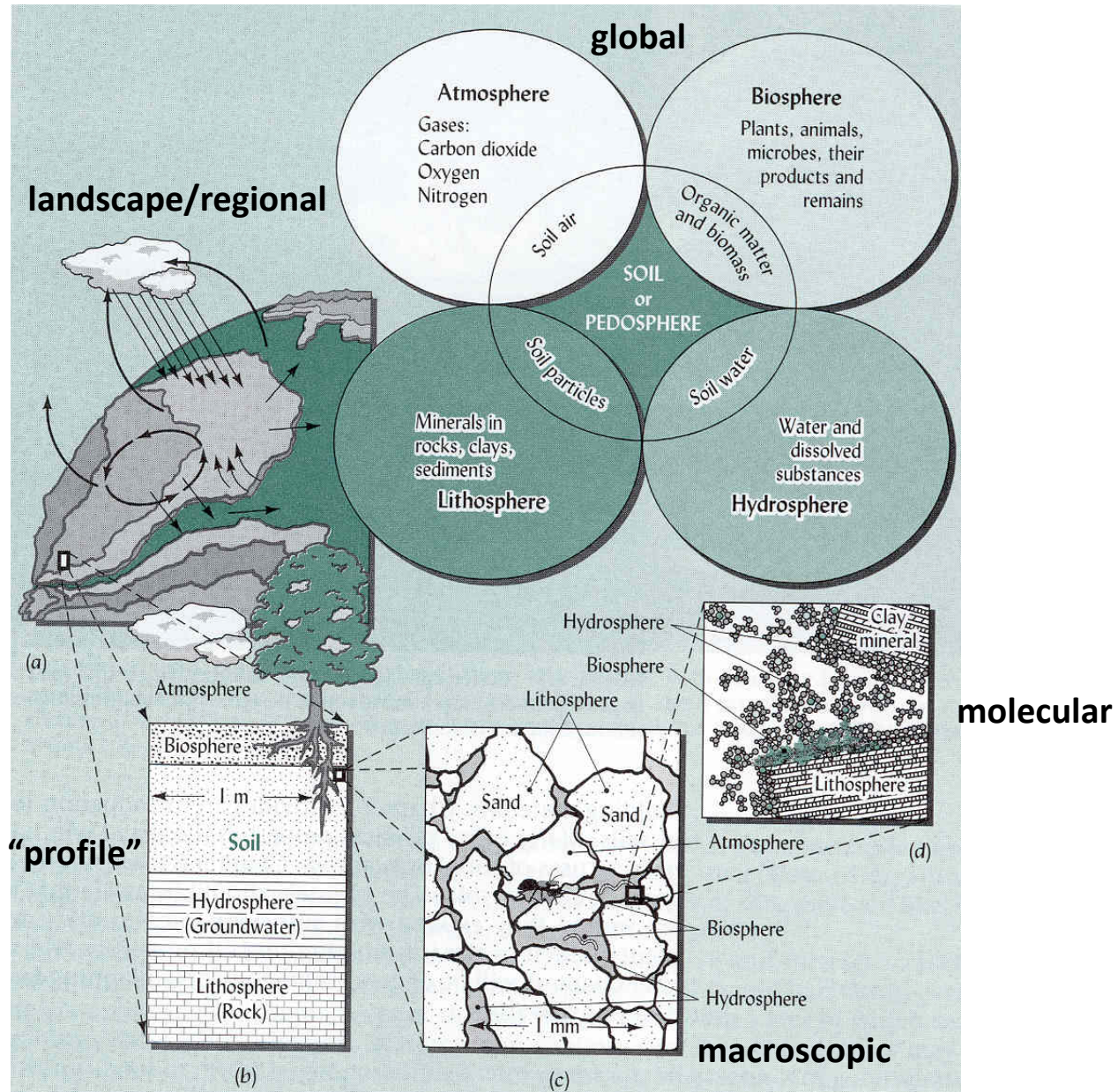


Soil Colloids

**Scales
to study
soils**

Interfaces



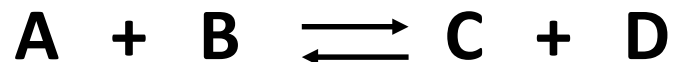
Chemical Principles:

First law of thermodynamics (conservation):

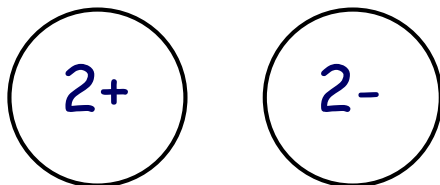
Energy (matter) is neither created nor destroyed, it changes from one form to another.

The total amount of energy and matter in the Universe remains constant, merely changing from one form to another.

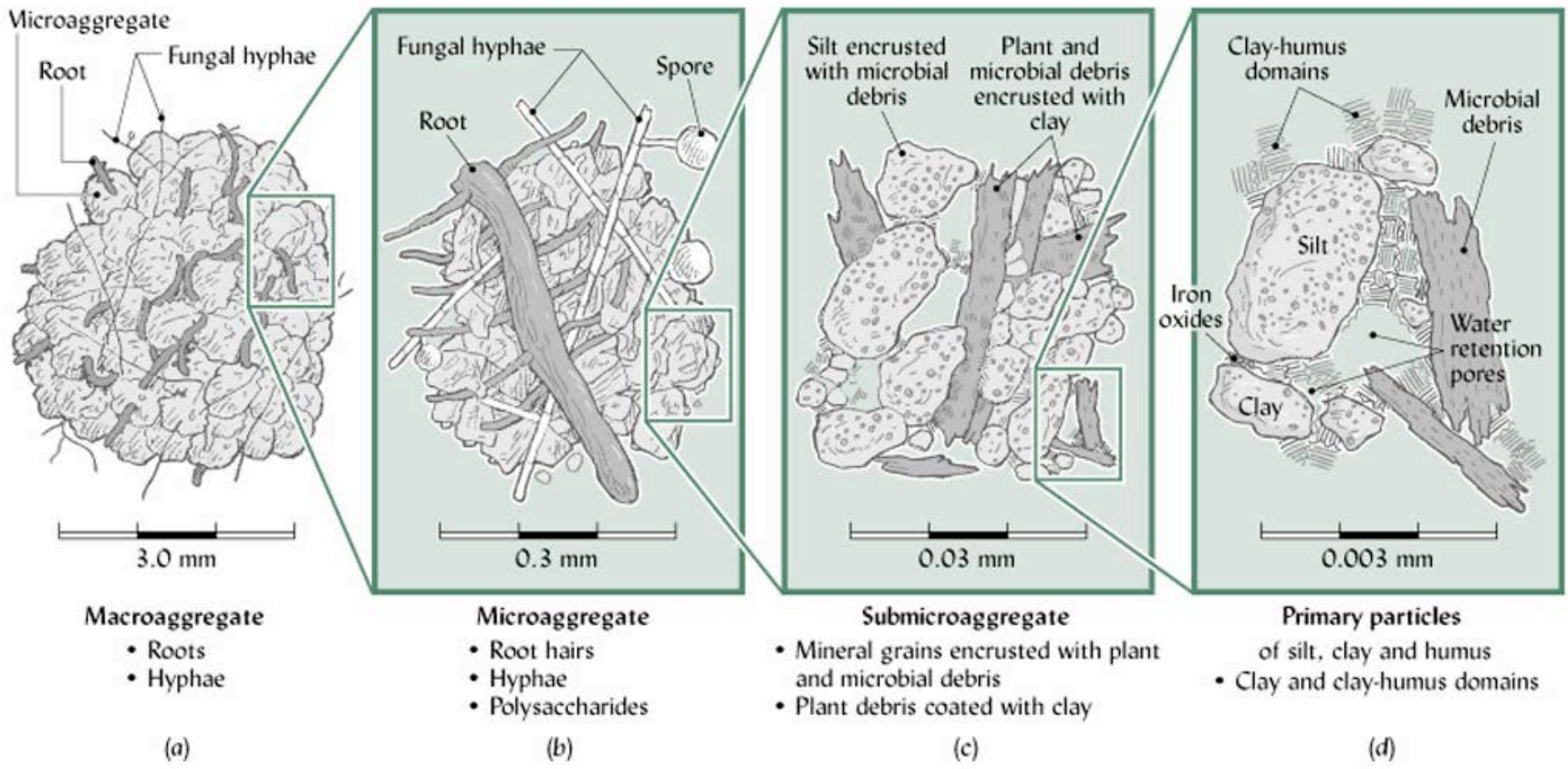
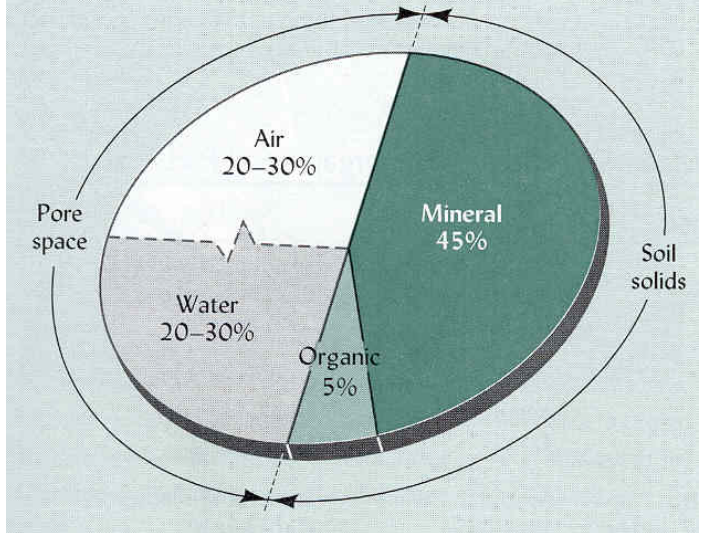
Mass Action



Charge Balance



Soil Colloids



Soil Colloids

increases

Atomic size (radii)

GROUP

1 2 13 14 15 16 17 18

1 H 1.0079

3 Li 6.941 4 Be 9.0122

11 Na 22.990 12 Mg 24.305

19 K 39.098 20 Ca 40.078

37 Rb 85.468 38 Sr 87.62 39 Y 88.906 40 Zr 91.224 41 Nb 92.906 42 Mo 95.94 43 Tc 98.906* 44 Ru 101.07 45 Rh 102.91 46 Pd 106.42 47 Ag 107.87 48 Cd 112.41 49 In 114.82 50 Sn 118.71 51 Sb 121.76 52 Te 127.60 53 I 126.90 54 Xe 131.29

55 Cs 132.91 56 Ba 137.33 57 La 138.91 72 Hf 178.49 73 Ta 180.95 74 W 183.84 75 Re 186.21 76 Os 190.23 77 Ir 192.22 78 Pt 195.08 79 Au 196.97 80 Hg 200.59 81 Tl 204.38 82 Pb 207.2 83 Bi 208.98 84 Po 209.98* 85 At 209.99* 86 Rn 222.02

87 Fr 223.02 88 Ra 226.03* 89 Ac 227.03 104 Rf (261) 105 Db (262) 106 Sg (266) 107 Bh (262) 108 Hs (269) 109 Mt (266) 110 (273) 111 (272) 112 (294)

26 Fe 55.845

13 Al 26.982 14 Si 28.086 15 P 30.974 16 S 32.066

5 B 10.811 6 C 12.011 7 N 14.007 8 O 15.999 9 F 18.998 10 Ne 20.180

31 Ga 69.723 32 Ge 72.61 33 As 74.922 34 Se 78.96 35 Br 79.904 36 Kr 83.80

increases

★Lanthanide series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.91	144.24	146.92*	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97

▲Actinide series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.04*	231.04*	238.03	237.05*	239.05*	241.06*	244.06*	249.08*	252.08*	252.08*	257.10*	258.10*	259.10*	262.11*

Note: Atomic masses shown here are the 1993 IUPAC values with a maximum of five significant figures (T. B. Coplen *et al.*, *Inorg. Chim. Acta* 1994, 217, 217). An asterisk indicates the mass of a commonly known radioisotope. Numbers in parentheses are the mass numbers of the corresponding longer-lived isotope.

Elemental Composition of Soils

TABLE 1.2 Mean elemental content (in mg kg^{-1}) of soil and crustal rocks, and the soil enrichment factor (EF)

Element	Soil ^{a,b}	Crust ^b	EF ^c	Element	Soil ^{a,b}	Crust ^b	EF ^c
Li	24	20	1.2	Zn	60	75	0.80
Be	0.92	2.6	0.35	Ga	17	18	0.94
B	33	10	3.3	Ge	1.2	1.8	0.67
C	25,000	480	52	As	7.2	1.5	4.8
N	2,000	25	80	Se	0.39	0.05	7.8
O	490,000	474,000	1.0	Br	0.85	0.37	2.3
F	950	430	2.2	Rb	67	90	0.74
Na	12,000	23,000	0.52	Sr	240	370	0.65
Mg	9,000	23,000	0.39	Y	25	30	0.83
Al	72,000	82,000	0.88	Zr	230	190	1.2
Si	310,000	277,000	1.1	Nb	11	20	0.55
P	430	1,000	0.43	Mo	0.97	1.5	0.65
S	1,600	260	6.2	Ag	0.05	0.07	0.71
Cl	100	130	0.77	Cd	0.35	0.11	3.2
K	15,000	21,000	0.71	Sn	1.3	2.2	0.59
Ca	24,000	41,000	0.59	Sb	0.66	0.20	3.3
Sc	8.9	16	0.56	I	1.2	0.14	8.6
Ti	2,900	5,600	0.52	Cs	4.0	3.0	1.3
V	80	160	0.50	Ba	580	500	1.2
Cr	54	100	0.54	La	37	32	1.2
Mn	550	950	0.58	Hg	0.09	0.05	1.8
Fe	26,000	41,000	0.63	Pb	19	14	1.4
Co	9.1	20	0.46	Nd	46	38	1.2
Ni	19	80	0.24	Th	9.4	12	0.78
Cu	25	50	0.50	U	2.7	2.4	1.1

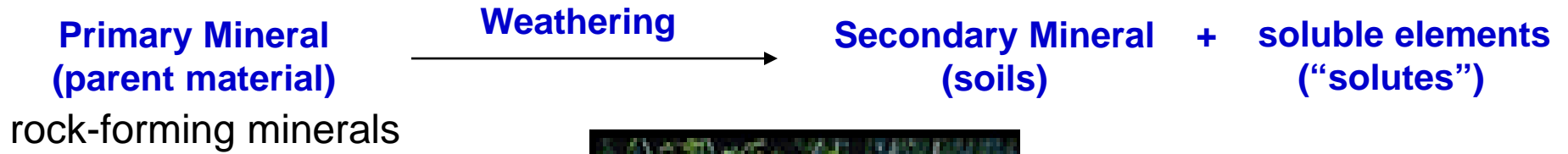
Enrichment or depletion

EF 0.5 – 2.0 is not significant (large std. dev.)

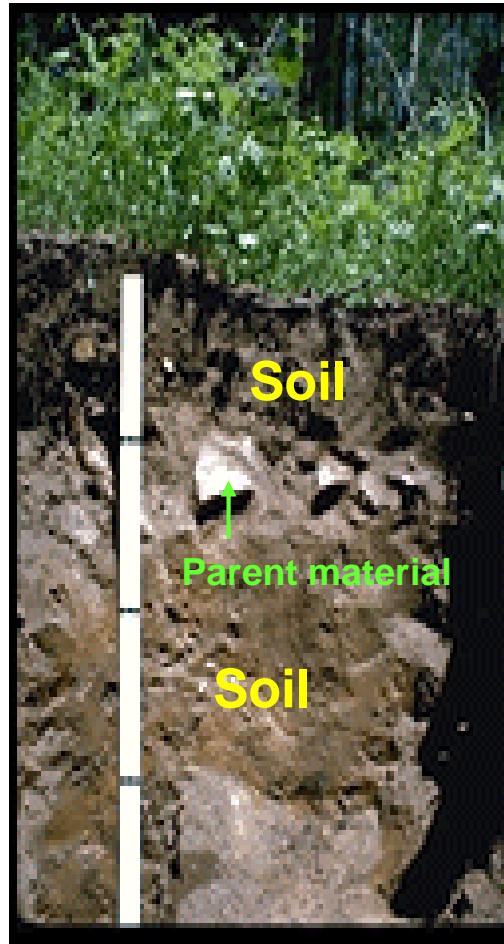
O, Si, and Al: the most abundant

Trace element: mass concentration in the solid phase is $\leq 100 \text{ mg kg}^{-1}$

Conversion of primary minerals to secondary minerals with the release of plant nutrient elements in soluble forms



- formed at high temperatures and pressures
- therefore, unstable under current atmospheric conditions



- form under current atmospheric conditions
- may be unstable if conditions change from those of their formation

typically clay sized: $< 2 \mu\text{m}$

Types of Colloids found in Soils:

Crystalline silicate clays

Phyllosilicates → tetrahedral and octahedral crystal sheets

Non-crystalline silicate clays (Andisols)

Dominately amorphous clays (allophane and imogolite)

Iron and aluminum oxides (Oxisols & ...)

