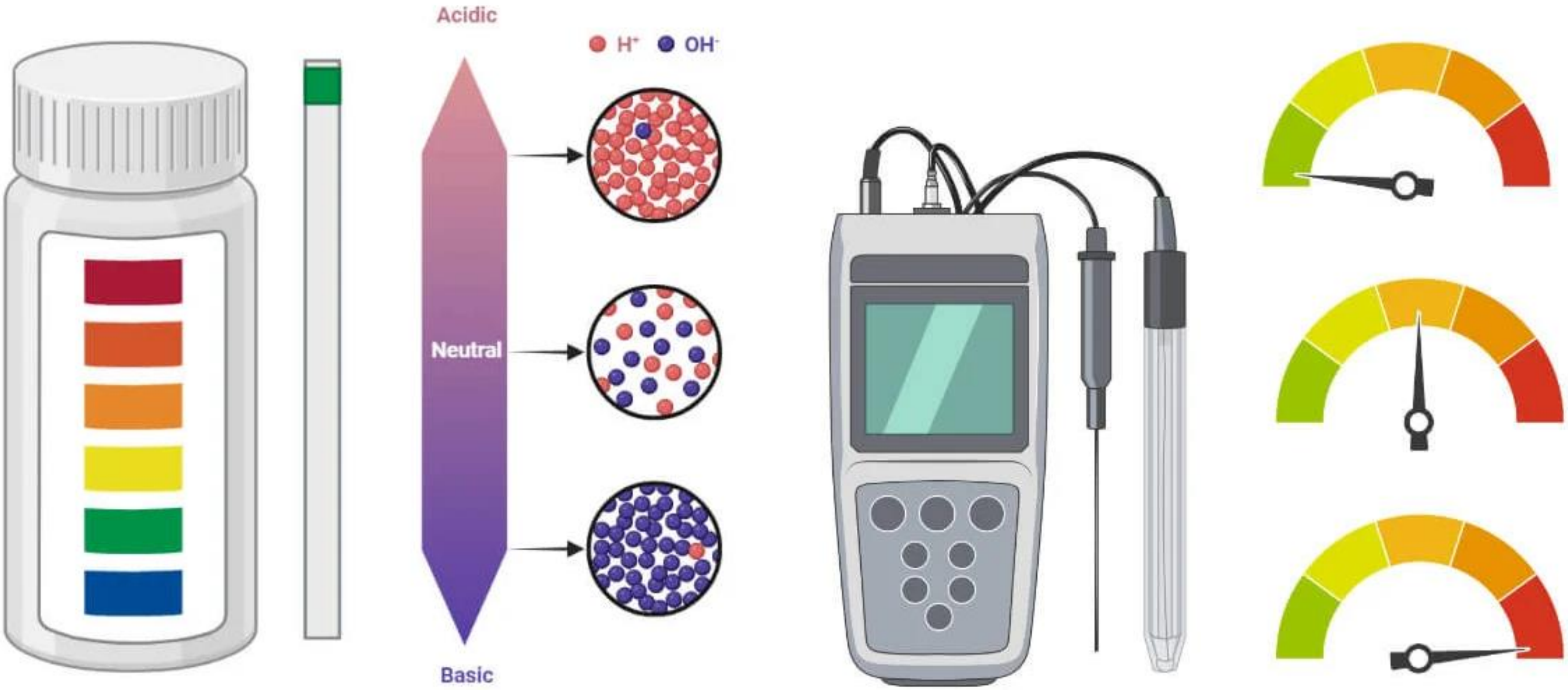
Measurement of soil pH

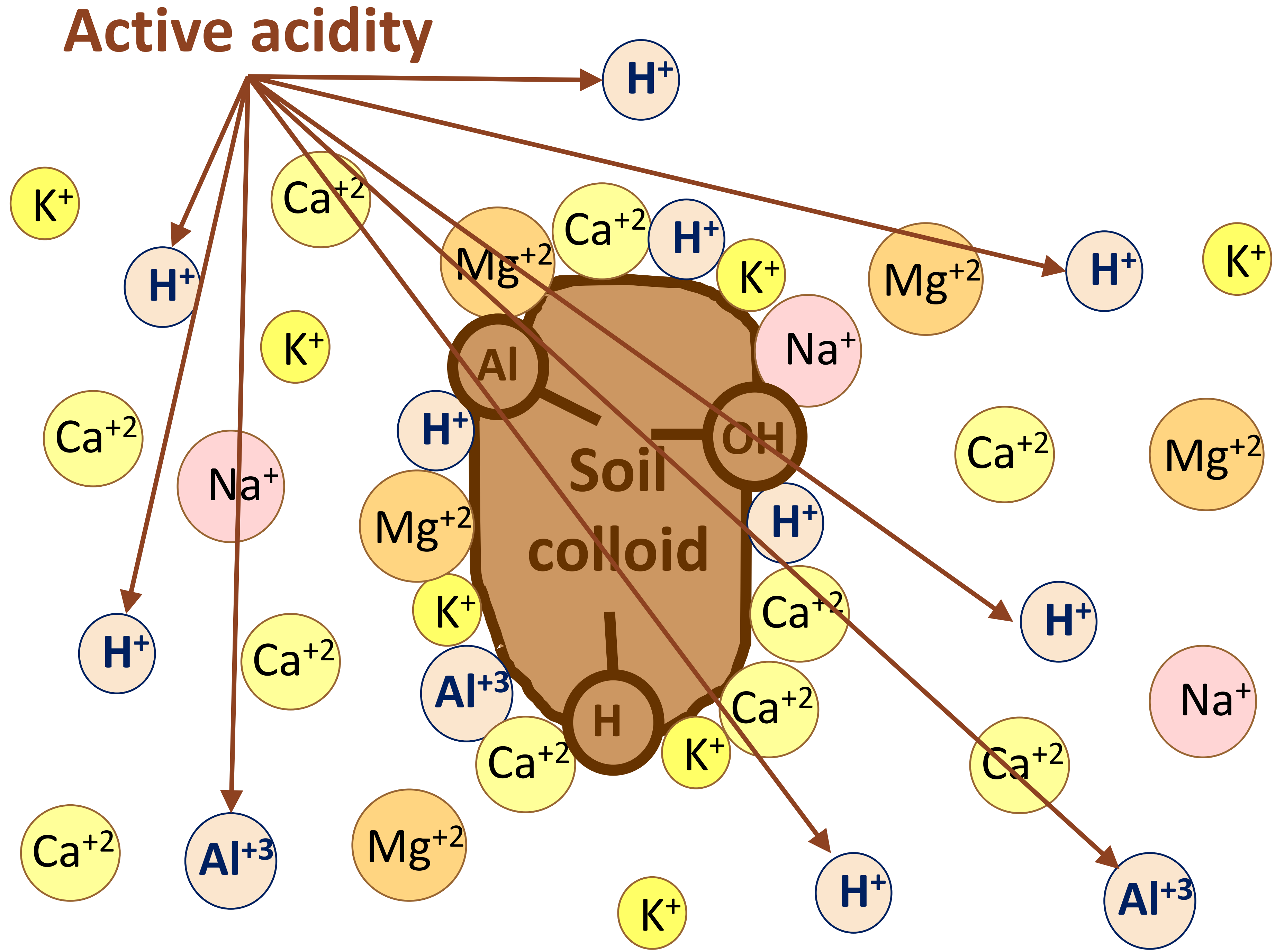
Colourimetric determination

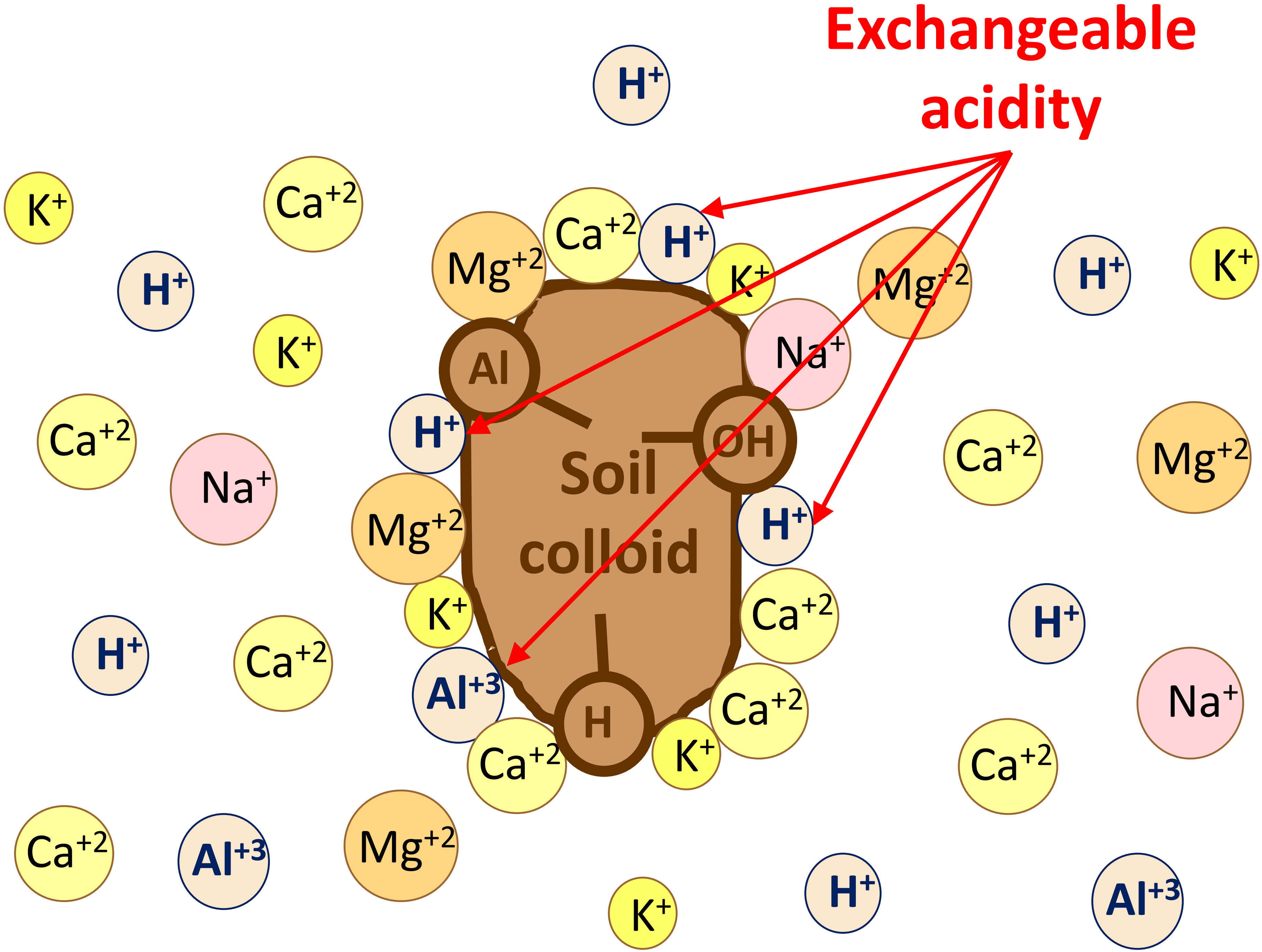
→ indicator paper/solution

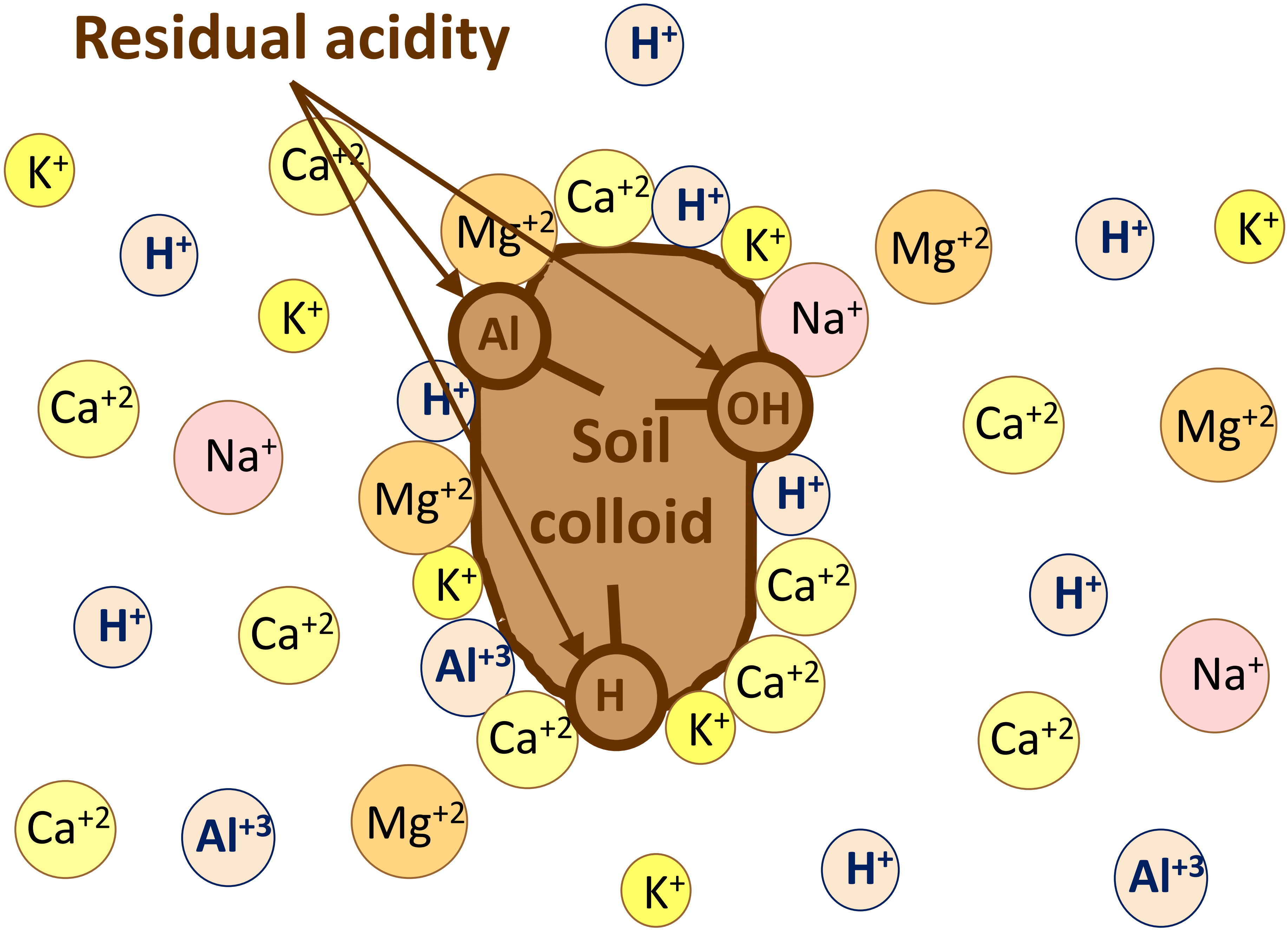
Potentiometric determination

→ measuring the potential difference between two appropriate electrodes




Active acidity
H+
K+
Ca+2
H+
Mg+2
Ca+2
H+
K+
Mg+2
H+
K+
K+
Na+
Al
Ca+2
H+
OH
Soil
colloid
Ca+2
Mg+2
Na+
Mg+2
H+
K+
Ca+2
H+
H+
Ca+2
Al+3
H
Ca+2
Na+
Ca+2
K+
Ca+2
Ca+2
Al+3
Mg+2
H+
Al+3
K+


Exchangeable acidity
Soil colloid
Al
OH
H
H+
K+
Ca+2
Mg+2
Na+
Al+3



Residual acidity
Soil colloid
Al
OH
H
H+
K+
Ca+2
Mg+2
Na+
Al+3

Soil acidity

Active acidity is the quantity of hydrogen ions that are present in the soil water solution (can be measured by the pH meter.

Potential or exchangeable acidity refers to hydrogen and aluminum ions retained on the exchange complex of the soil, i.e. on the surfaces of soil colloids. It is many times higher than the active acidity and is due to the adsorbed H^+ and Al^{3+}.

The active pool of hydrogen ions **is in equilibrium** with the exchangeable hydrogen ions adsorbed on the surfaces of the colloids.

