

Types of Soil Colloids

- **Crystalline silicate clays**
 - Phyllosilicates → tetrahedral and octahedral crystal sheets
- **Non-crystalline silicate clays (Andisols)**
 - Dominantly amorphous clays (allophane and imogolite)
- **Iron and aluminum oxides (Oxisols & ...)**
 - Dominantly gibbsite (Al-oxide) and goethite (Fe-oxide)
- **Organic (humus) colloids (Histosols &...)**
 - Non-crystalline colloids dominated by long C-chain molecules

Sources of Charges on Soil Colloids

- Constant Charge (structural)
 - through Isomorphic substitution
 - both negative and positive charges
 - predominately NEGATIVE
- Variable or pH-Dependent Charge
 - both negative and positive charges
 - primarily associated with hydroxyl (OH) groups
 - Source of charge on humus, Fe & Al oxides, allophane and some phyllosilicates.

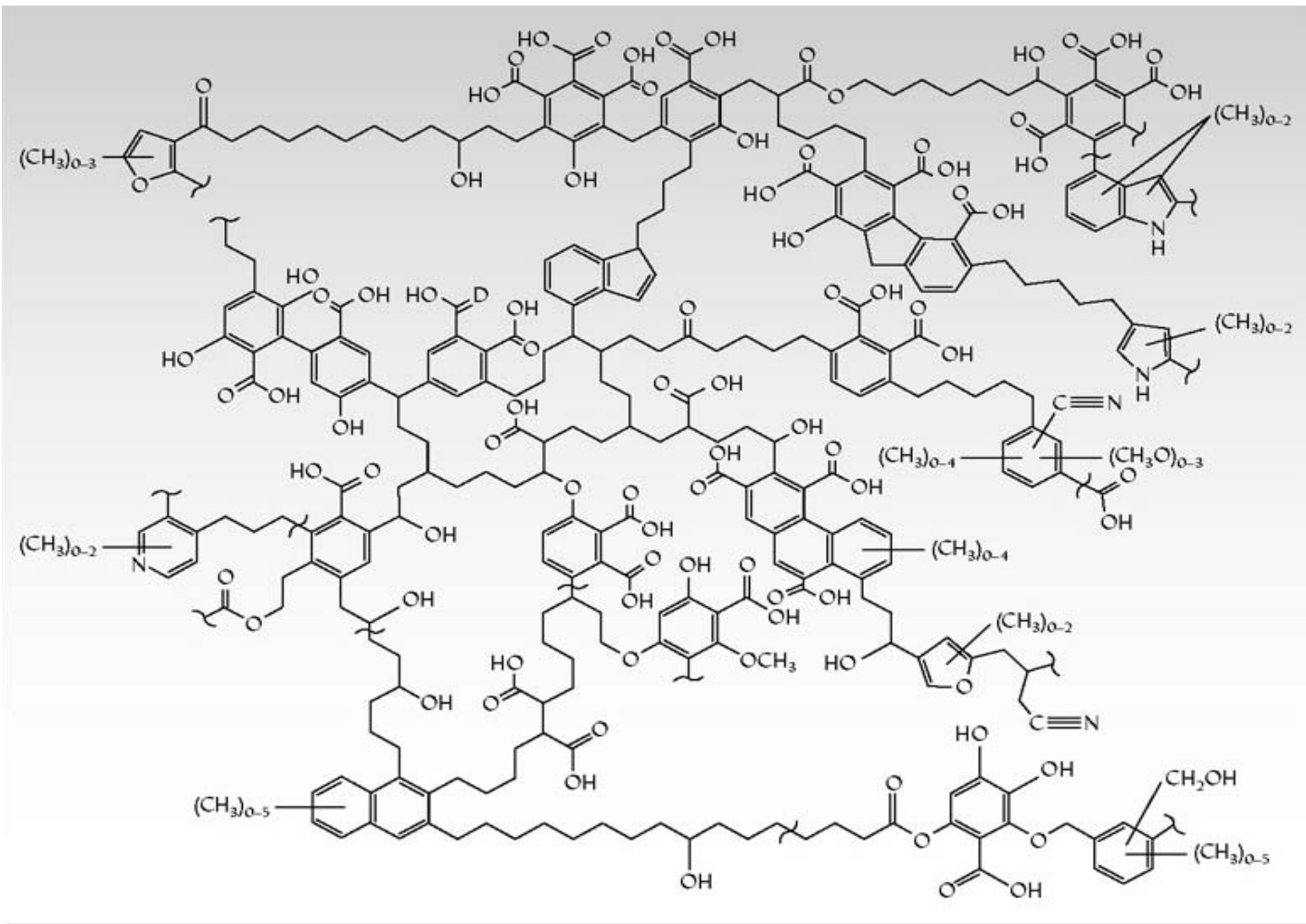
Constant Charge (structural)

TABLE 8.4 Typical Unit Layer Formulas of Several Clay and Other Silicate Minerals Showing Octahedral and Tetrahedral Cations as Well as Coordinating Anions, Charge per Unit Formula, and Fixed and Exchangeable Interlayer Components

Note that the charge per unit formula is the sum of the charges on the octahedral and tetrahedral sheets and that this negative charge is counterbalanced by equivalent positive charges in interlayer areas.

Mineral	Octahedral sheet	Tetrahedral sheet	Coordinating anions	Charge per unit formula	Interlayer components	
					Fixed	Exchangeable ^a
<i>1:1-Type</i>						
Kaolinite (dioctahedral)	Al ₂	Si ₂	O ₅ (OH) ₄	0	None	None
Serpentine (trioctahedral)	Mg ₃	Si ₂	O ₅ (OH) ₄	0	None	None
<i>2:1-Type Dioctahedral Minerals</i>						
Pyrophyllite	Al ₂	Si ₄	O ₁₀ (OH) ₂	0	None	None
Montmorillonite	Al _{1.7} Mg _{0.3} -0.3	Si _{3.9} Al _{0.1} -0.1	O ₁₀ (OH) ₂	-0.4 ↑	None	M _{0.4} ⁺
Beidellite	Al ₂	Si _{3.6} Al _{0.4} -0.4	O ₁₀ (OH) ₂	-0.4 ↑	None	M _{0.4} ⁺
Nontronite	Fe ₂	Si _{3.6} Al _{0.4} -0.4	O ₁₀ (OH) ₂	-0.4 ↑	None	M _{0.4} ⁺
Vermiculite	Al _{1.7} Mg _{0.3} -0.3	Si _{3.6} Al _{0.4} -0.4	O ₁₀ (OH) ₂	-0.7 ↑	xH ₂ O	M _{0.7} ⁺
Fine mica (illite)	Al ₂	Si _{3.2} Al _{0.8} -0.8	O ₁₀ (OH) ₂	-0.8 ↑	K _{0.7} ⁺	M _{0.1} ⁺
Muscovite	Al ₂	Si ₃ Al -1.0	O ₁₀ (OH) ₂	-1.0 ↑	K ⁺	None
<i>2:1-Type Trioctahedral Minerals</i>						
Talc	Mg ₃	Si ₄	O ₁₀ (OH) ₂	0	None	None
Vermiculite	Mg _{2.7} Fe _{0.3} ²⁺ +0.3	Si ₃ Al -1.0	O ₁₀ (OH) ₂	-0.7 ↑	xH ₂ O	M _{0.7} ⁺
Chlorite	Mg _{2.6} Fe _{0.4} ³⁺ +0.4	Si _{2.5} (Al,Fe) _{1.5} -1.5	O ₁₀ (OH) ₂	-1.1 ↑	Mg ₂ Al(OH) ₆ ⁺	M _{0.1} ⁺

^a Exchangeable cations such as Ca²⁺, Mg²⁺, and H⁺ are indicated by the singly charged cation M⁺.