Gibbsite (Al-oxide) and goethite (Fe-oxide)

Organic (humus) colloids (Histosols &...)

Colloidal sized soil organic matter

Permanent charge minerals

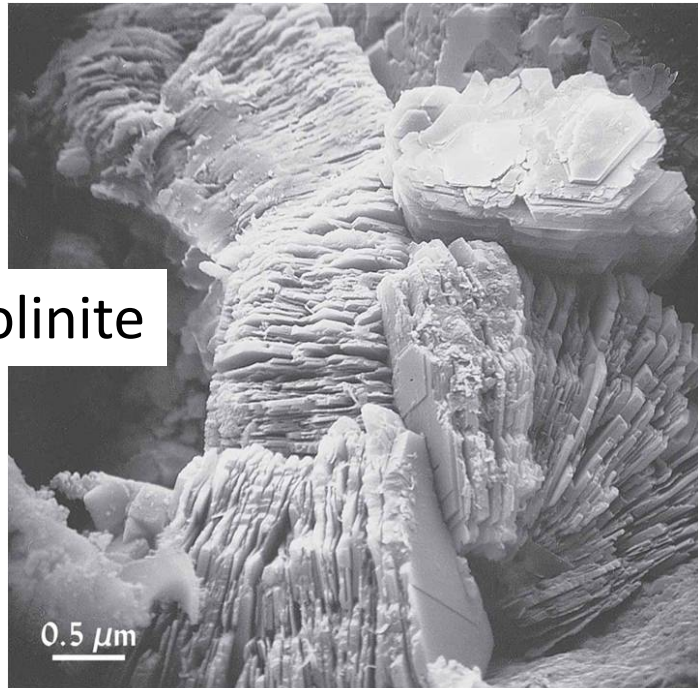
layer silicate clays with structural negative charge

Variable (pH-dependent) charge minerals

surface charge that is pH dependent

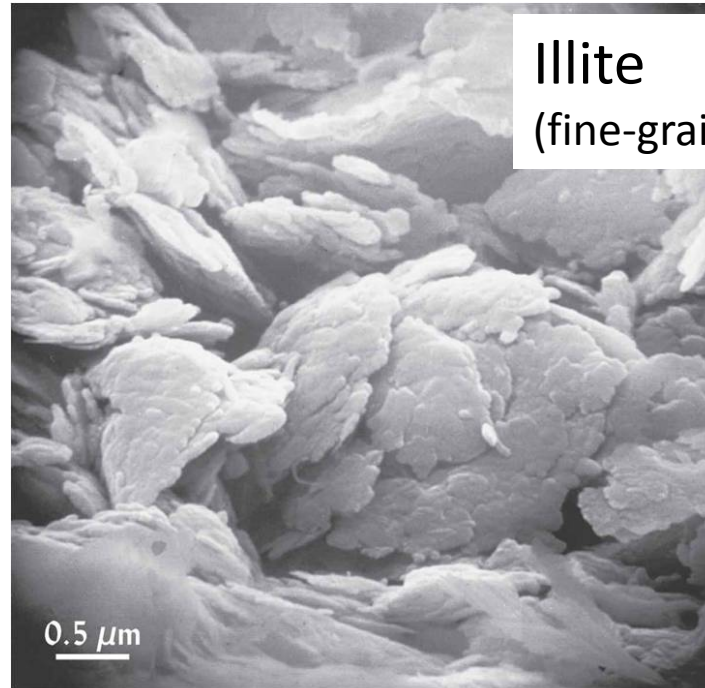
(allophanes (amorphous, high charge); Fe/Al oxide (more crystalline, low charge); organic molecules

kaolinite



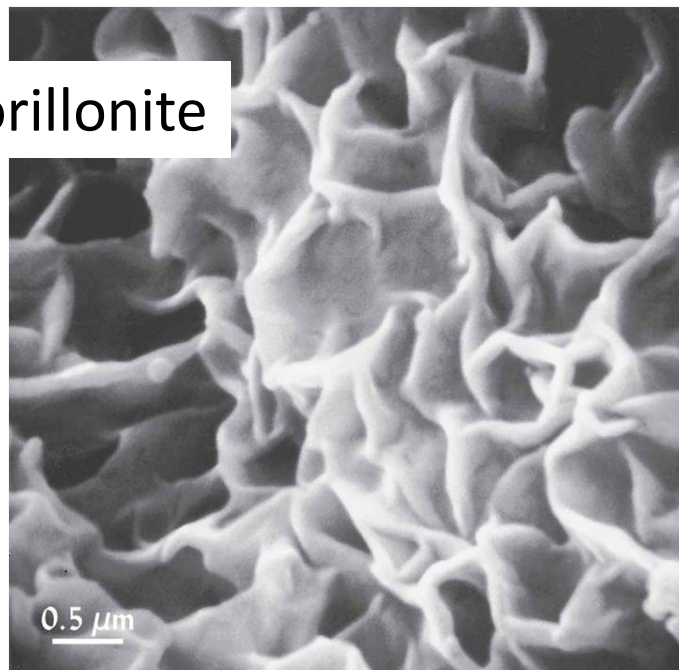
(a)

Illite
(fine-grained mica)

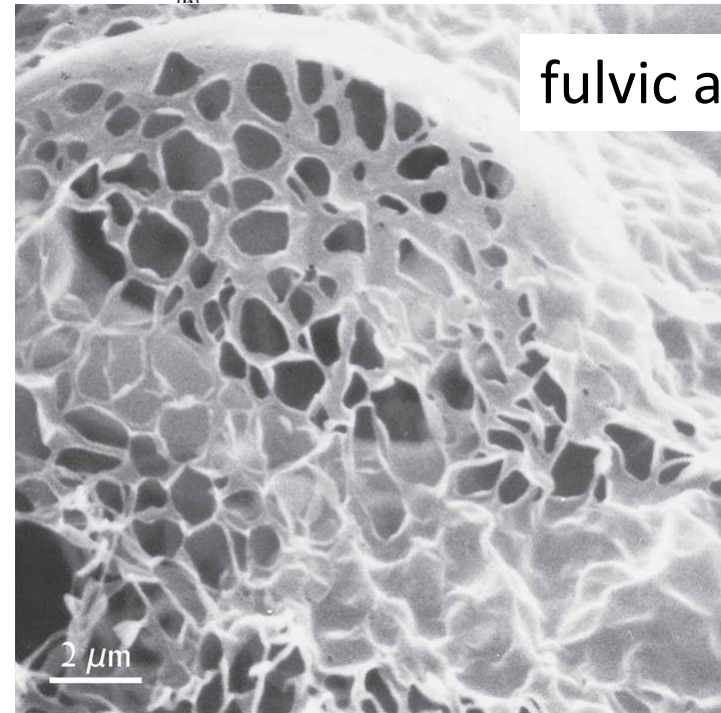


(b)

montmorillonite

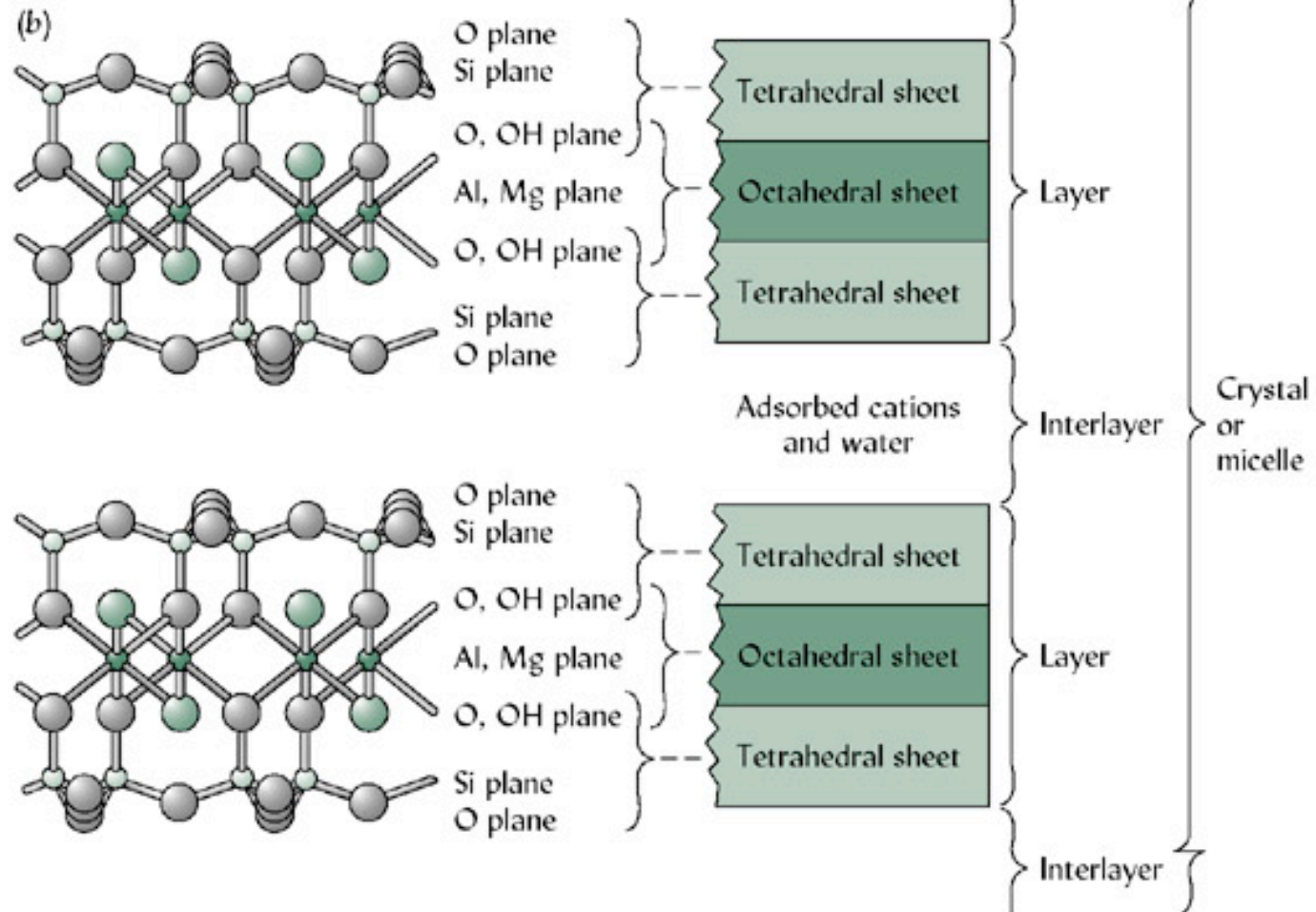
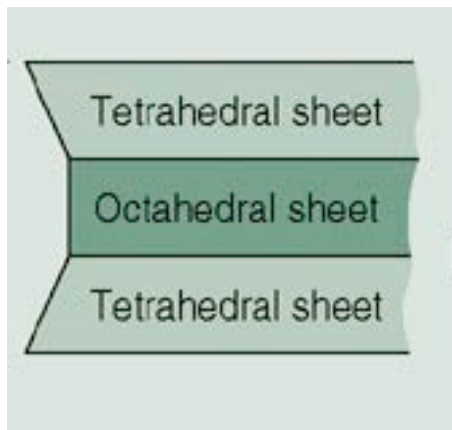


fulvic acid



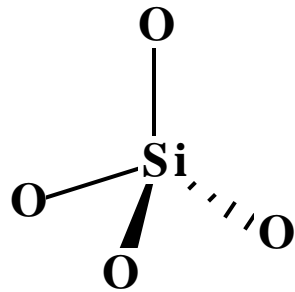
Aim to understand the structures of soil minerals (typically represented like this):

2:1 mineral

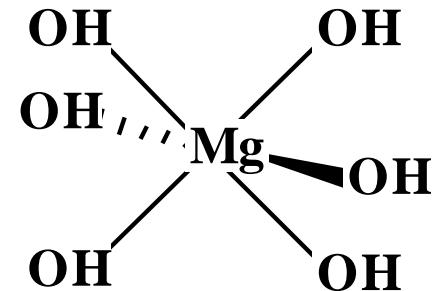
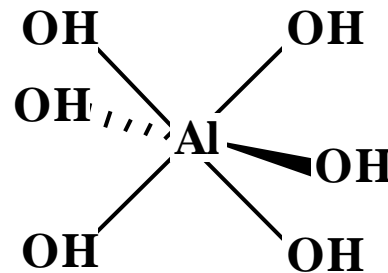


Building Blocks of Soil Minerals – molecular scale

Si and Al tetrahedra - (MO_4)



Al, Fe, Mg octahedra - (MO_6)



What determines the expected ion coordination?

TABLE 8.2 Ionic Radii of Elements Found in Silicate Clays and an Indication of Which Are Found in the Tetrahedral and Octahedral Sheets **Size (relative size)**

Note that Al, Fe, ~~O~~, and ~~OH~~ can fit in either.

Ion	Radius, nm ^a	Minimum Radius Ratio	Found in
Si ⁴⁺	0.042	CN = 4	Tetrahedral sheet
Al ³⁺	0.051		
Fe ³⁺	0.064	0.225	Octahedral sheet
Mg ²⁺	0.066		
Zn ²⁺	0.074		
Fe ²⁺	0.070	0.414	Exchange sites
Na ⁺	0.097		
Ca ²⁺	0.099	CN = 6	Both sheets
K ⁺	0.133		
O ²⁻	0.140	0.414	Both sheets
OH ⁻	0.155		

^a1 nm = 10⁻⁹m.

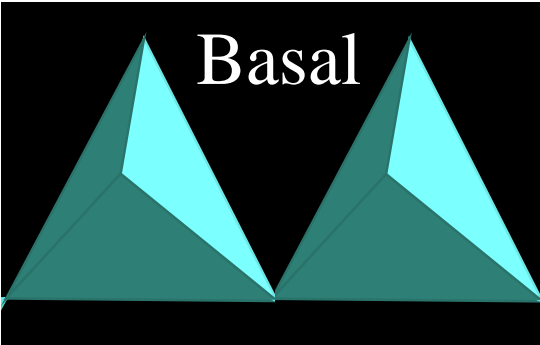
Linking Tetrahedra and Octahedra to Form Sheets

Main class of soil minerals (phyllosilicates) are formed by:

linking Si (Al) tetrahedra \longrightarrow form tetrahedral sheets

linking Al (Mg, Fe) octahedra \longrightarrow form octahedral sheets

Linking Tetrahedra:



Linking Octahedra:

Corner

Edge

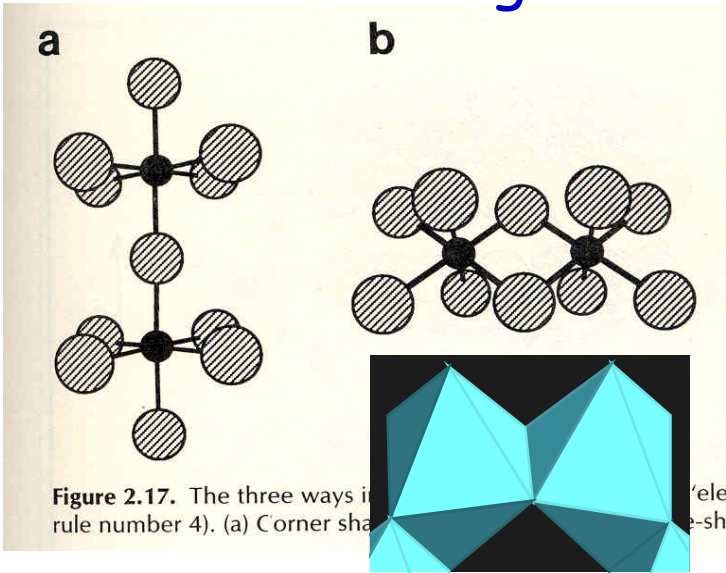


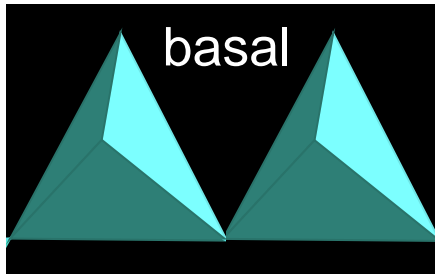
Figure 2.17. The three ways in which octahedra can be linked (rule number 4). (a) Corner sharing (1 point sharing) (b) Edge sharing (2 point sharing)