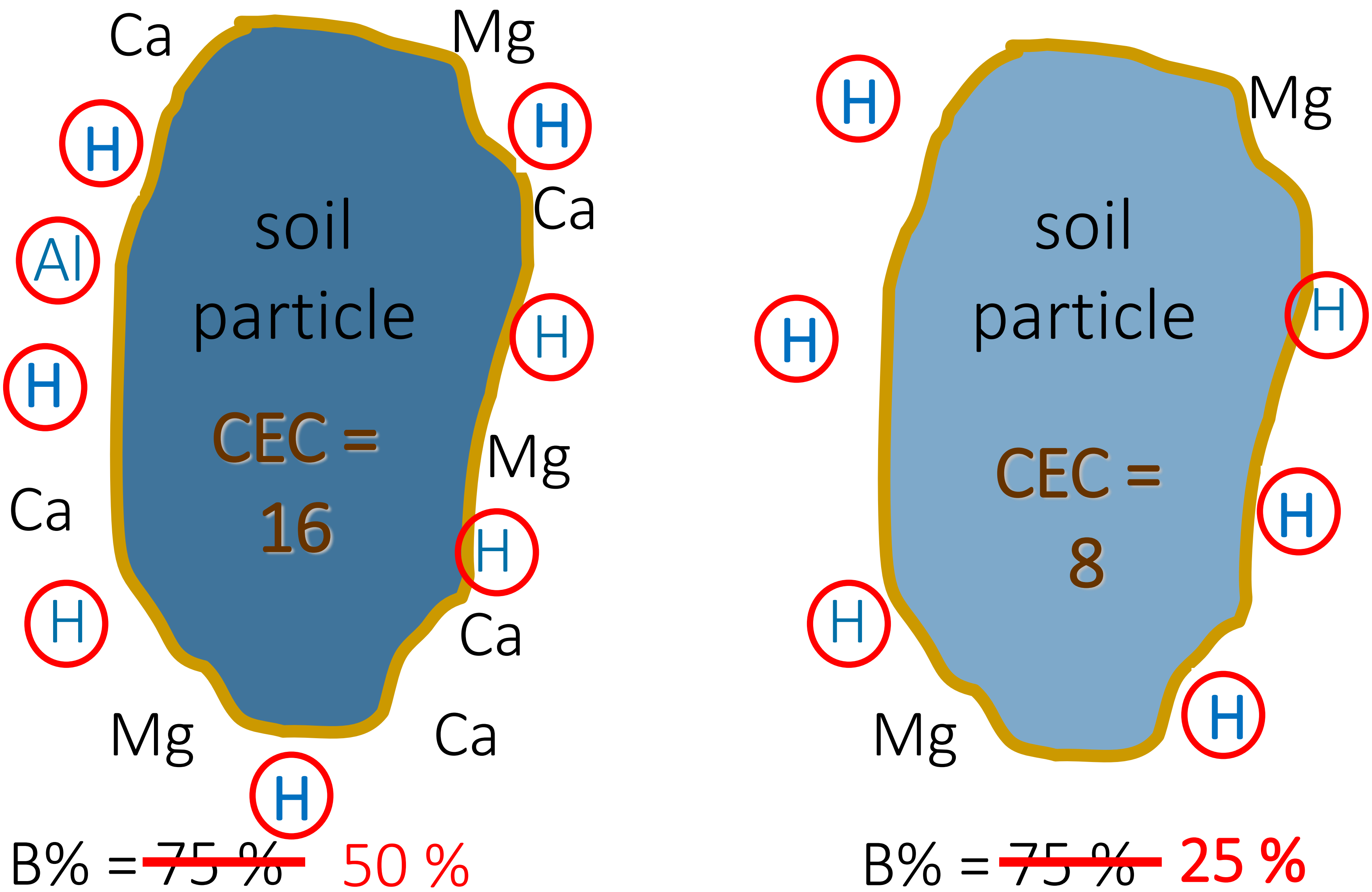
Soil Buffering Capacity

- Resistance to change in pH
- Buffering capacity increases as CEC increases

Illustration of Buffering Capacity
(Each symbol is 1 cmol(+)/kg)

4 H
Adding acid

4 H
Adding acid




I ♥ SOIL