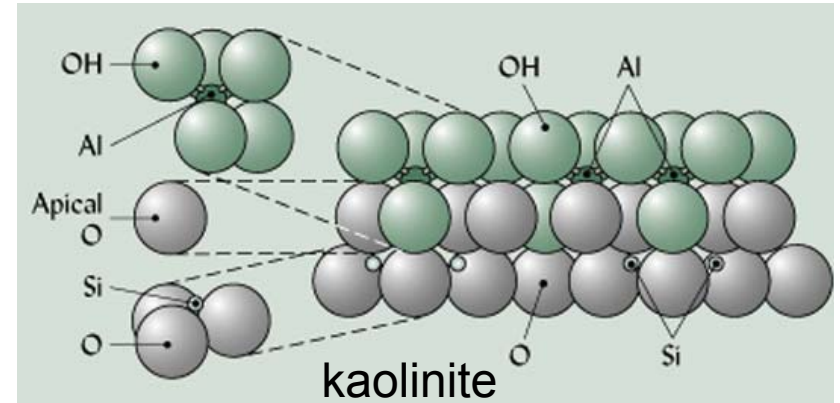
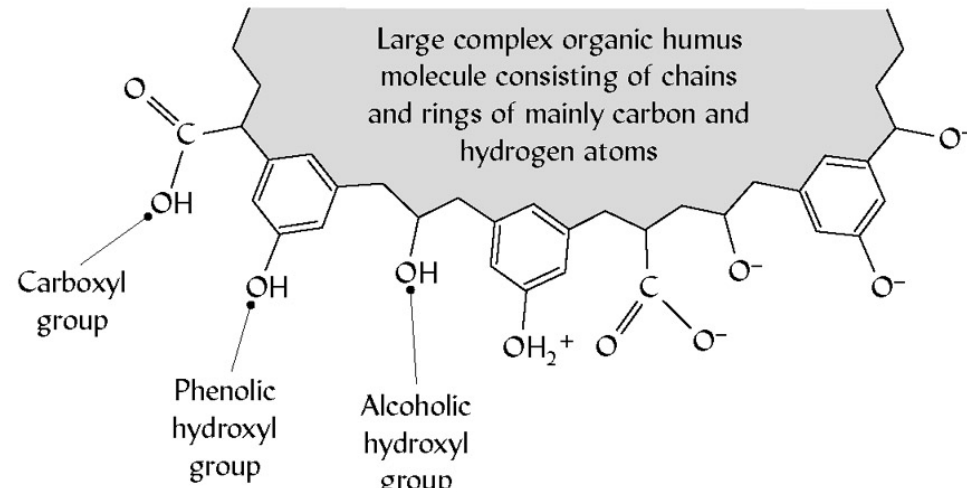


Variable or pH-Dependent Charge

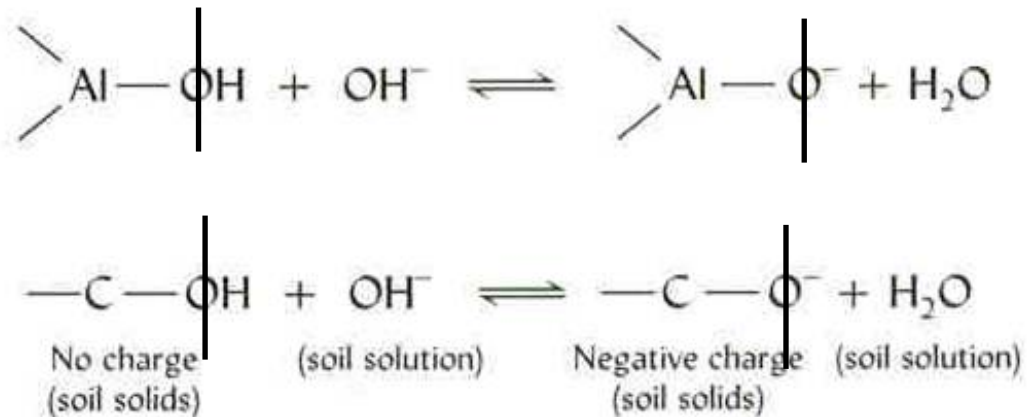
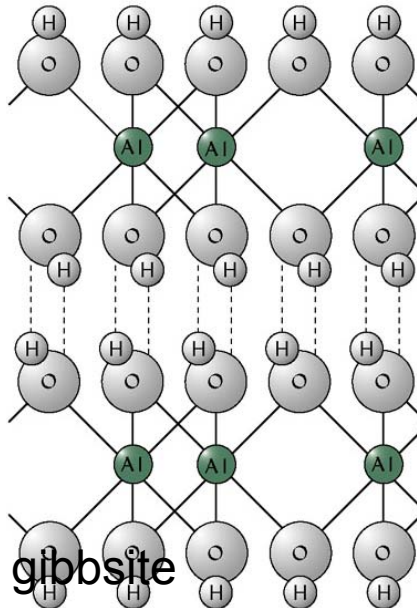
- both negative and positive charges
- primarily associated with hydroxyl (OH) groups
- Source of charge on humus, Fe & Al oxides, allophane and some phyllosilicates.