1 point sharing

2 point sharing

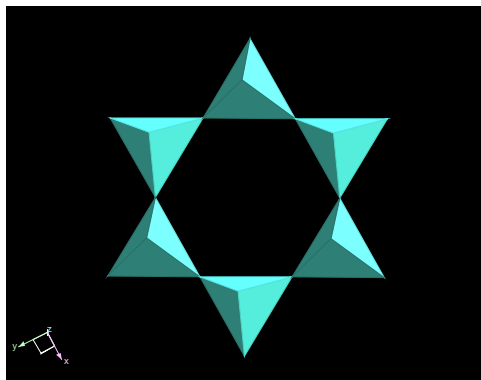
Tetrahedral Sheet

Formed by a sharing of 3 O to form hexagonal rings



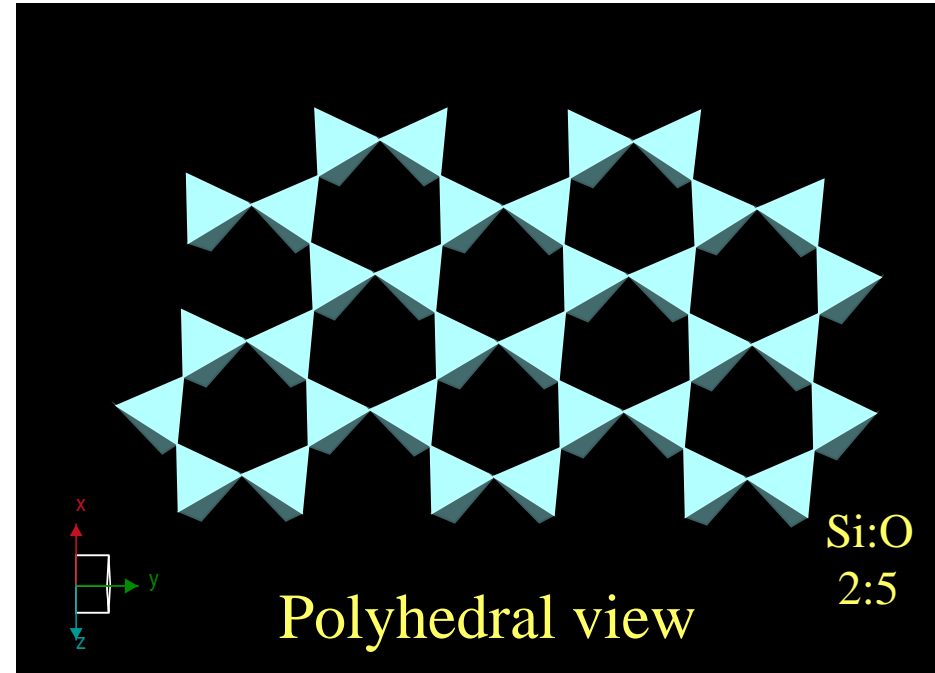
linking

A blue arrow points from the "basal" diagram down to the "Hexagonal ring" diagram. The word "linking" is written in green text above the arrow.



linking

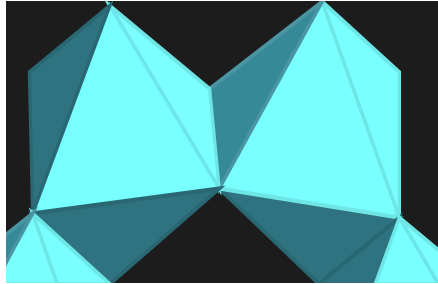
A blue arrow points from the "Hexagonal ring" diagram to the "Polyhedral view" diagram. The word "linking" is written in green text above the arrow.



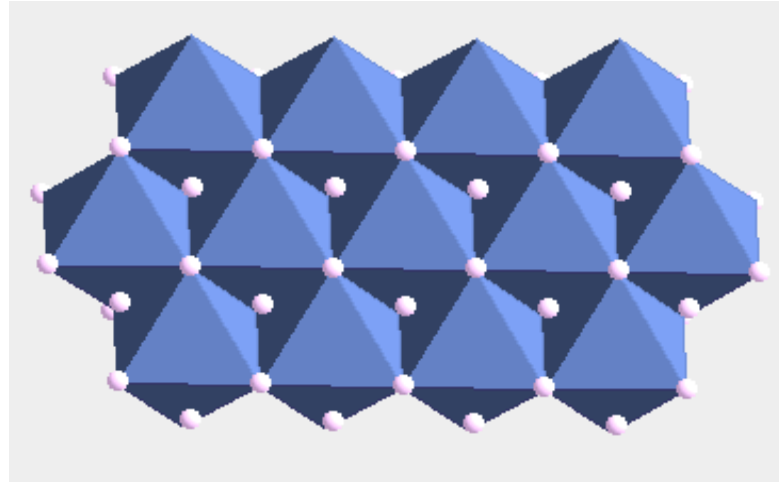
Si tetrahedra only share corners

Octahedral Sheets – polyhedral view

Octahedral



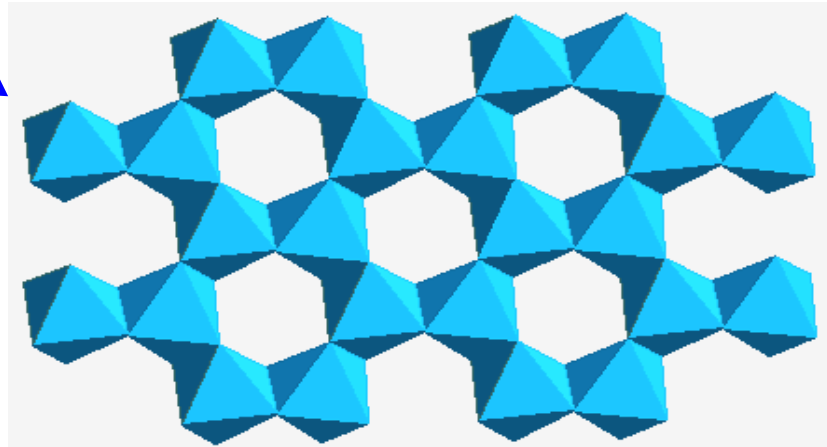
linking



Trioctahedral
(divalent cation)

3 of 3 sites
occupied by M^{2+}

linking



Dioctahedral
(trivalent cation)

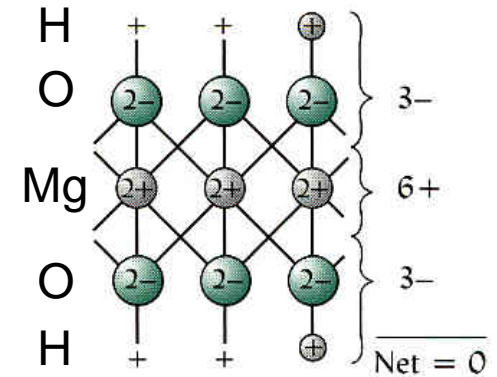
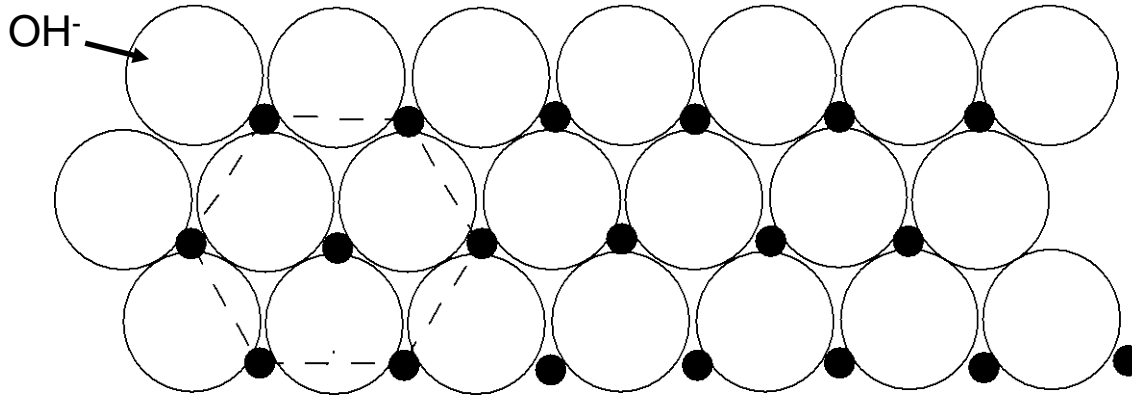
2 of 3 sites
occupied by M^{3+}

Octahedral Cation Occupancy

position of divalent and trivalent cations

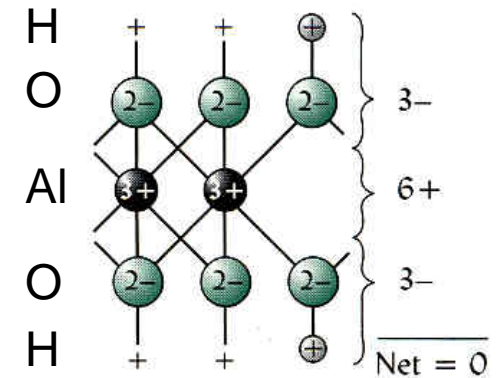
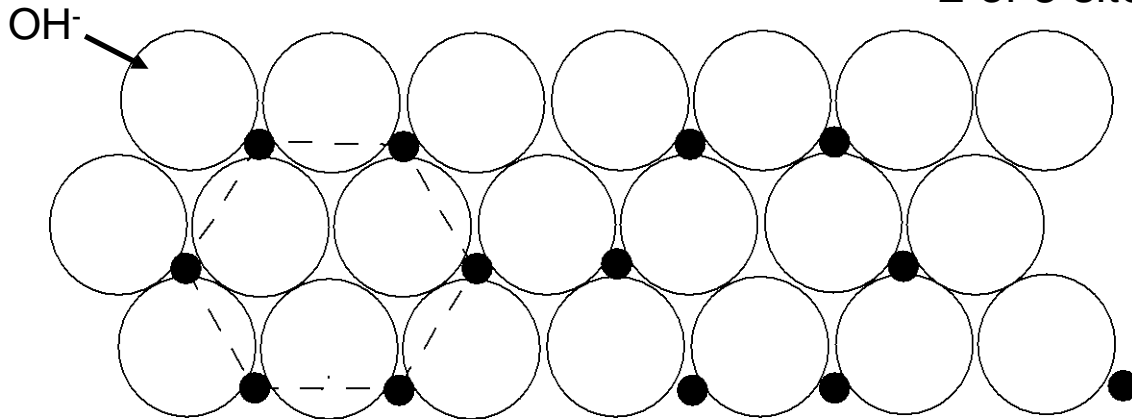
● = Mg

Trioctahedral → 3 of 3 sites occupied by M^{2+}



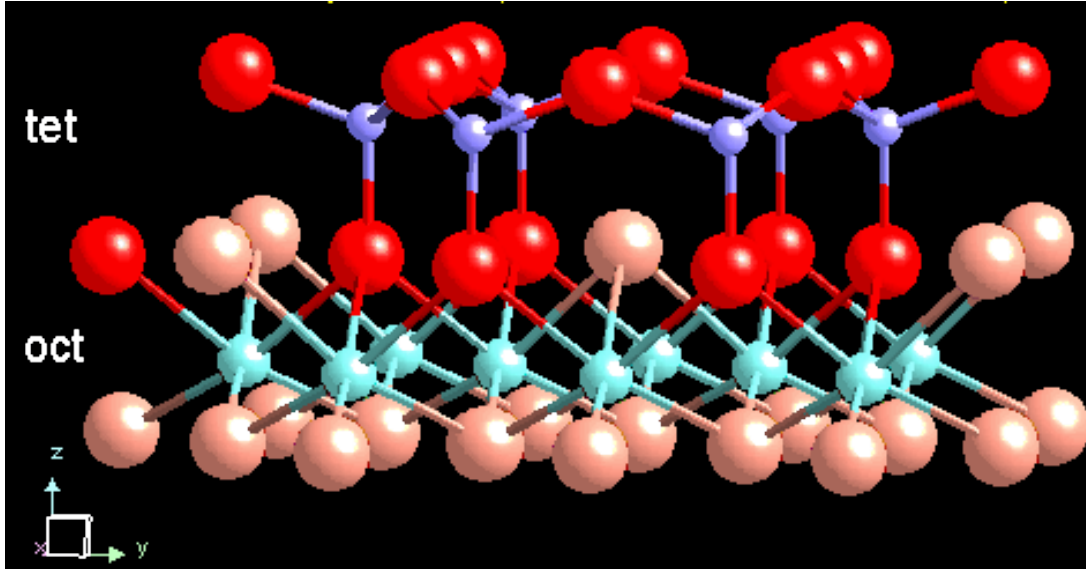
● = Al

Dioctahedral → 2 of 3 sites occupied by M^{3+}



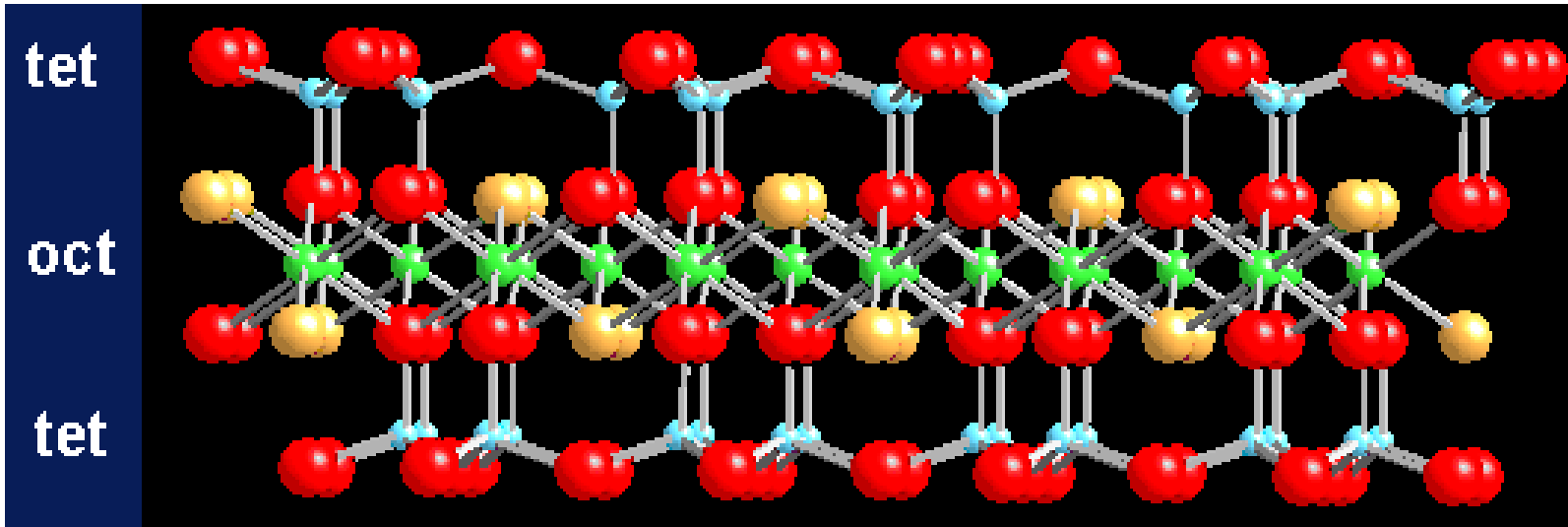
Tetrahedra-Octahedra linkage

Sharing apical oxygens in tetrahedral sheet with hydroxyls of octahedral sheet



1:1 mineral

2:1 mineral



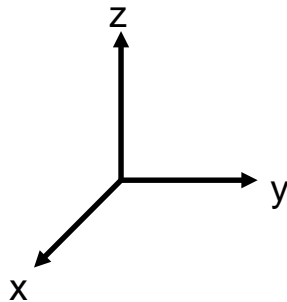
Secondary Minerals: Layer Silicates or Phyllosilicates

composed of Si, Al tetrahedra; Mg, Al, Fe octahedra

“aluminosilicates”

Classification based on:

- **number** of tetrahedra and octahedra in a layer
- **octahedral site occupancy** (octahedral composition: who and how many cations in octahedral positions)
- **charge** for each layer (**layer charge**)