Variable or pH-Dependent Charge

via protonation / deprotonation of hydroxyl groups

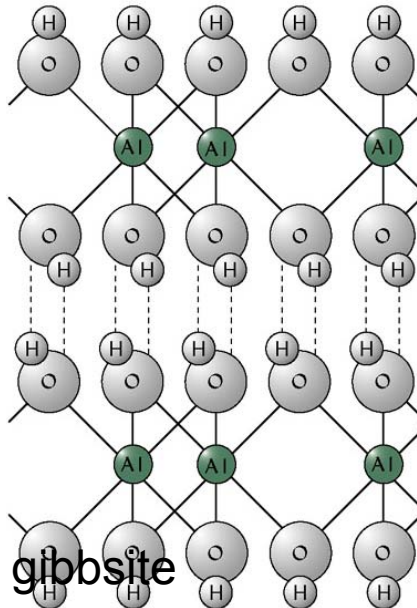
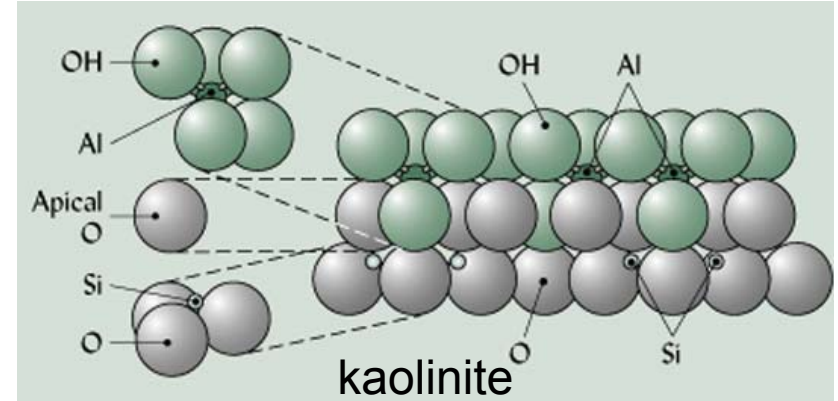
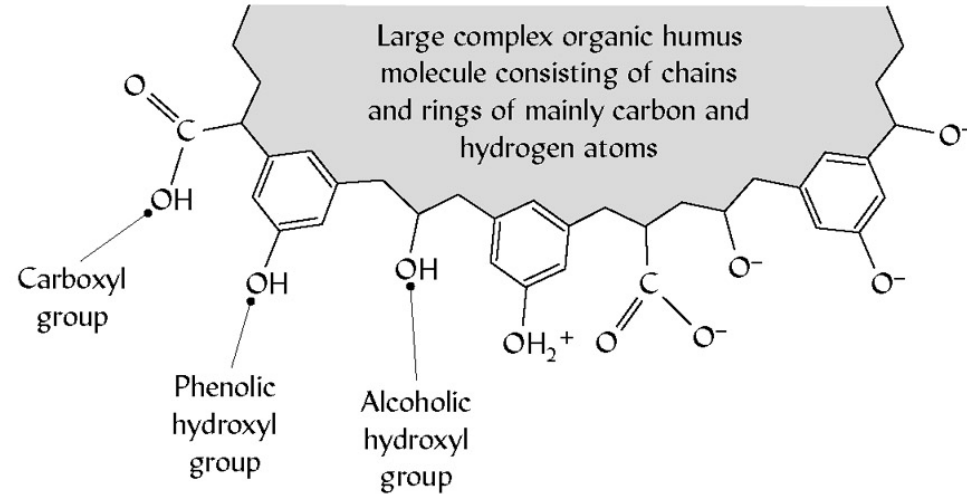