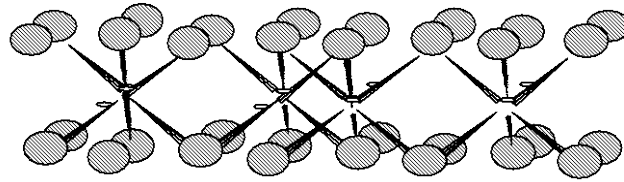
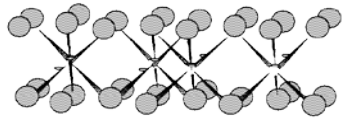


platy morphology

x-y dimensions: $\sim 10^{-6}$ m

z dimensions: $\sim 10^{-9}$ m

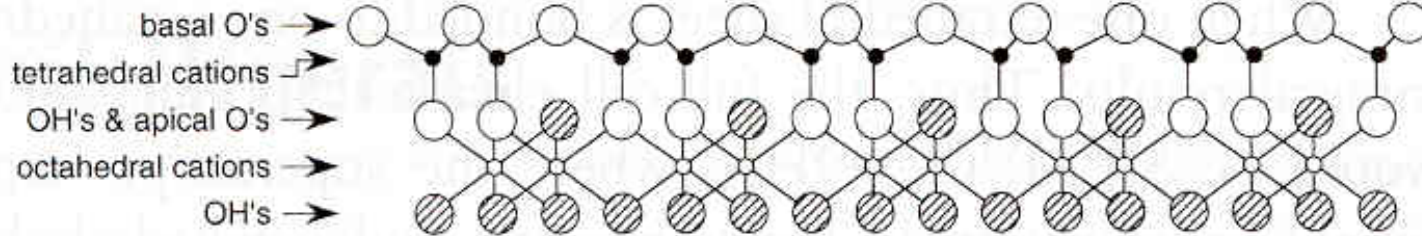
Secondary minerals: number of tetrahedra and octahedra in a layer



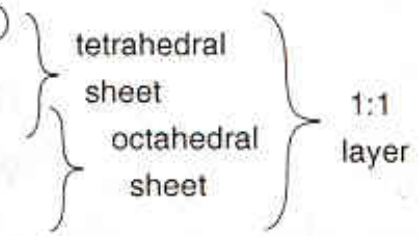
simplest – single octahedra

1:1 mineral (1 tetrahedra + 1 octahedra)

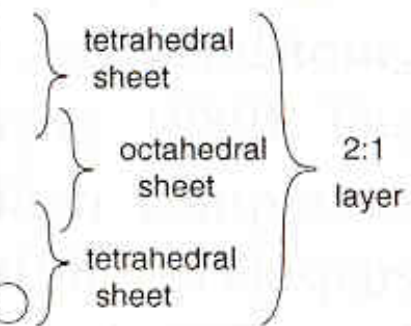
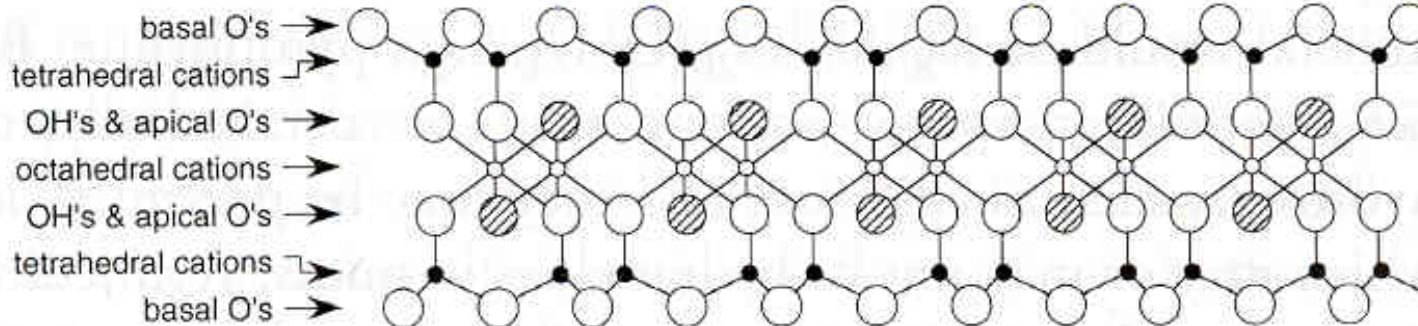
PLANES OF IONS



SHEETS, LAYERS

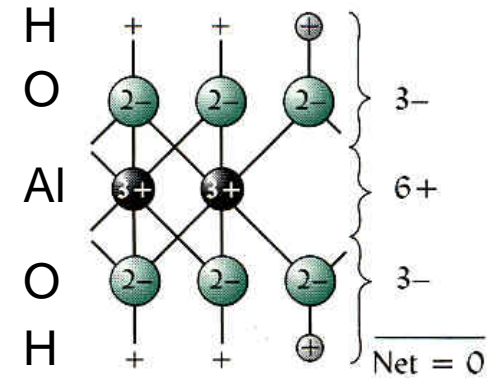
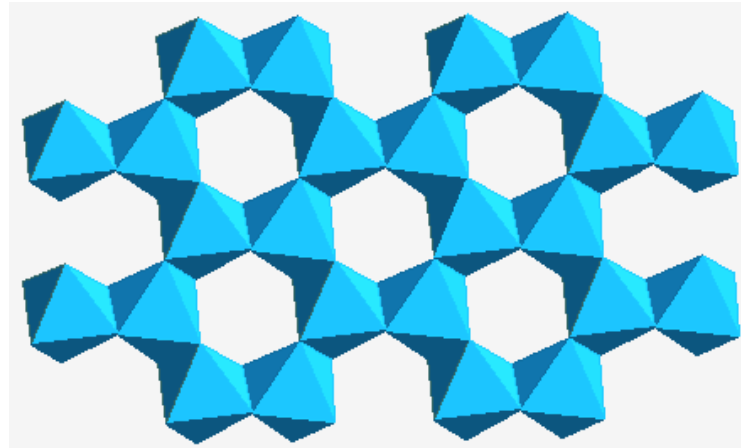


2:1 mineral (2 tetrahedra + 1 octahedra)

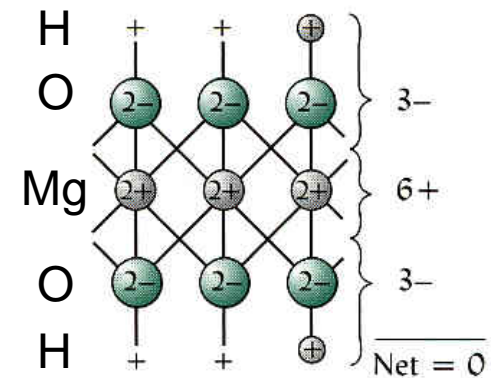
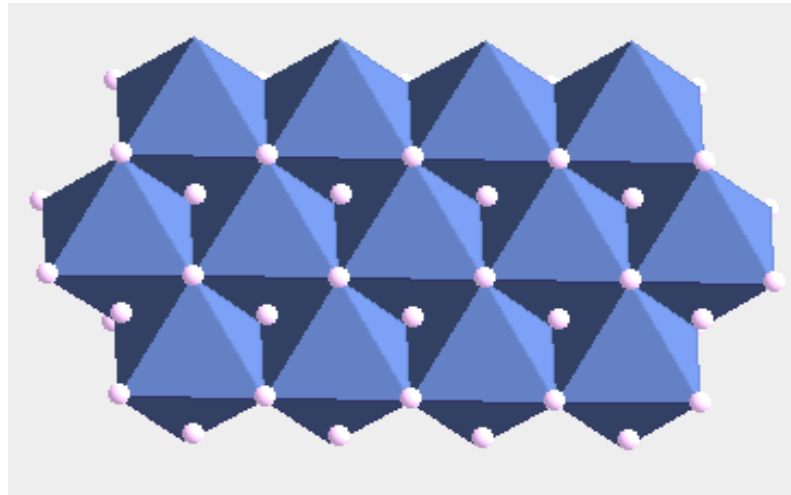


Secondary minerals: octahedral site occupancy
 position of divalent and trivalent cations

Di-octahedral → 2 of 3 sites occupied by M^{3+}



Tri-octahedral → 3 of 3 sites occupied by M^{2+}



Charge:

“Soils are negatively charged”

“Minerals exert a charge”

How?

1. **Isomorphic substitution** (results in pH independent charge)

Al^{3+} for Si^{4+} substitution in tetrahedral sheet

$\text{Mg}^{2+}/\text{Fe}^{2+}$ substitution for $\text{Al}^{3+}/\text{Fe}^{3+}$ in octahedral sheet

2. **Terminal broken bonds** (pH dependent charge)

Dissociation of pH-dependent functional groups: surface hydroxyl (OH) groups in minerals and organic matter

Why is charge important?

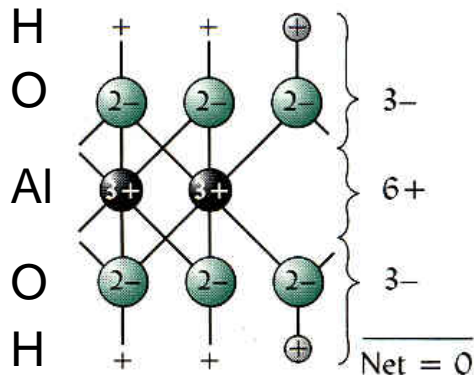
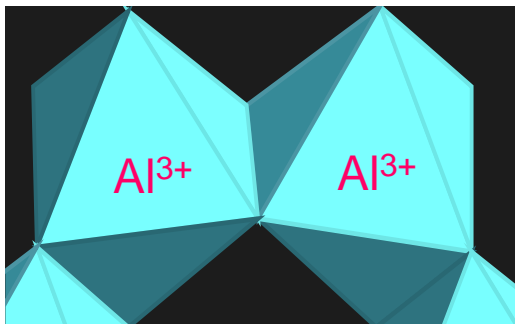
Reactivity towards everything

1. Isomorphous substitution: develops a charge within a mineral layer

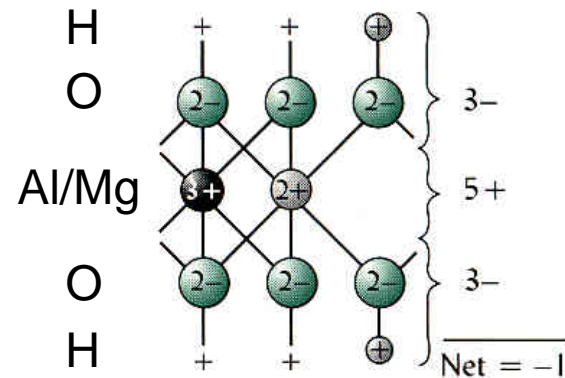
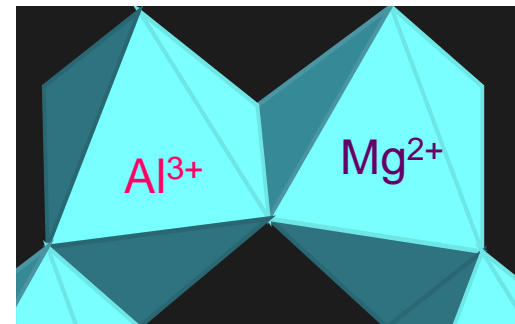
Permanent or Structural Charge: it is pH independent

replacement of one ion with another having a different charge but with no change in the mineral structure

Dioctahedral

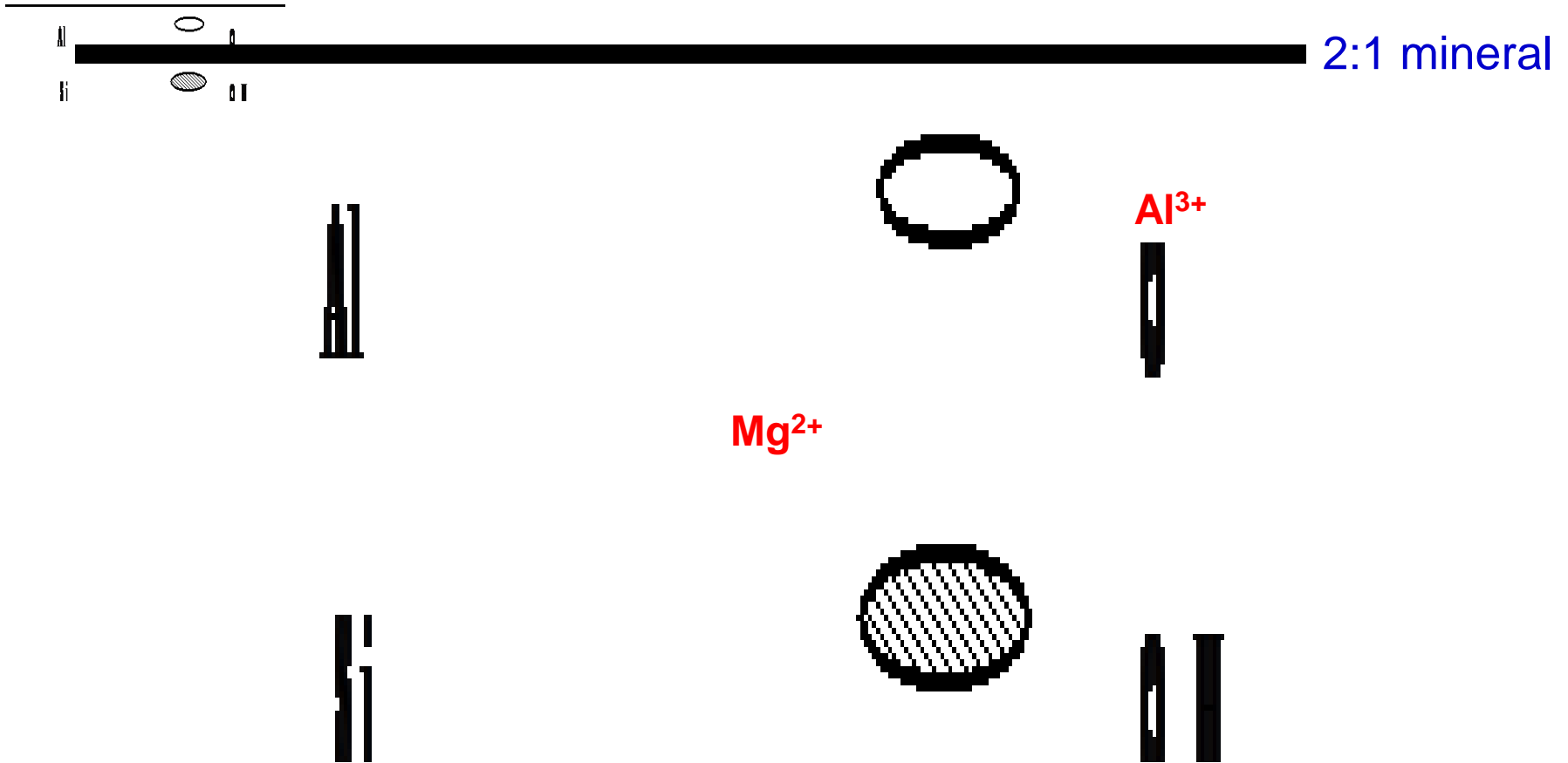


Dioctahedral with substitution



Secondary minerals: charge within a layer

Permanent or Structural Charge: it is pH independent

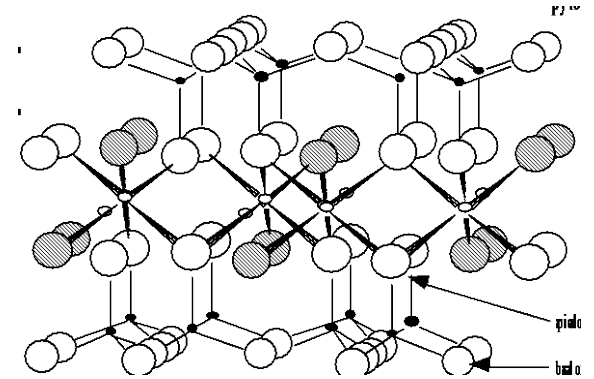
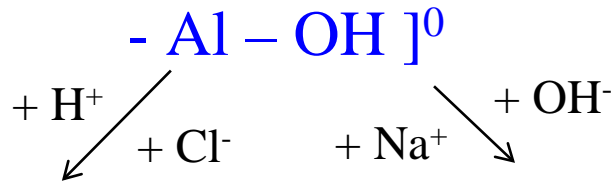


Charge sites located within the tetrahedral (Al^{3+} for Si^{4+}) or/and octahedral (Mg^{2+} for Al^{3+}) sheet