A negative charge comes with increasing pH

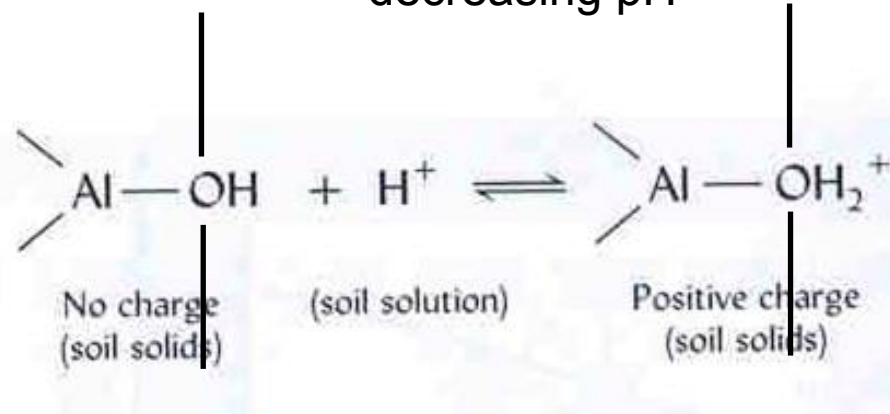


Variable or pH-Dependent Charge

via protonation / deprotonation of hydroxyl groups



A positive charge comes with decreasing pH



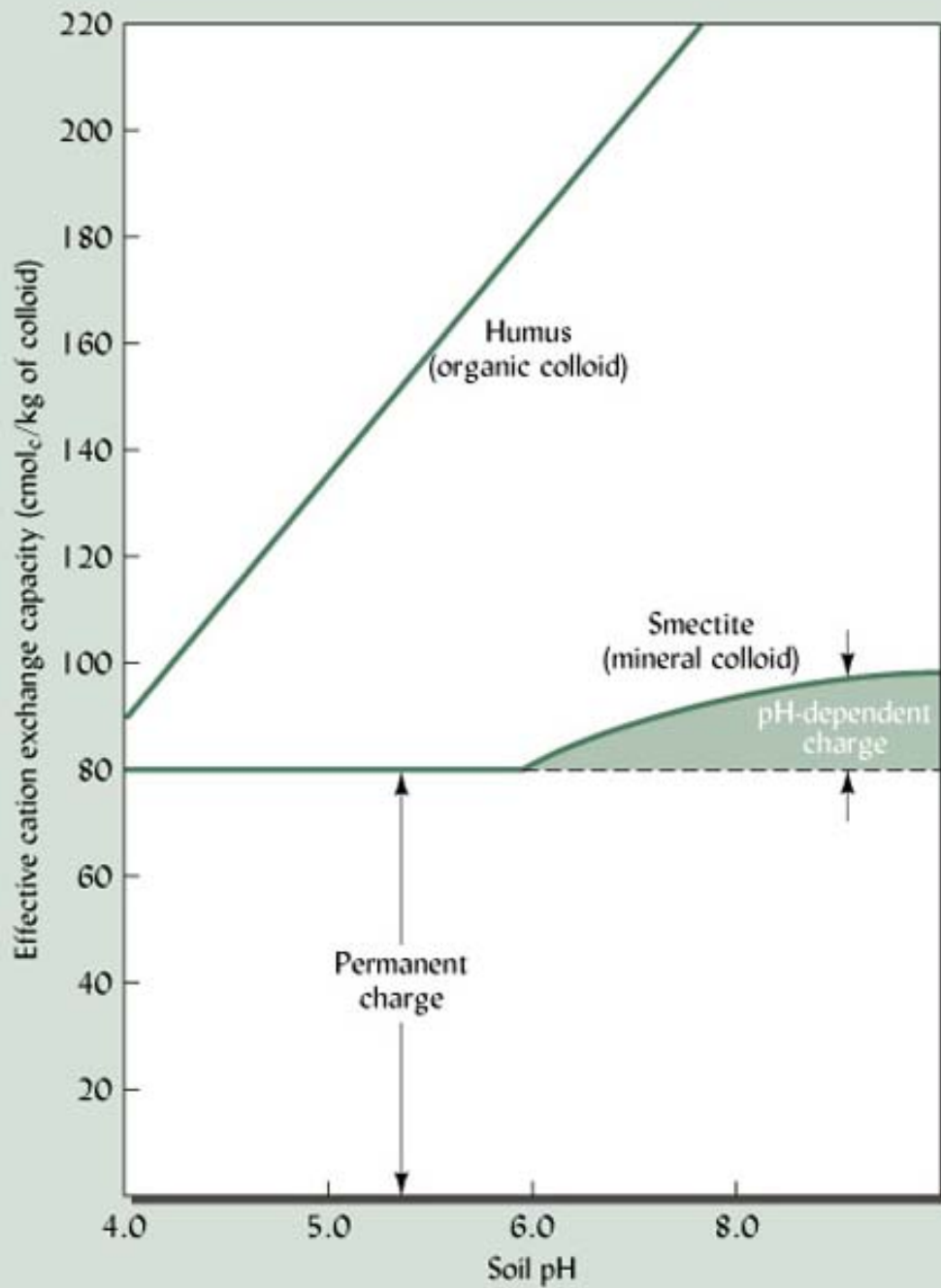


TABLE 8.5 Charge Characteristics of Representative Colloids Showing Comparative Levels of Permanent (Constant) and pH-Dependent Negative Charges as Well as pH-Dependent Positive Charges

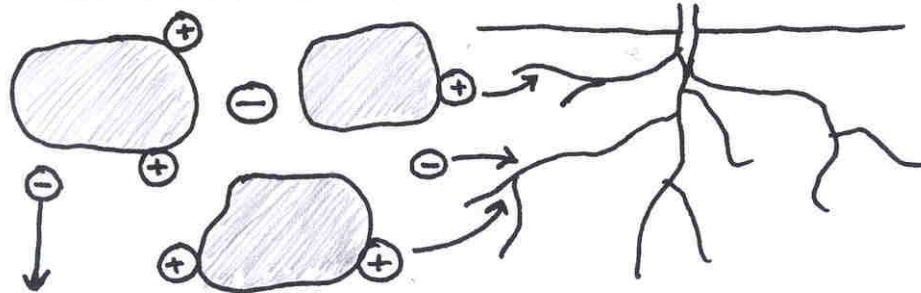
<i>Colloid type</i>	<i>Negative charge</i>			<i>Positive charge, cmol_c/kg</i>
	<i>Total at pH 7, cmol_c/kg</i>	<i>Constant, %</i>	<i>pH dependent, %</i>	
Organic	200	10	90	0
Smectite	100	95	5	0
Vermiculite	150	95	5	0
Fine-grained micas	30	80	20	0
Chlorite	30	80	20	0
Kaolinite	8	5	95	2
Gibbsite (Al)	4	0	100	5
Goethite (Fe)	4	0	100	5
Allophane	30	10	90	15

So where do the ions come from?

&

Which ions bind to the exchange sites?

SOLID-LIQUID INTERACTIONS



Almost all ions or molecules are ...

- absorbed by roots

or - leached away

But first the ions must be released from solids by/from ...

- cation exchange

- anion exchange

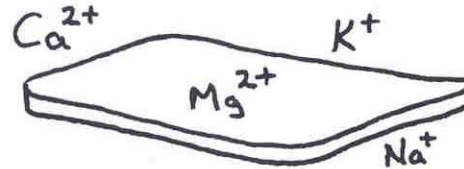
- ligand exchange

- dissolution / precipitation

or - surface chelation

A. Cation Exchange

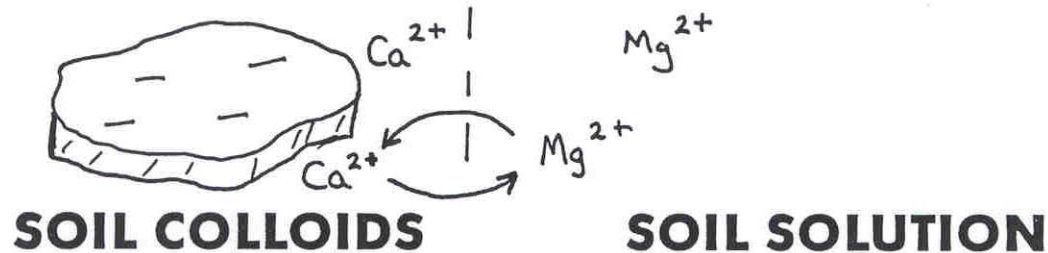
- clays have negative charge from isomorphous substitution



- organic matter has negative charge:



- cations are loosely bonded to these sites by electrostatic attraction.
- ion exchange occurs easily and rapidly between solution & surface.



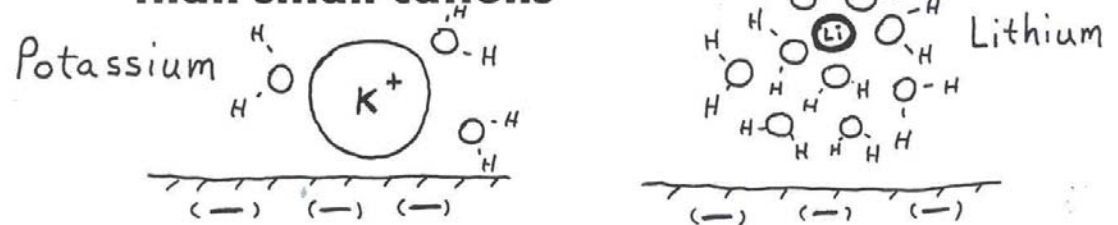
Importance of ion exchange:

- 1) exchange complex retains ions necessary for plant growth (Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , etc.)**
- 2) Exchangeable ions are not leached away from roots.**
- 3) exchangeable ions are rapidly available to plants**
- 4) many more cations reside on exchange complex than in solution**
- 5) ion exchange can purify metal-polluted wastewater.**

Rules of Cation Exchange:

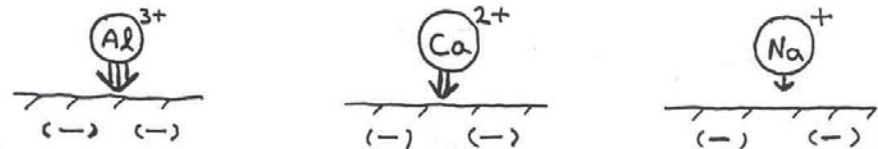
Cation Selectivity

1. Large cations are held more tightly than small cations

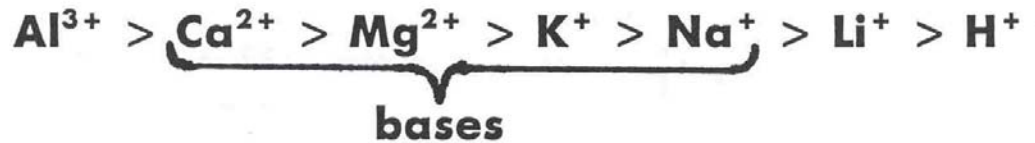


2. High-charge cations are held more tightly than low-charge cations

Charge Equivalence



Result:



Ratio Law

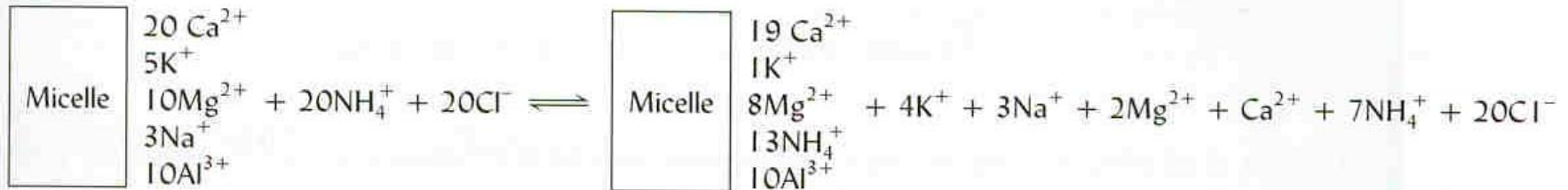
3. Any one cation can replace any other if its concentration is high enough.

(MASS-ACTION RULE)

Reversibility = all exchanges are reversible

Complementary Cations

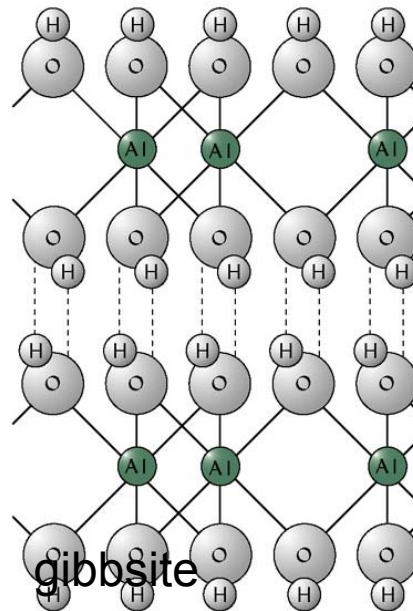
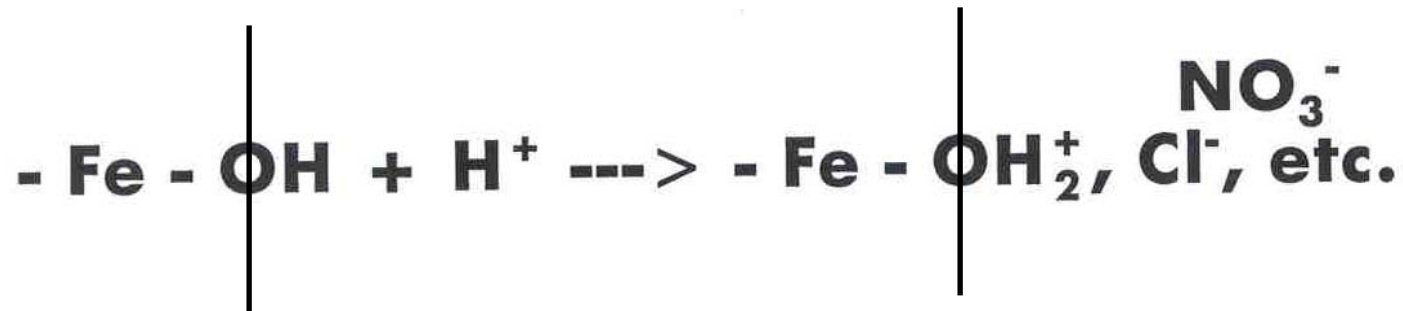
4. the combined influence of charge equivalencies, ion selectivity and complementary ions drive the exchange of cations



Generally it is the cations with the largest ionic radii and the lowest hydration energies that adsorb most strongly on the permanent charge sites of clay minerals.

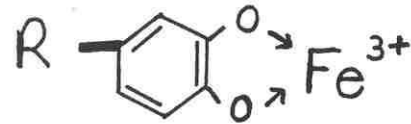
B. Anion Exchange (AEC)

- Generally much smaller than CEC
- Attraction of anions to oxide minerals



E. Surface Chelation

Chelate-ring structure formed when two or more ligands bond to a metal cation:



- **important in strongly binding many micronutrients into organic matter**

Fe³⁺, Cu²⁺, Zn²⁺, Mn²⁺, etc.

- **very slow release**

So where do the ions come from?

Answer: through dissolution processes into the soil solution and exchange processes from the soil solids in the soil solution

&

Which ions bind to the exchange sites?

Answer : an interaction of size, charge, charge strength and concentration determine the net residency of ions on exchange sites

NB – this is a dynamic environment with exchanges happening constantly

How do we quantitatively measure this characteristic of soil?

Answer: **Cation Exchange Capacity (CEC)**

and to a lesser extent Anion Exchange Capacity (AEC)

Cation Exchange Capacity (CEC)

CEC = total amount of exchangeable cations (expressed in moles of charge) that can be held by a given mass of soil.

$$\text{Units: } \frac{\text{milliequivalents}}{100 \text{ grams}} \text{ or } \frac{\text{centimoles (-)}}{\text{kg}}$$