2. Terminal broken bonds: pH dependent (variable) charge

addition or release of protons from the surface results in different charges

Minerals



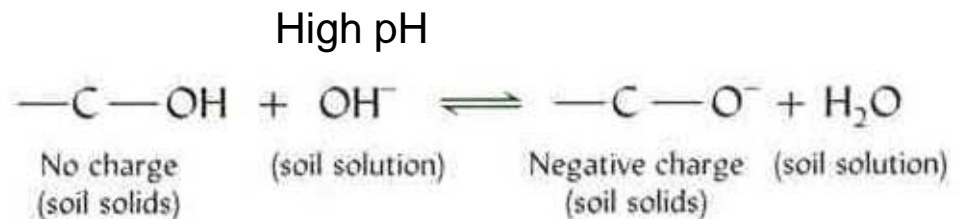
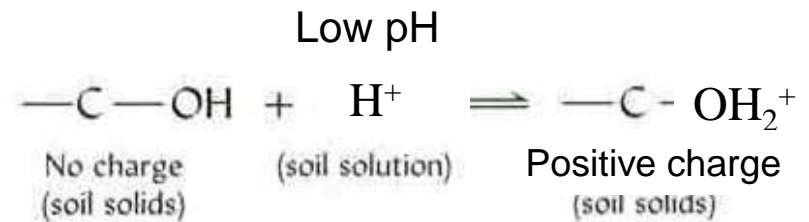
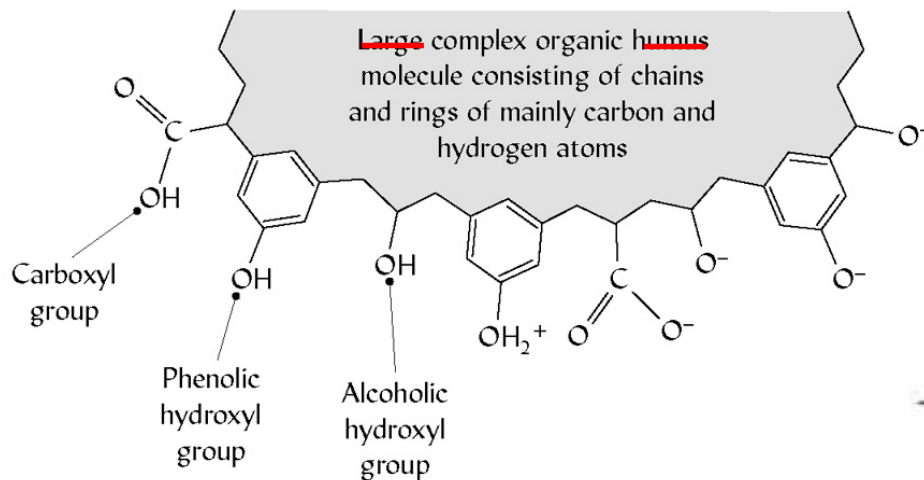
- Al - OH₂⁺ ... Cl⁻
Anion Exchange Sites

Low pH (protonation)

- Al - O⁻ ... Na⁺
Cation Exchange Sites

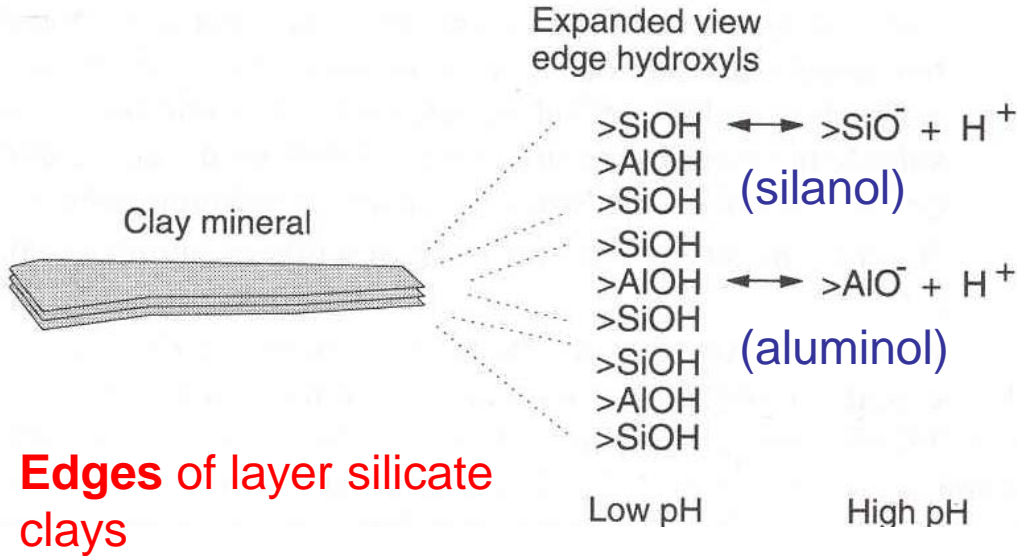
High pH

Soil Organic Matter

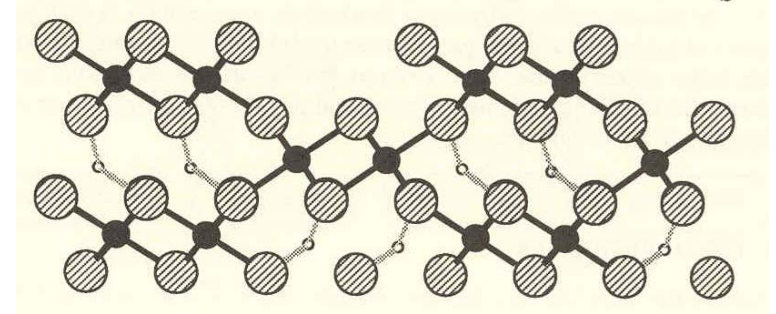


2. Terminal broken bonds: pH dependent (variable) charge

Where do they develop?



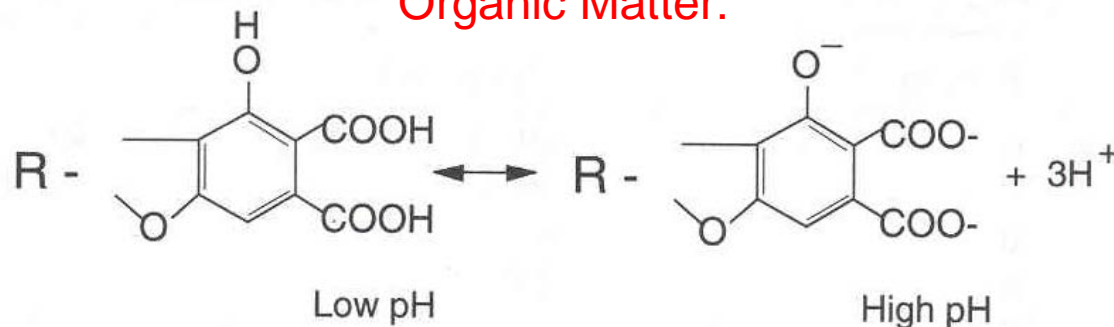
goethite - α -FeOOH



all faces of (hydrous) oxides

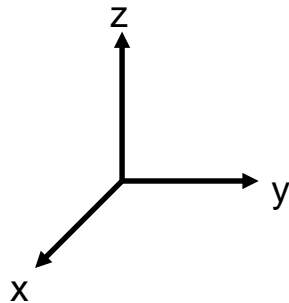
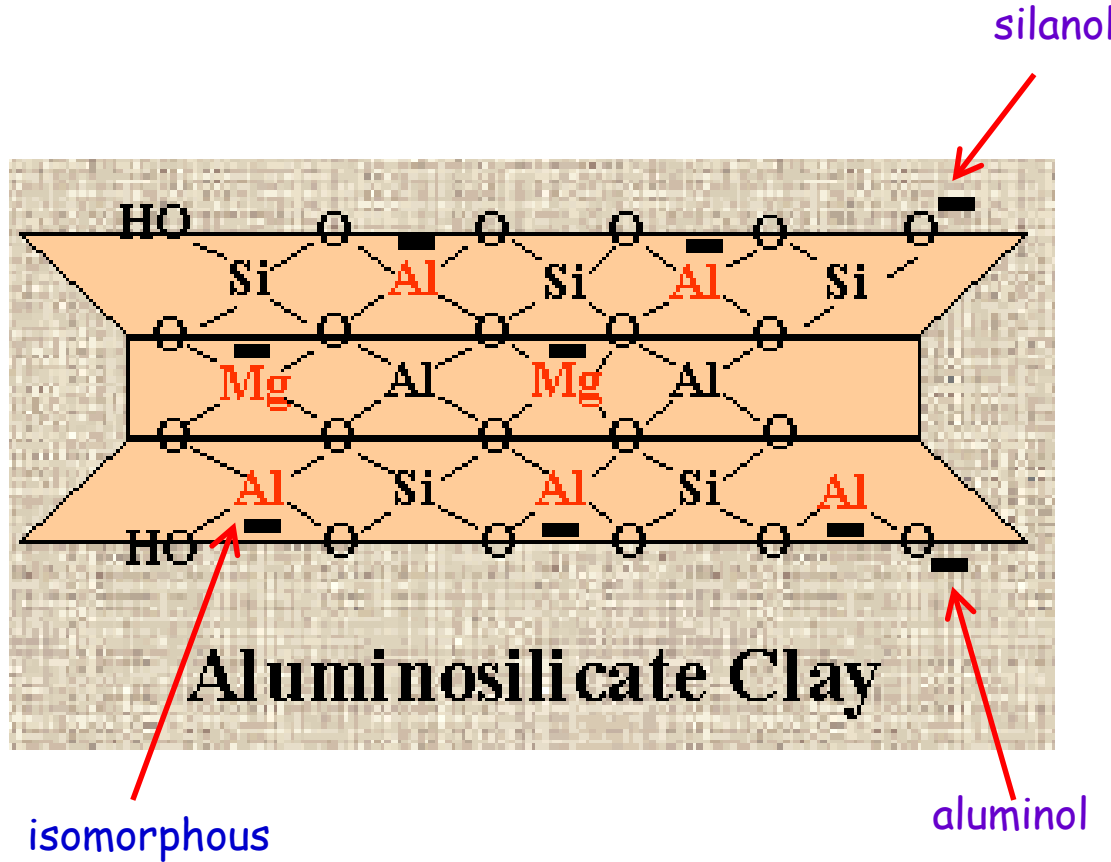
- Surface hydroxyl (OH) groups of Al/Fe oxides (crystalline minerals)
- Amorphous (noncrystalline) minerals (allophane)

Organic Matter:



Secondary layer aluminosilicate minerals:

Charge: permanent (structural) and pH-dependent



platy morphology

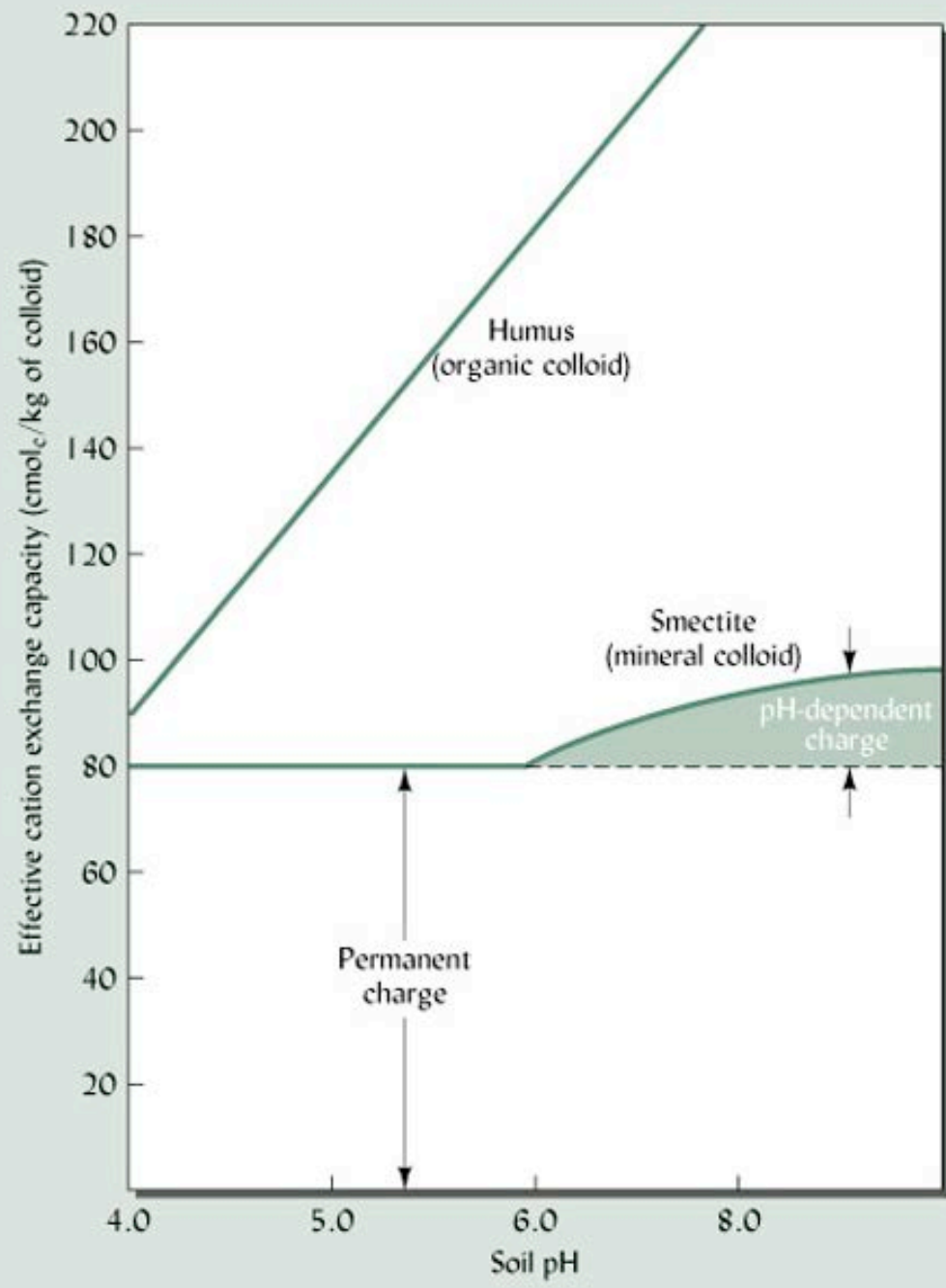
x-y dimensions: $\sim 10^{-6}$ m

z dimensions: $\sim 10^{-9}$ m

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

Colloid type	Negative charge			Positive charge, cmol _c /kg
	Total at pH 7, cmol _c /kg	Constant, %	pH dependent, %	
Organic	200	10	90	0
Smectite	100	95	5	0
Vermiculite	150	95	5	0
Fine-grained micas (illite)	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

Cations (K⁺, Na⁺, Ca²⁺, Mg²⁺) and anions sorbed between sheets and on the edges balance the charge





Smectite
(mont)
2:1

0.3g

Keolinite
1:1

0.3g

gibbsite
(Al ox.)

0.3g

Ferric
(Fe oxide)

0.3g

Org matter
(peat)

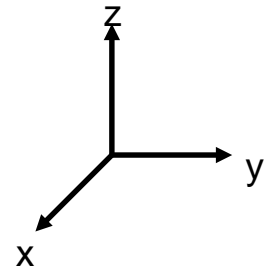
Layer Silicates: Mineral Groups

Classification based on:

Number of tetrahedra and octahedra

Octahedral site occupancy (tri- and dioctahedral)

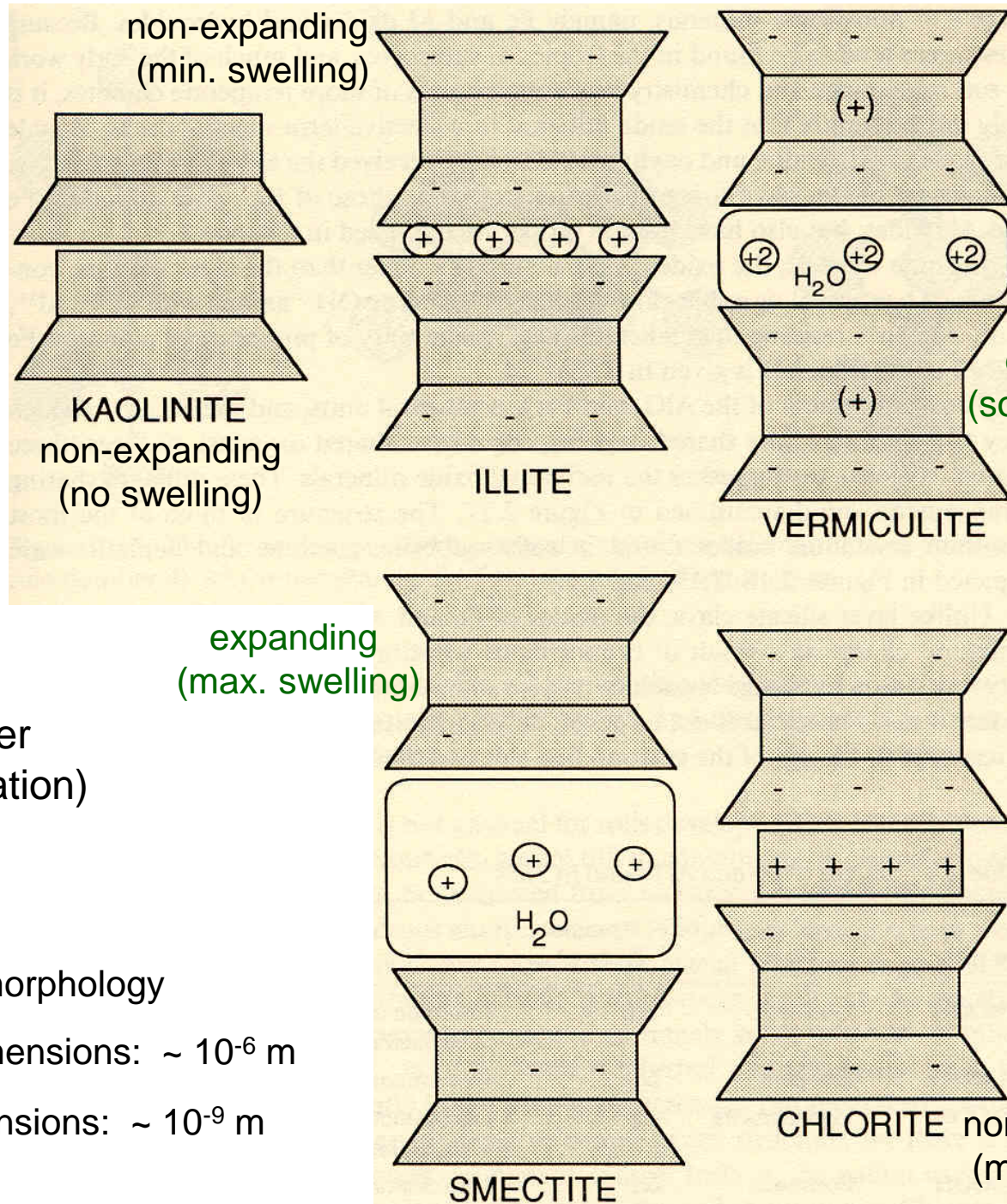
Charge for each layer (magnitude and location)



platy morphology

x-y dimensions: $\sim 10^{-6}$ m

z dimensions: $\sim 10^{-9}$ m

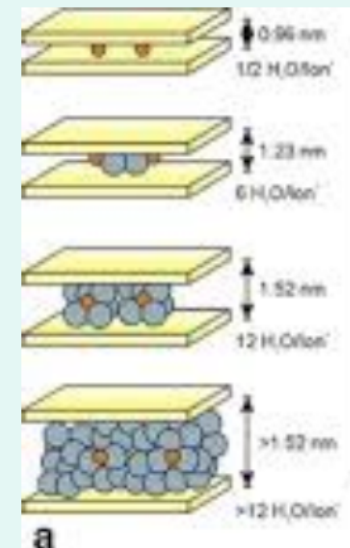




Clay swelling in water depends on:

- Magnitude of layer charge (vermiculite vs. smectite)
- Location of charge in 2:1 layer (tetrahedral vs. octahedral)
- Exchange cation charge (and hydration)

Na⁺ clays freely expand, Ca²⁺ and Mg²⁺ clays do not



Chicago – suburb built on drained wetland



example: engineering medium

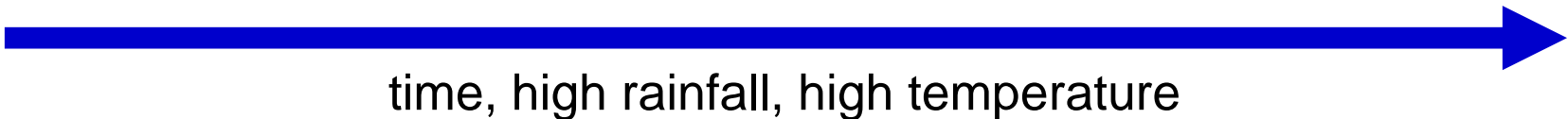
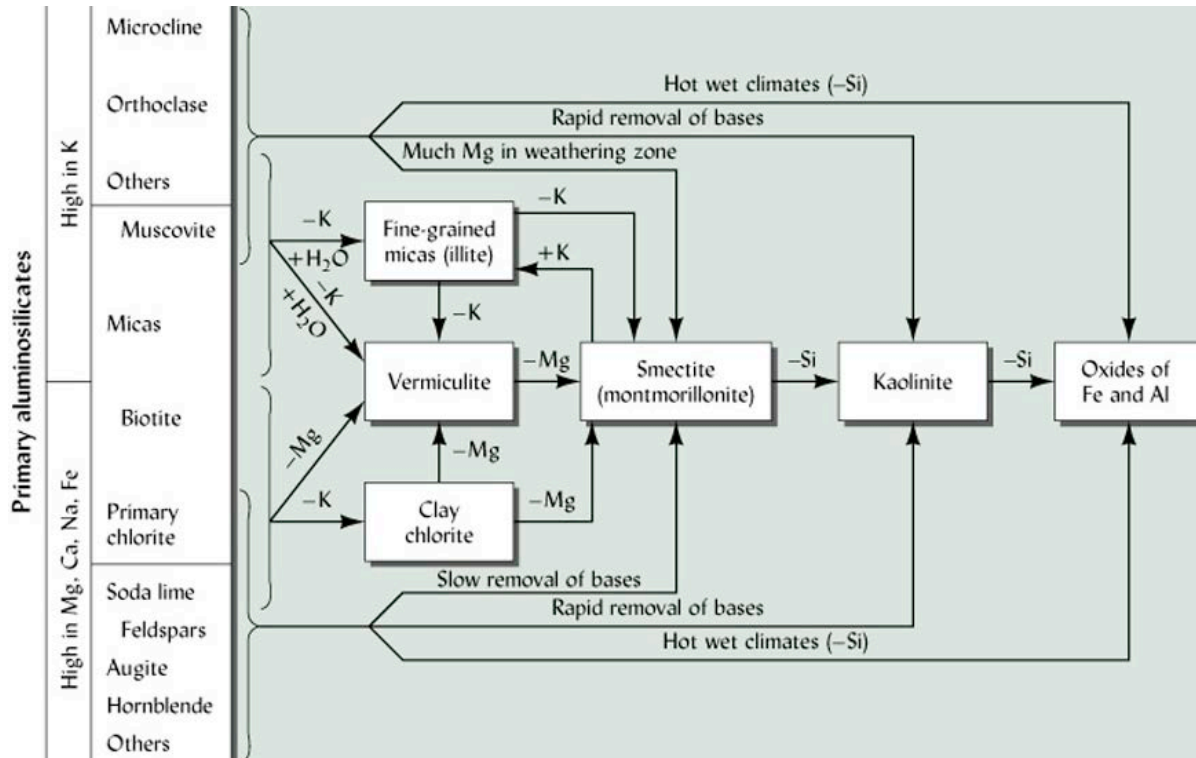
organic matter decomposition, “wrong” clays

shoring up the house: > \$30,000

Weathering

Mineralogical transformations - a slow transition from primary (rock-forming) to secondary (soil-formed) minerals

Chemical composition - a long-term result of losses in base cations, silica



Ideal Weathering Series

Soil Orders

Rock



Entisol



Inceptisol



Mollisol



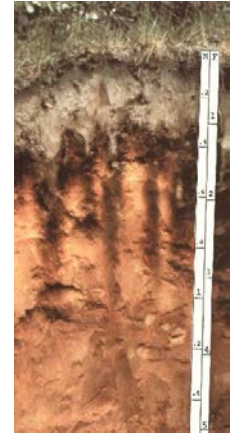
Alfisol



Vertisol
(mineralogy, cracks)



Spodosols
(leached horizon)



Ultisol



Oxisol



Oxides of Al and Fe dominate

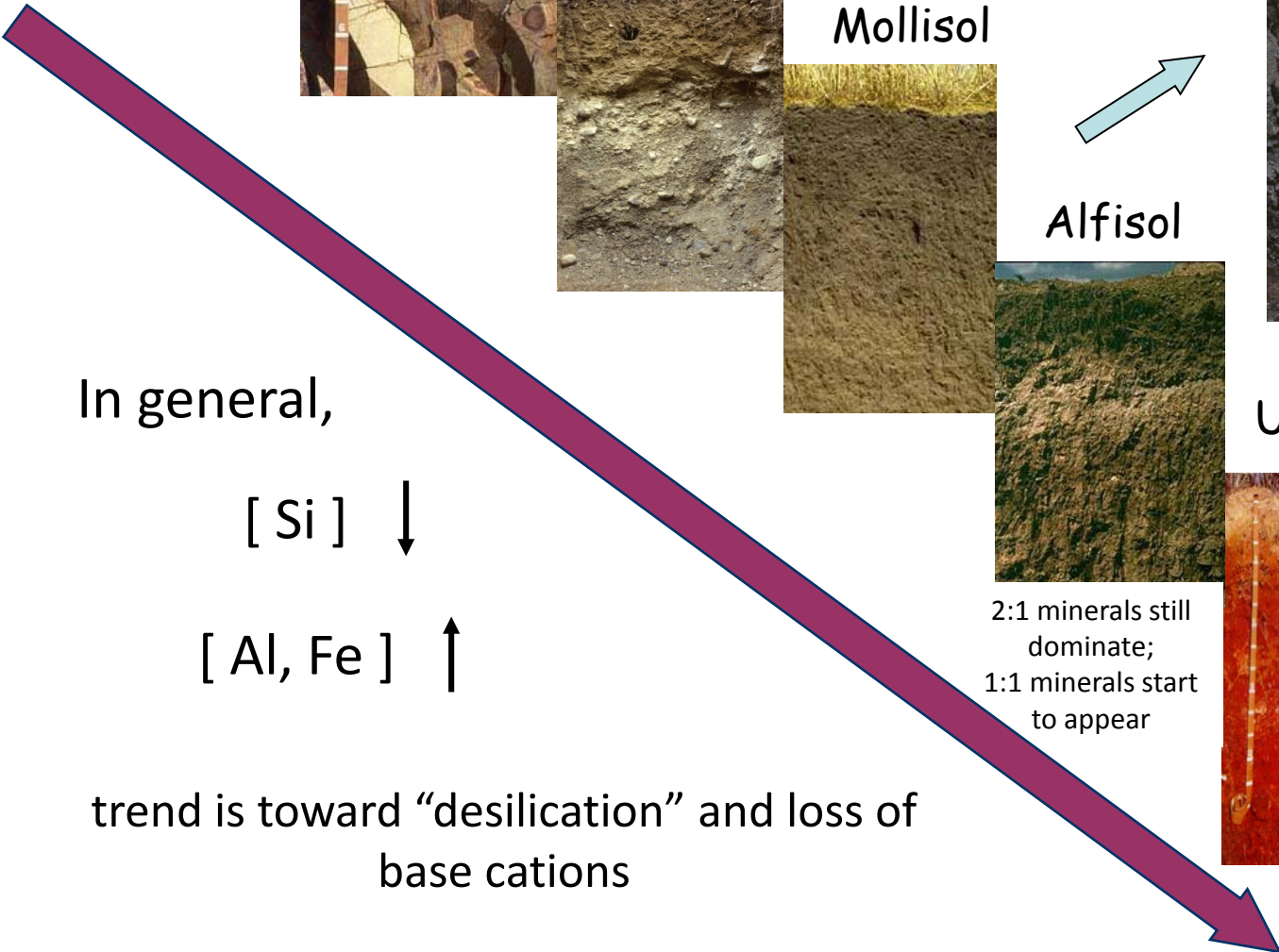
2:1 minerals still dominate;
1:1 minerals start to appear

In general,

[Si] ↓

[Al, Fe] ↑

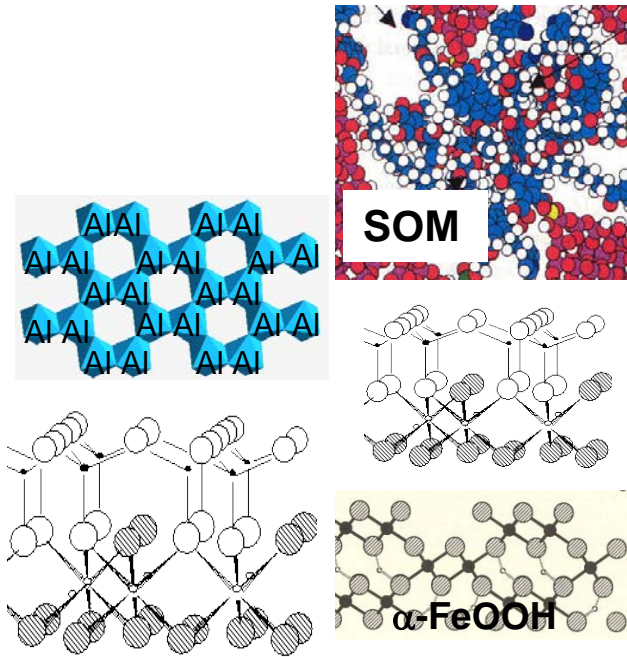
trend is toward “desilication” and loss of base cations



Reactions at the Solid-Solution Interface – Retention Mechanisms

Soil Solids/Colloids

Soil Solution

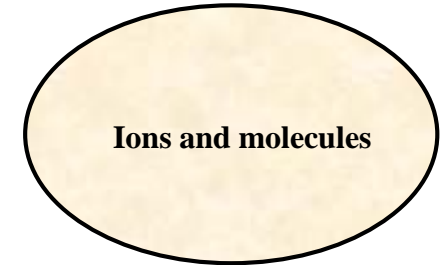


Reactions at the Interface



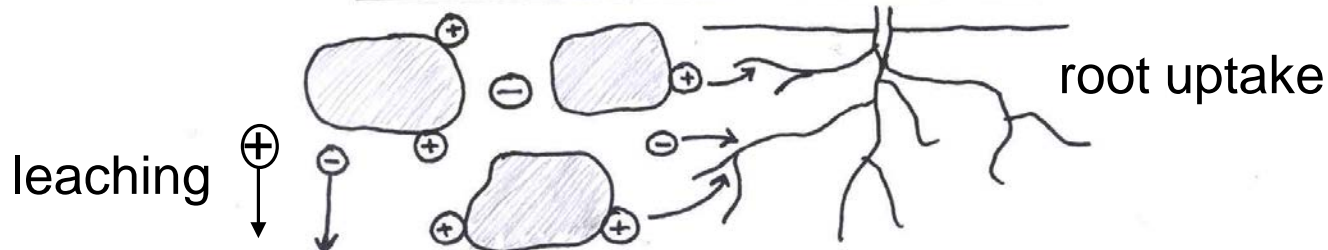
Ion Exchange

Adsorption



Ions and molecules

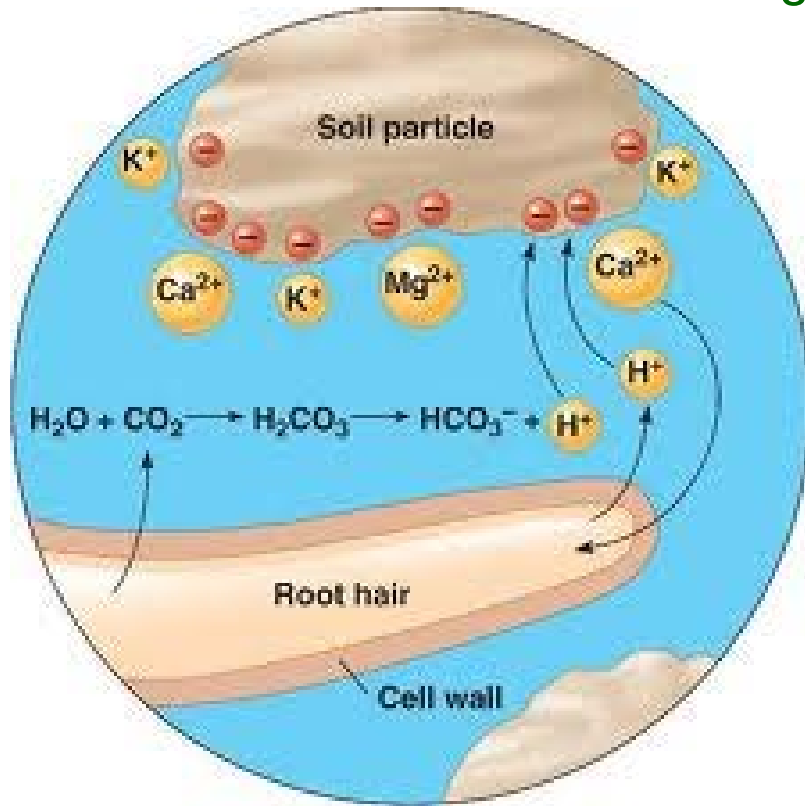
SOLID-LIQUID INTERACTIONS



Retention: net accumulation of matter at the interface between a solid phase and an aqueous solution phase
(ability of soils/colloids to remove ions from solution)

Ion Exchange on Soil Colloids

one of the mechanisms by which (soil) colloids **hold ions against leaching loss**, **hold nutrients in ecosystems** and **keep pollutants out of ground and surface water**