An equivalent is the quantity of ion which possesses one mole of charge

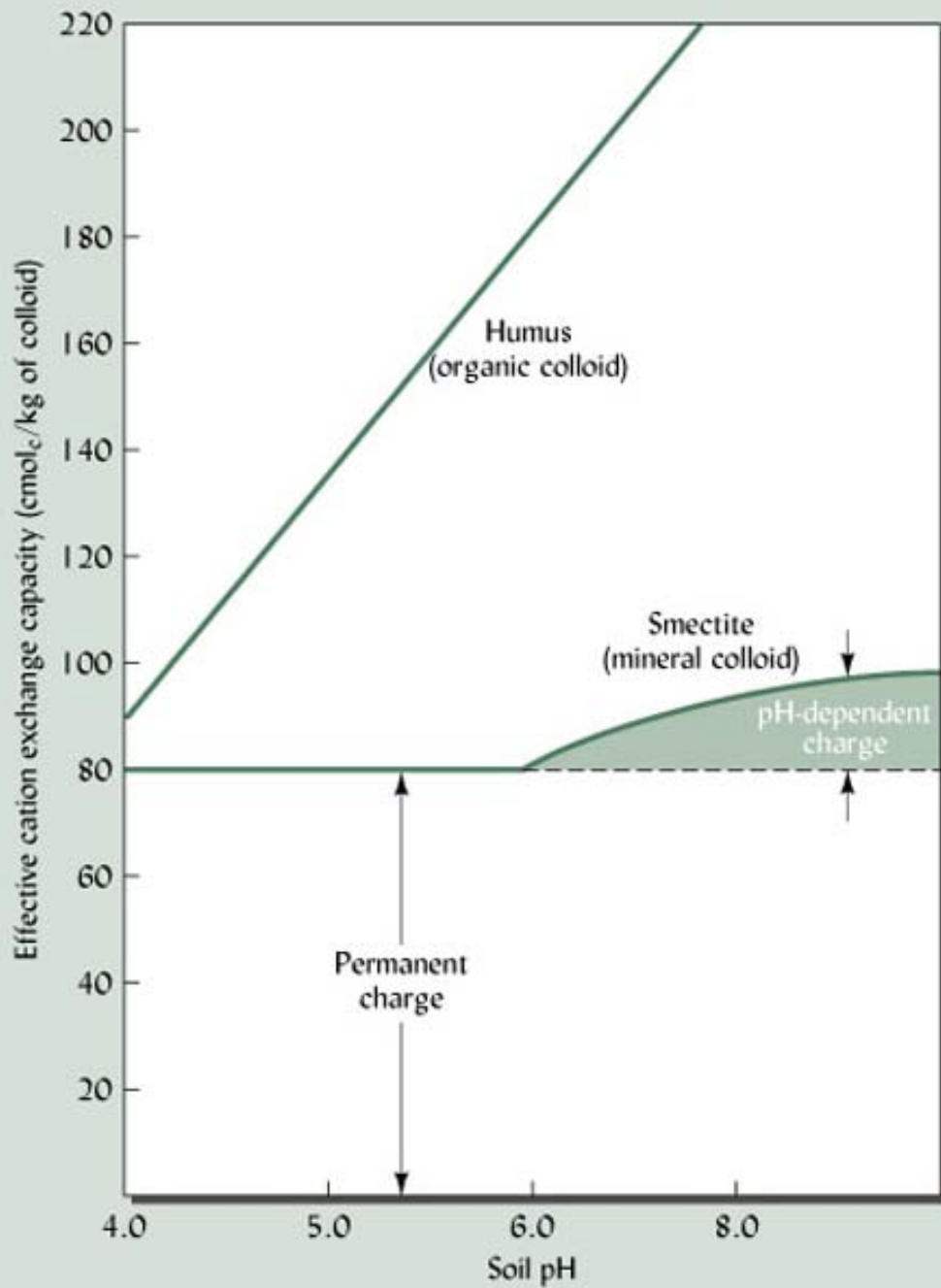
$$\text{Equivalent weight} = \frac{\text{atomic weight}}{\text{ionic charge}}$$

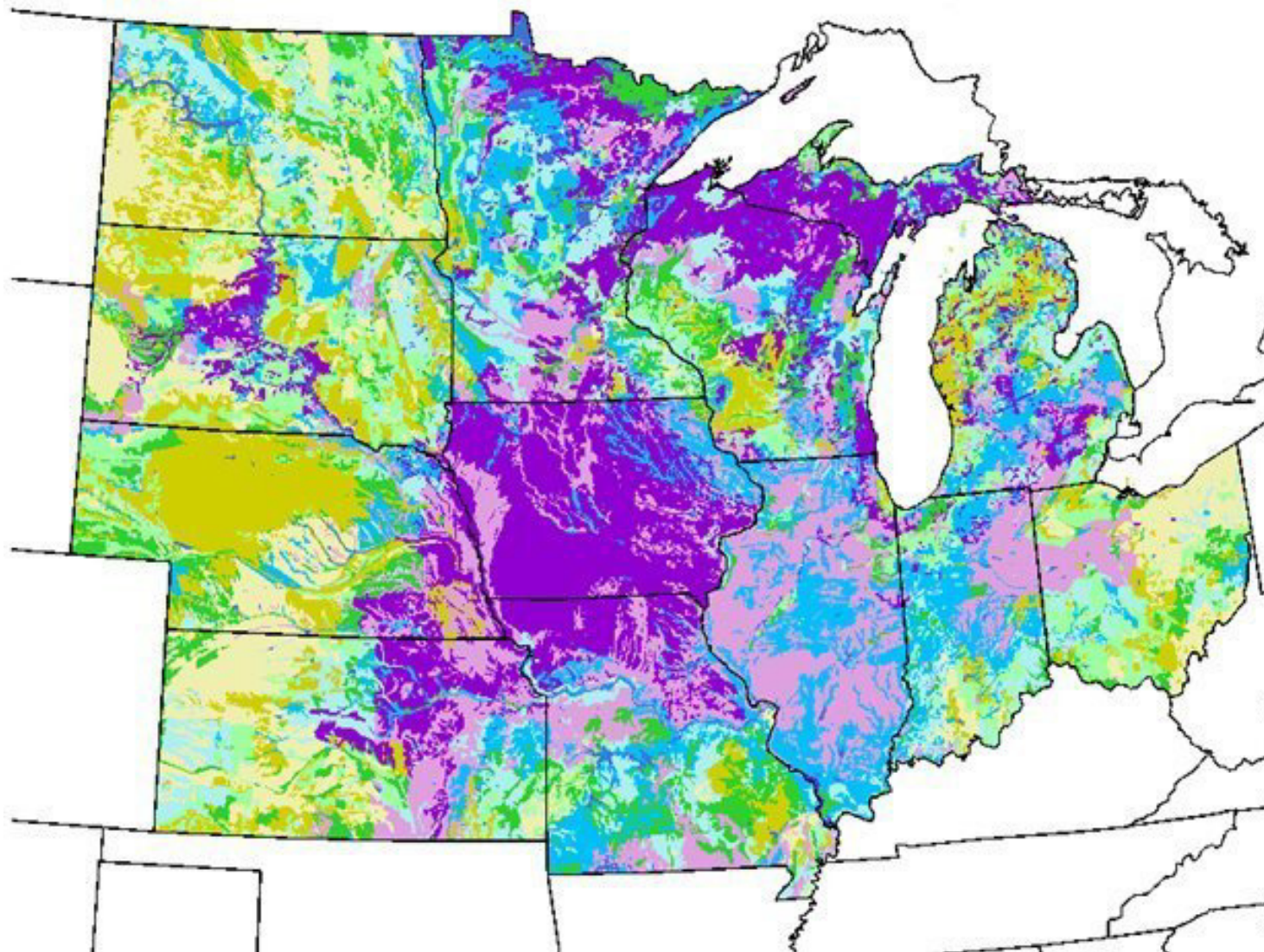
CEC largely determined by clay & organic matter content of soil.