Electroneutrality

Clay	Solution
Ca ²⁺	Cl ⁻ Ca ²⁺
Na ⁺	Na ⁺ SO ₄ ²⁻
Mg ²⁺	HCO ₃ ⁻ Ca ²⁺
Ca ²⁺	HCO ₃ ⁻
Mg ²⁺	Mg ²⁺ NO ₃ ⁻
K ⁺	SO ₄ ²⁻ K ⁺
10- = 10 Cation	8 anion = 8 Cation

exchangeable cations and surfaces \rightleftharpoons soluble cations and anions

Mass Action & Charge Balance

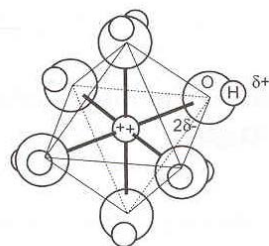
Ion exchange = the process
CEC = the property of the colloid/soil

Retention Mechanisms

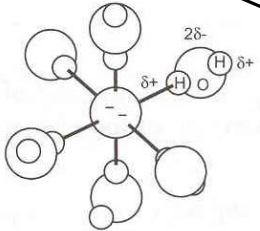
Outer- and Inner- Sphere Complexes

Ca ²⁺
Na ⁺
Mg ²⁺
Ca ²⁺
Mg ²⁺
K ⁺

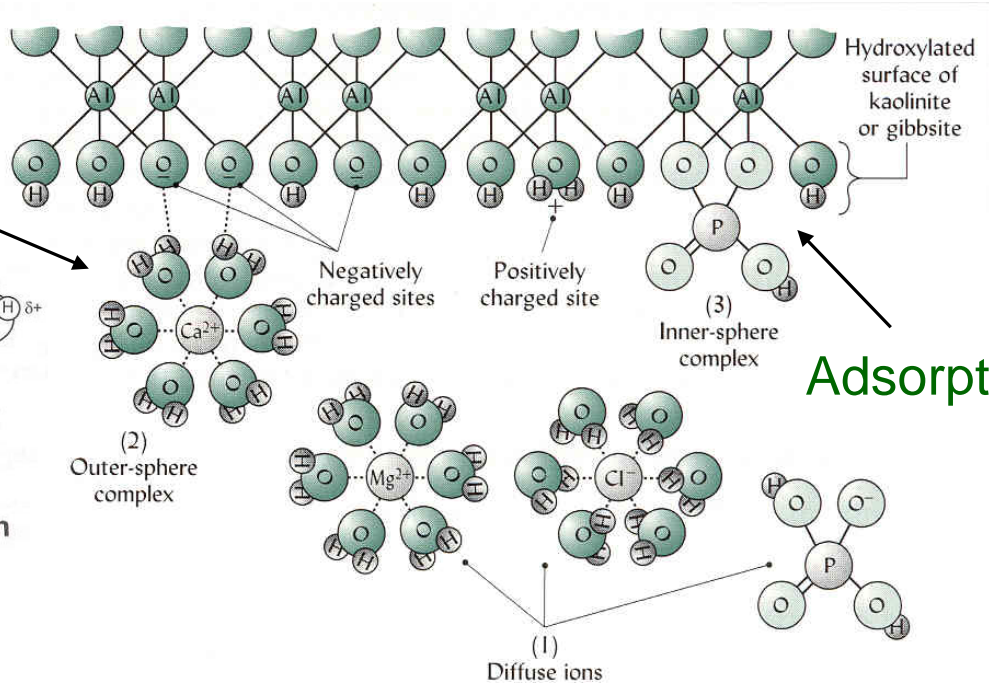
Ion Exchange



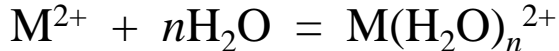
Hydrated Cation



Hydrated Anion



Adsorption

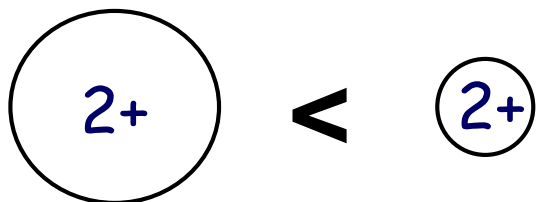


Ion Hydration:

ionic potential = z^2/r

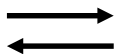
z = charge; r = radius

smaller and more charged ion:
 higher ionic potential
 hydrate most strongly



Ion Exchange: The Process

reversible



forward and backward reactions coincide

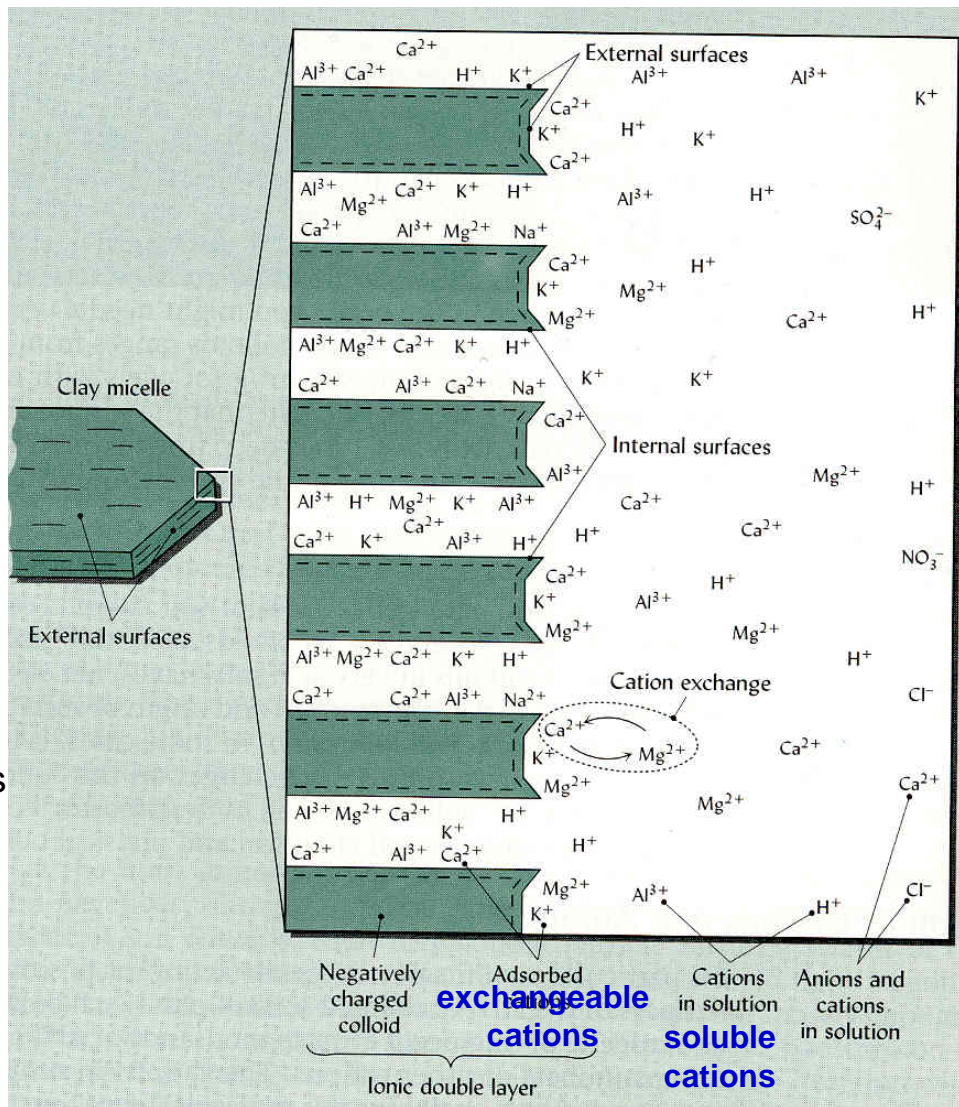
stoichiometric

- ions that leave colloid surface are replaced by equivalent amount of other ions

- exchange takes place in a **charge-for-charge** basis

(exchange reactions can occur between cations of equal or unequal charge)

(electroneutrality)



diffusion controlled

- molecular diffusion in aqueous environments

electrostatic

nonspecific
(outer-sphere)

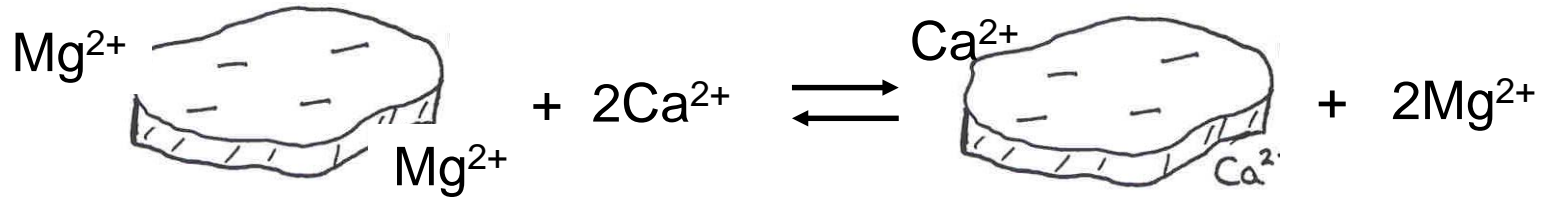
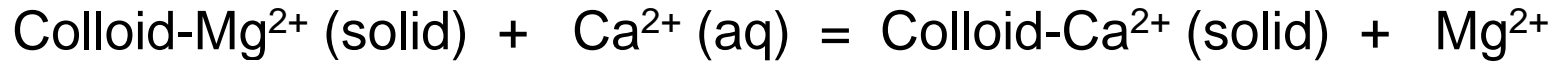
medium-long range

Mostly from permanent charge minerals and soil organic matter

Al and Fe oxides, kaolinite - no real contribution to CEC of soils

Cation Exchange on Permanent Charge Minerals (Layer Aluminosilicate Clays)

Exchange Equation:



General Rules:

selectivity of cation by exchanger based on the **ion's charge/size**
(ionic potential = z^2/r)

size:

the smaller the hydrated radius the greater the affinity (same charge)
(ions with small dehydrated radius have large hydrated)

charge:

the higher the charge the greater the exchanger preference
($3+ > 2+ > 1+$)

For example: $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ \sim \text{NH}_4^+ > \text{Na}^+$

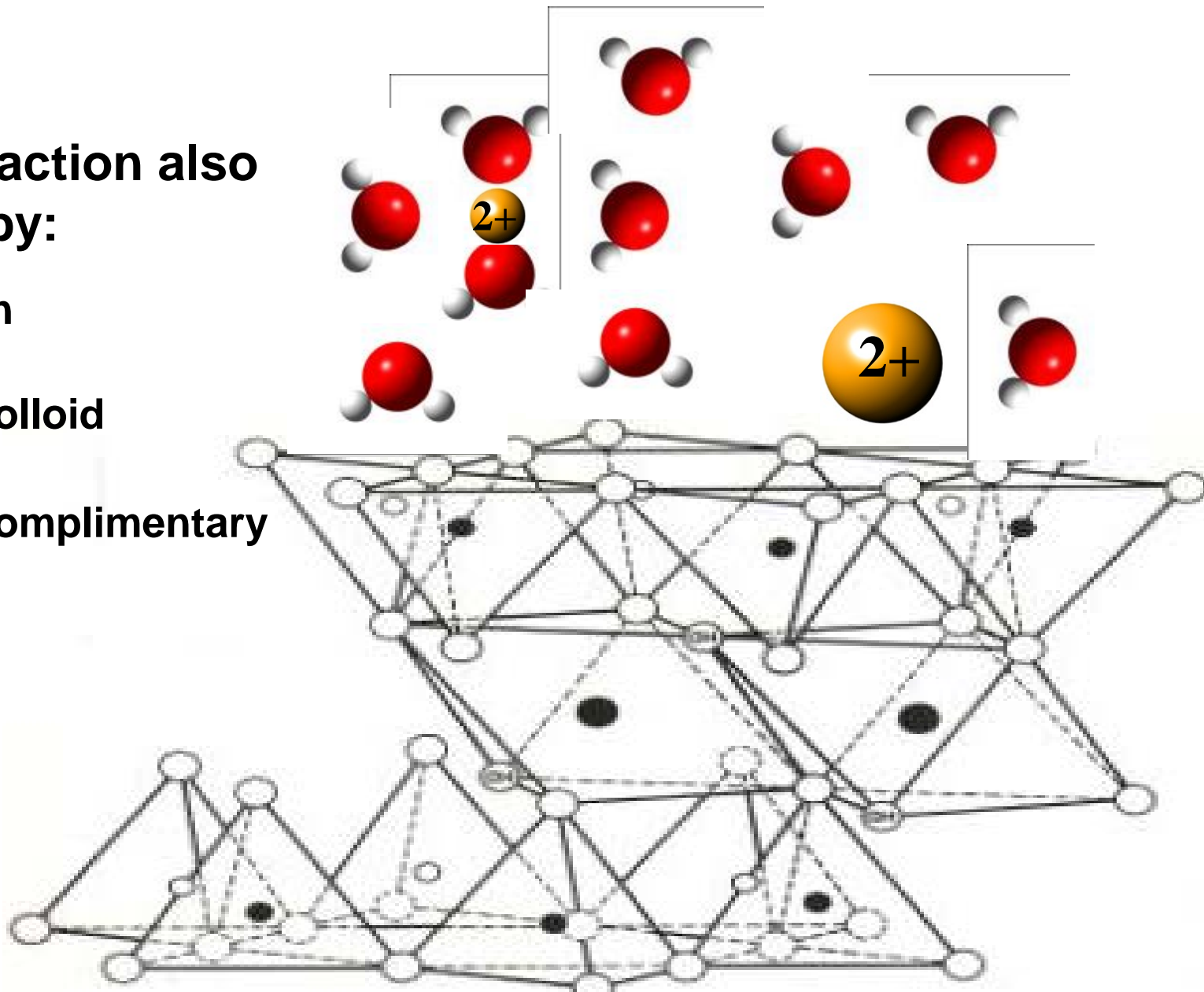
Cation selectivity is determined by extent of cation hydration

Extent of reaction also influenced by:

Mass action

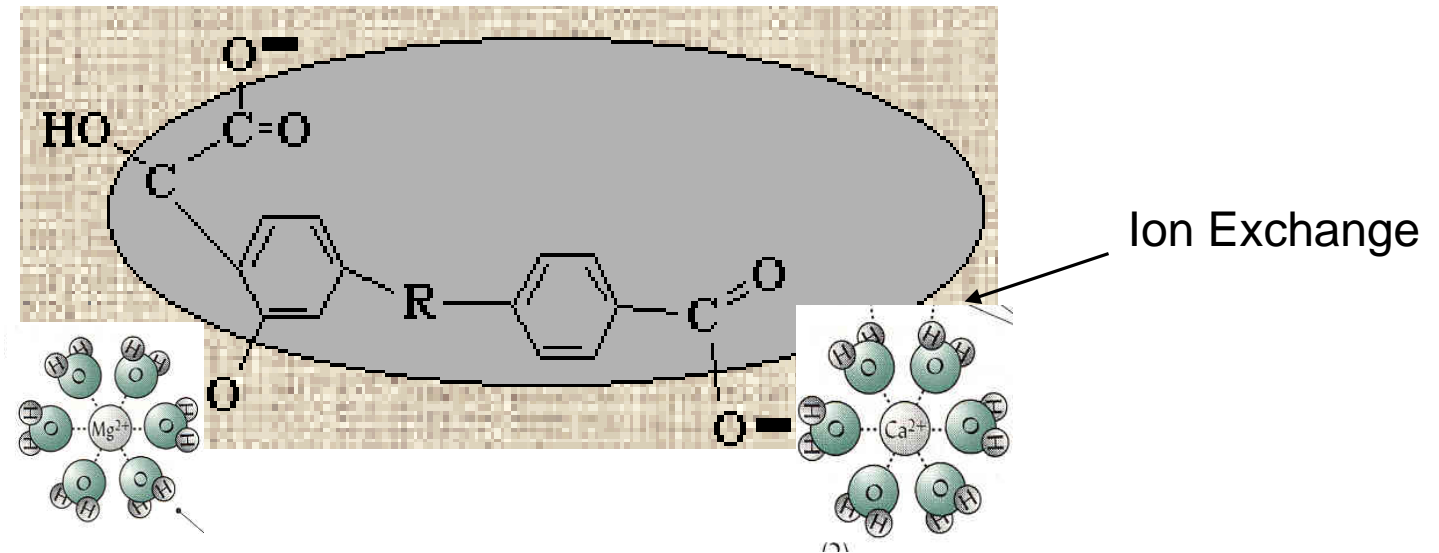
Nature of colloid

Nature of complimentary ions



Soil Organic Matter

Surface Functional Groups (hydroxyl, carboxylic, alcohols, phenols)