Order of contribution to CEC (by weight)









ORGANIC MATTER 200-1000	SMECTITE, VERMICULITE 90-150	ILLITE, CHLORITE 10-30	KAOLINITE OXIDES
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milliequivalents / kilogram





**Average Value
Milliequivalents
per 100 grams of
dry soil**

-  < 1.8
-  1.8-3.6
-  3.7-5.8
-  5.9-8.6
-  8.7-12.0
-  12.1-16.1
-  16.2-23.8
-  ≥ 23.9

-  Do not
meet criteria
-  Water

**Range of Results:
0 - 132.0**

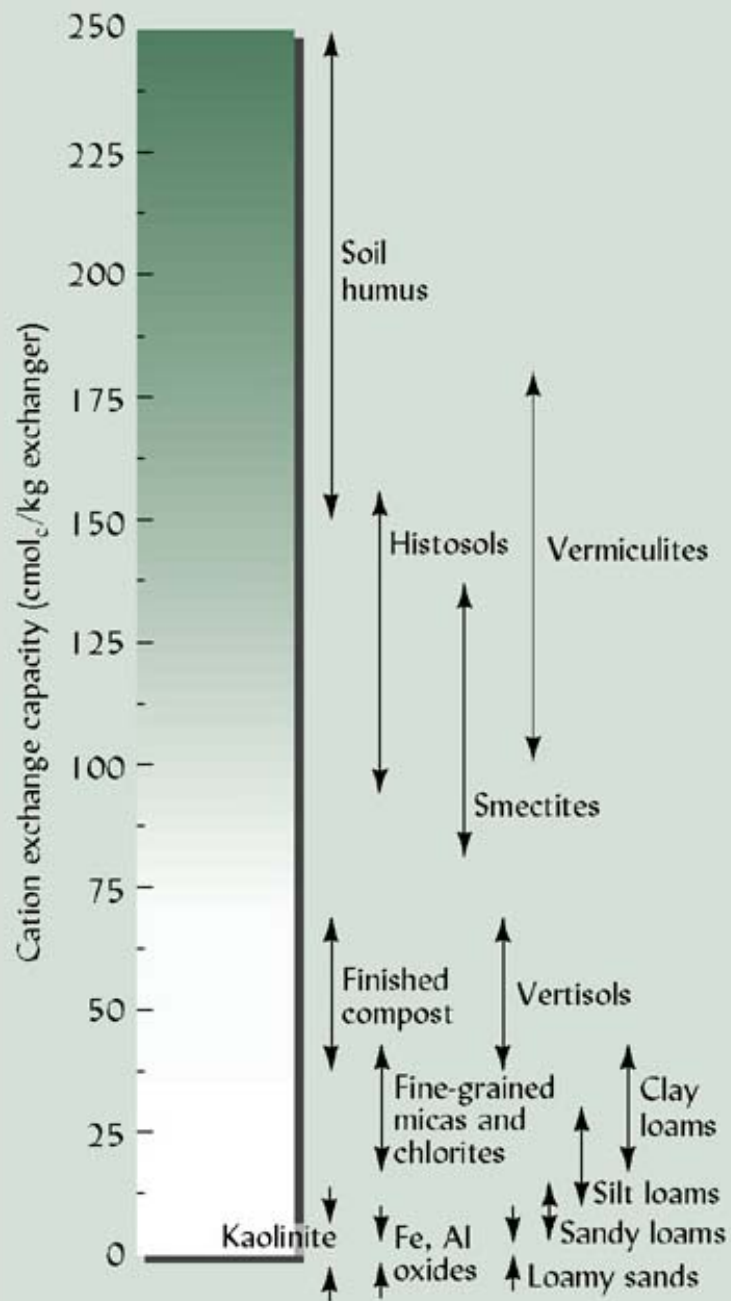
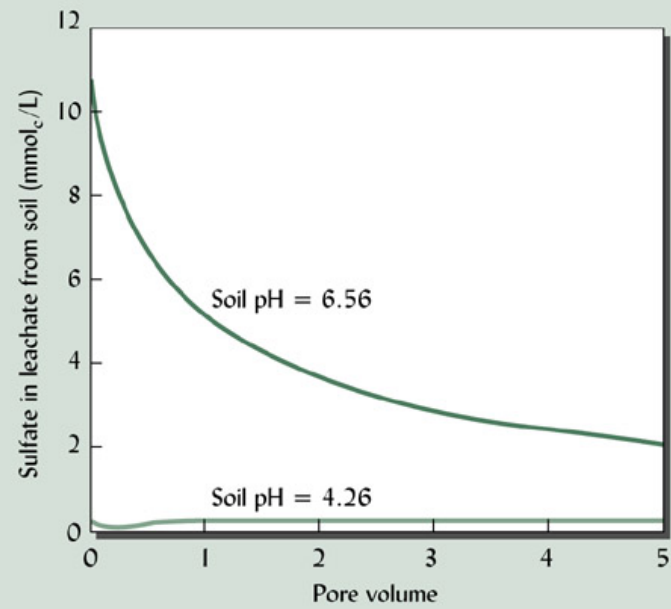
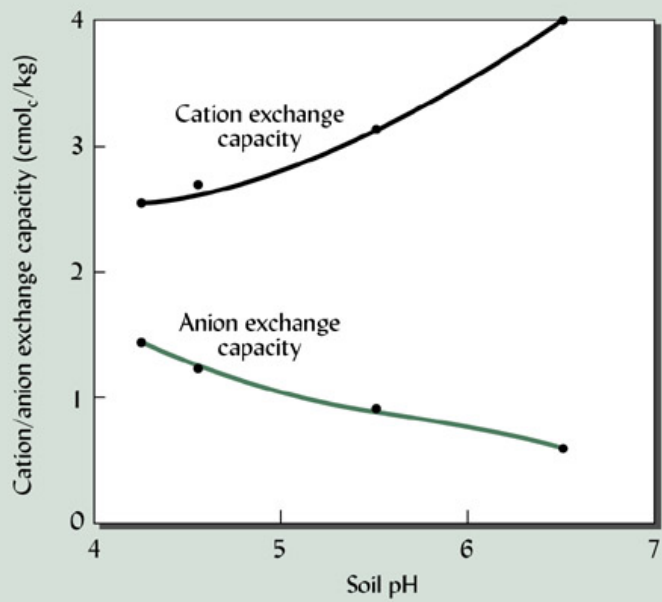


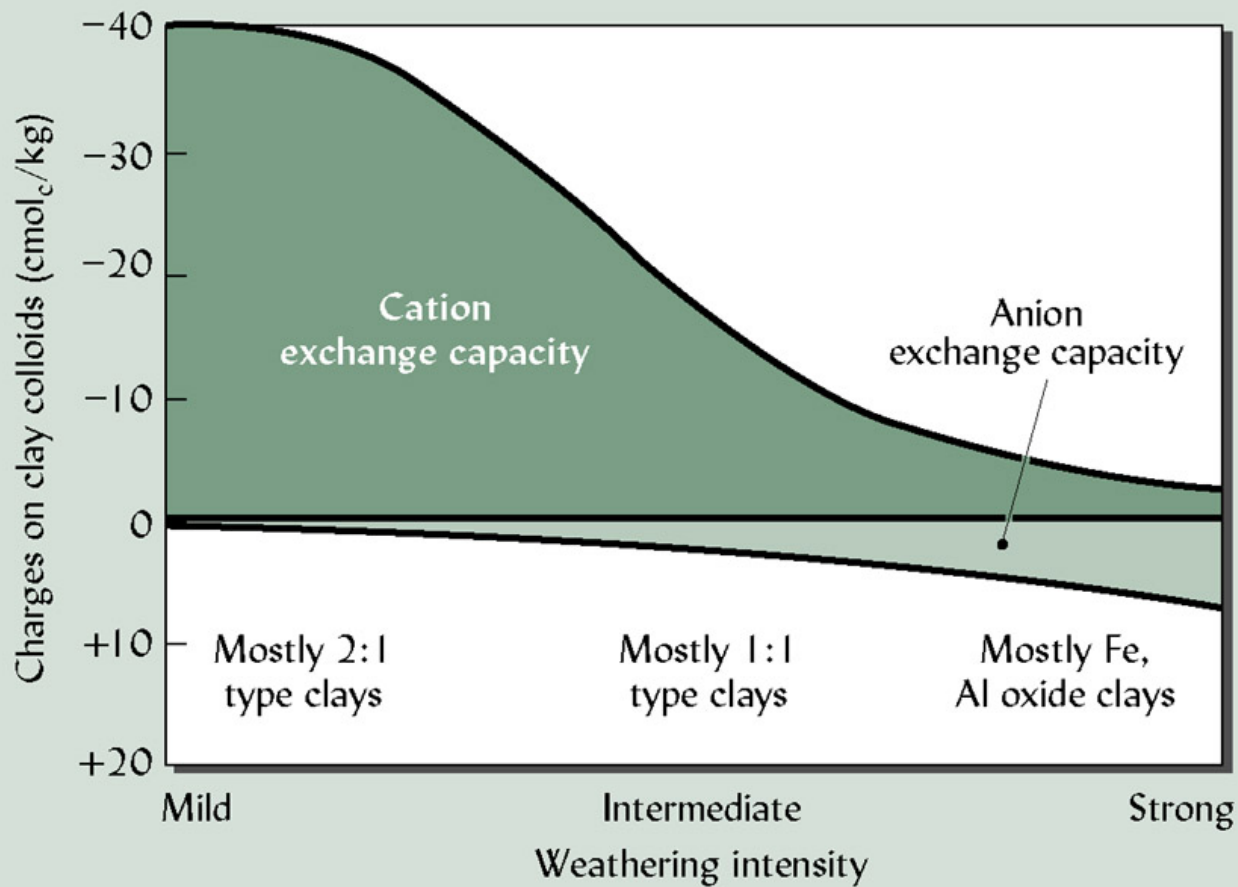
TABLE 8.7 The Average Cation Exchange Capacities (CEC) and pH Values of More Than 3000 Surface Soil Samples Representing Nine Different Soil Orders

Note the very high CEC of the Histosols and among the mineral soils of the Vertisols. Ultisols have the lowest CEC. The low average pH values of the Spodosols and high values for the Aridisols and Entisols (many of which were from low-rainfall areas) are noteworthy.

Soil order	CEC, cmol _c /kg	pH
Ultisols	3.5	5.60
Alfisols	9.0	6.00
Spodosols	9.3	4.93
Entisols	11.6	7.32
Inceptisols	14.6	6.08
Aridisols	15.2	7.26
Mollisols	18.7	6.51
Vertisols	35.6	6.72
Histosols	128.0	5.50

From Holmgren, et al. (1993).





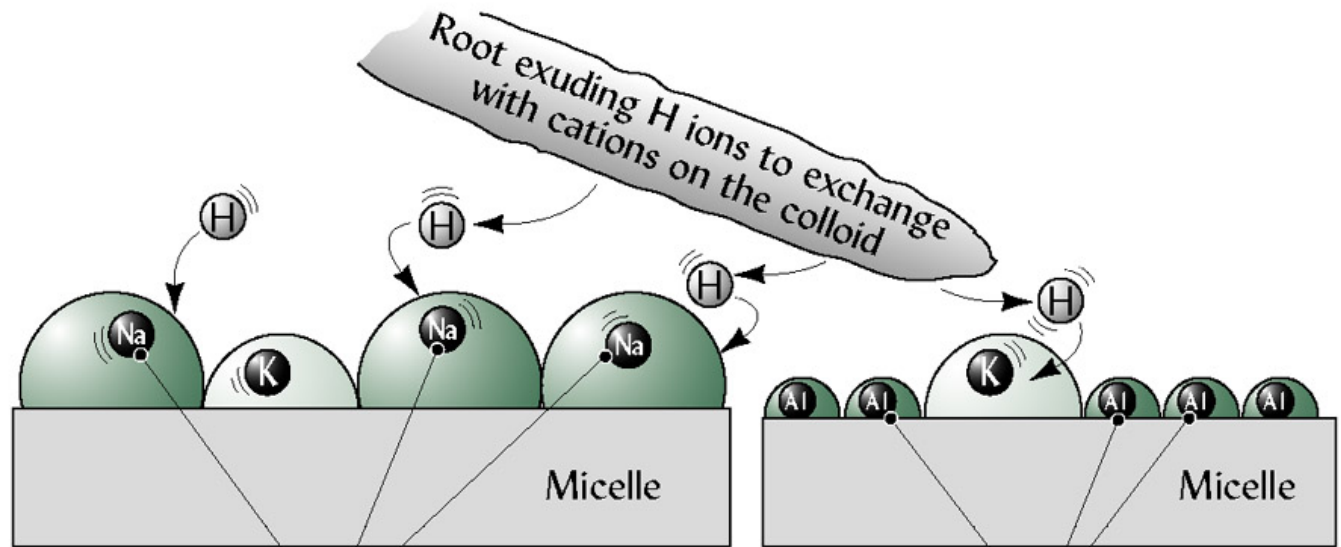
CEC only measures the capacity of a soil to hold exchangeable cations

Base Saturation is a measure of base cations located on the exchange sites.

Base Cations* (Ca, Mg, K and Na) or non-acid cations
vs.
Acid Cations (Al^{3+} and H^{+})

Base Saturation = the percentage of CEC sites occupied by bases

*Technically these non-acid base cations are not bases, but they do serve to reduce acidity and increase the pH in the soil solution – hence the term “base”



Root exuding H ions to exchange with cations on the colloid

Micelle

Micelle

Loosely held complementary ions with large oscillation zones

Tightly held complementary ions with small oscillation zones