General Rule: selectivity of cation by exchanger based on the ion's charge/size

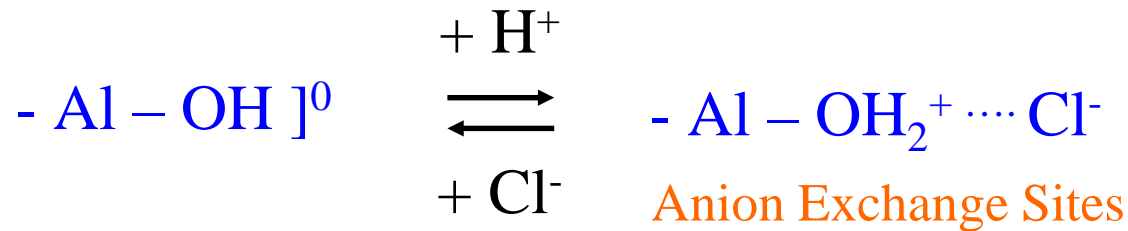
Order of Selectivity: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
 $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$
 $\text{Al}^{3+} > \text{M}^{2+} > \text{M}^+$

Anion Exchange Capacity (AEC)

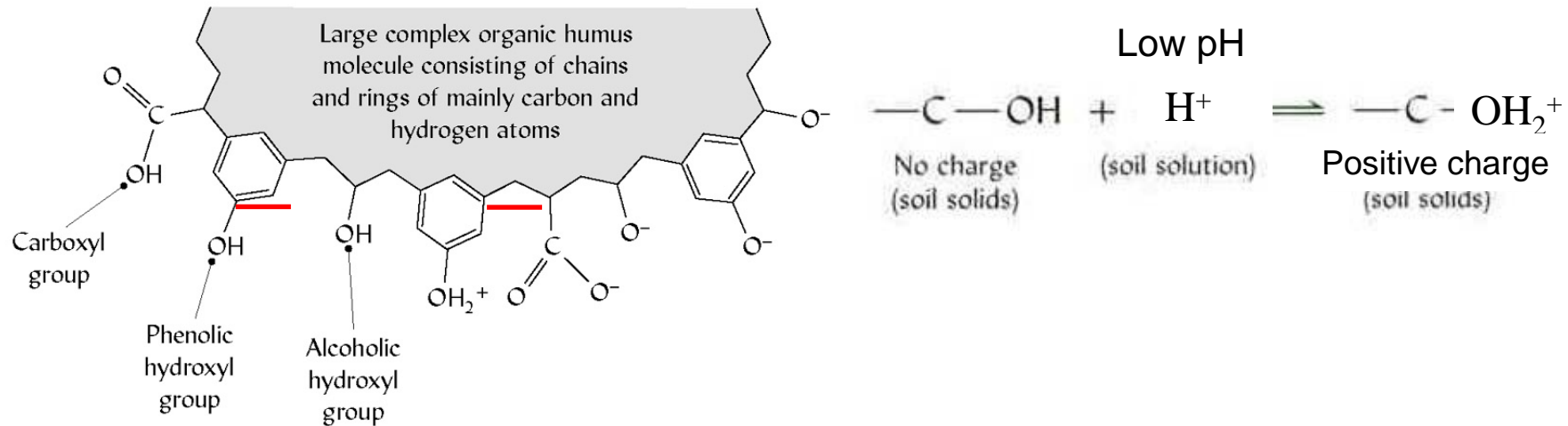
Terminal broken bonds: pH dependent (variable) charge

Minerals

Low pH (protonation)



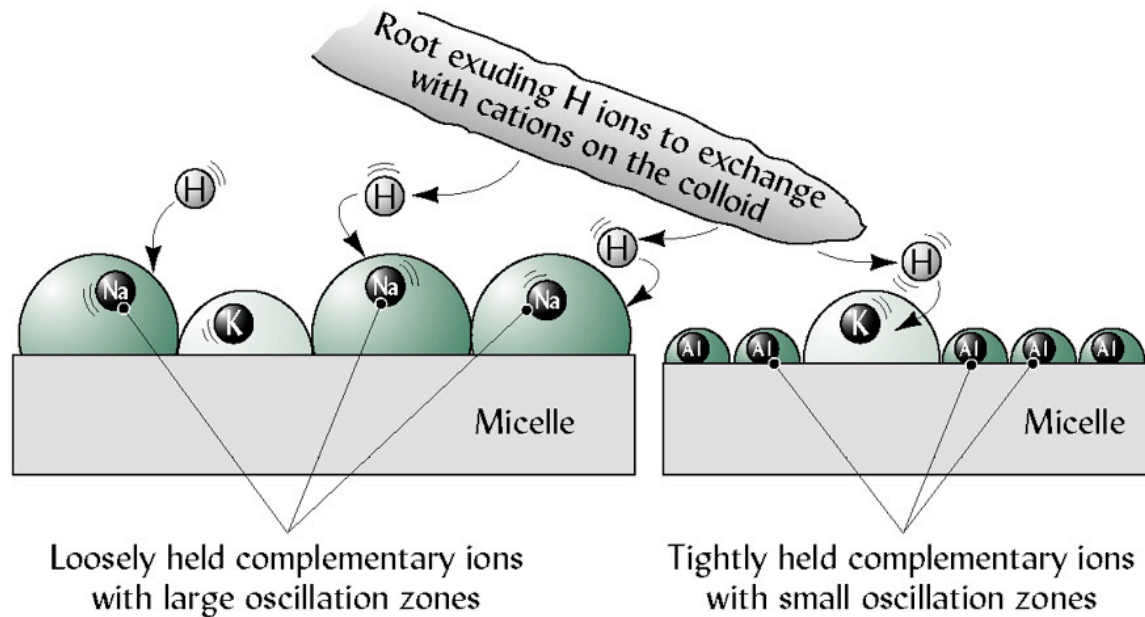
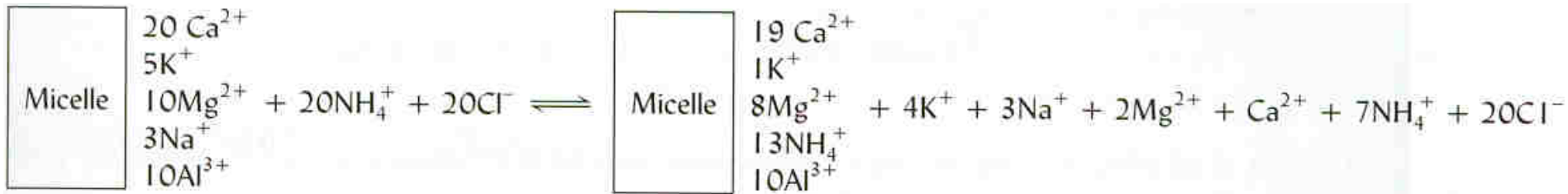
Soil Organic Matter



AEC is generally much smaller than CEC

Attraction of anions to oxide minerals and SOM





Complimentary cations: Influence plant uptake and leaching



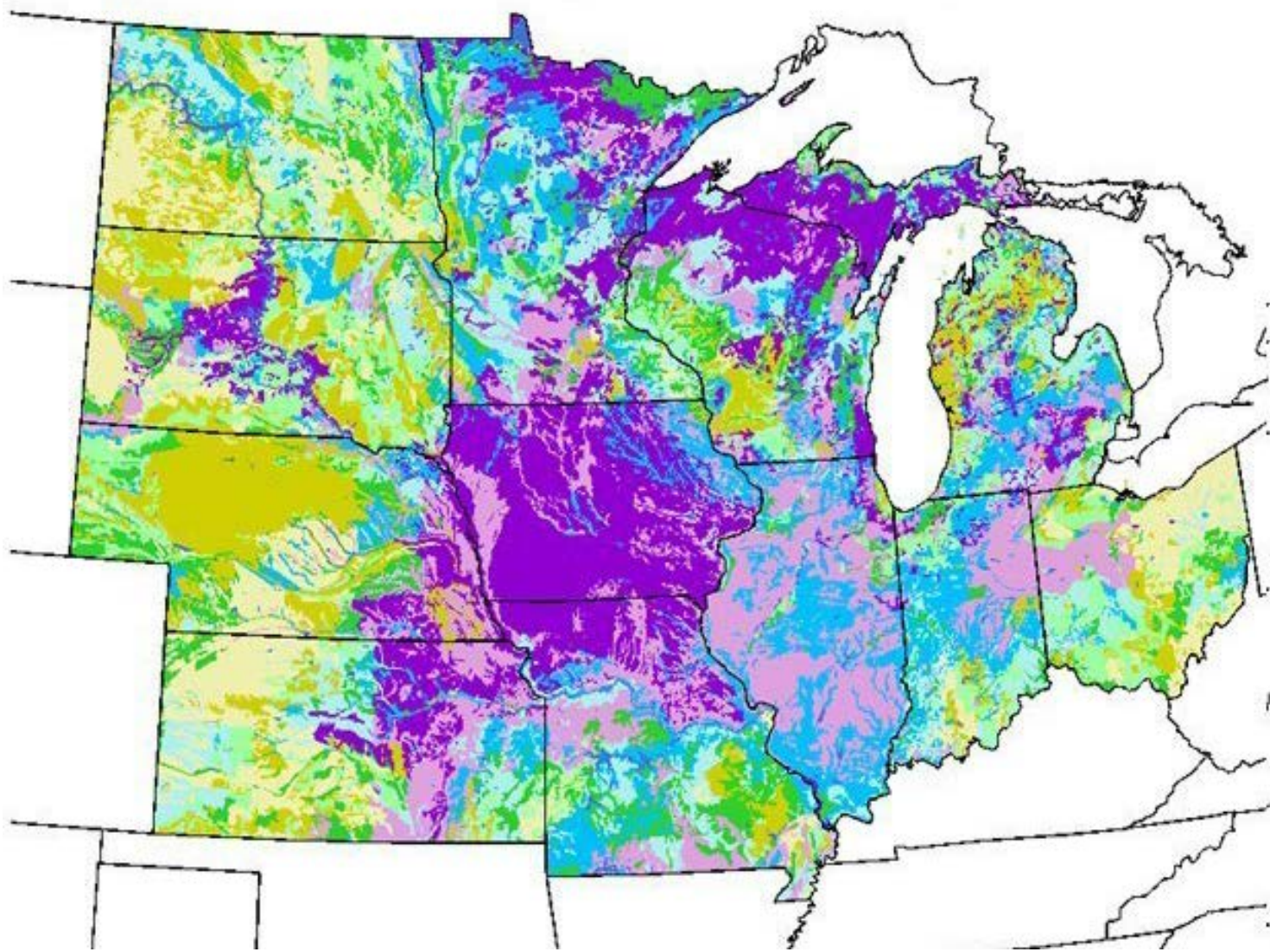
At a given %K⁺ saturation, K⁺ is more readily available for both plant uptake and leaching in acid soils (lots of Al³⁺) than in neutral to alkaline soils. Why?

CEC

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



Cation Exchange Capacity (CEC) – The Property

Assessment of the **quantity** of cations reversibly retained (electrostatic) per unit weight of mineral/organic matter/soil

mmol(+) charge / kg

Magnitude of CEC determined by the nature and content of clay minerals and organic matter

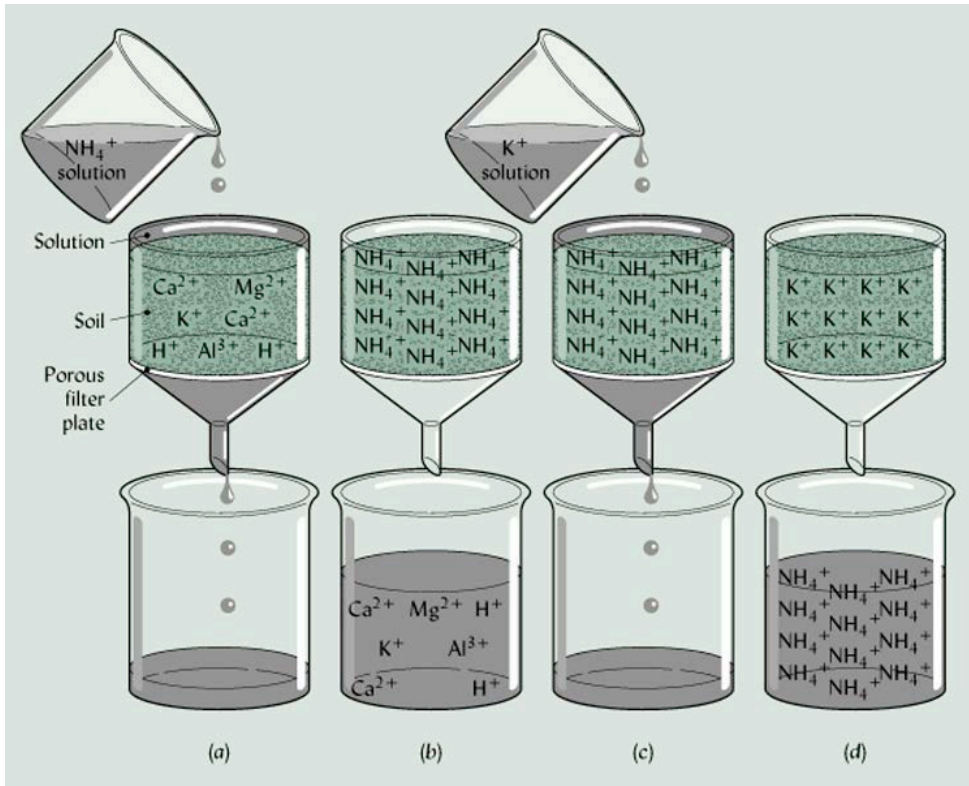
CEC is related to the negative charge of the soil colloids

CEC of soils is usually dominated by Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Al^{3+}

CEC (mmol charge) $\sim 2[\text{Ca}] + 2[\text{Mg}] + [\text{Na}] + [\text{K}] + 3[\text{Al}]$

Determination of Cation Exchange Capacity in Soils

Leach soil with a concentrated solution of an exchanger cation (NH_4^+ , Ba^{2+} , Sr^{2+})



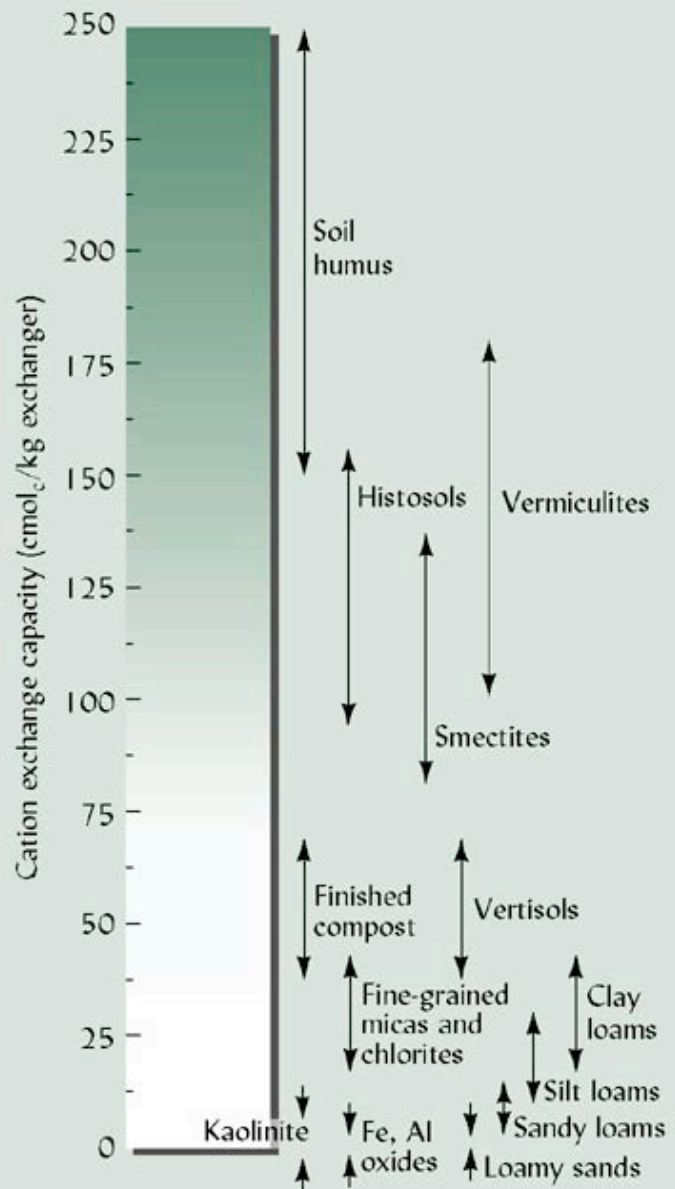
1. determine elements in the leachate (usually Ca, Mg, Na, K, Al)

2. measure exchanger cation adsorbed (requires an extra step: need to leach the exchanger cation)

Buffered (NH_4^+ at pH 7, Ba^{2+} at pH 8.2) and Unbuffered (soil pH) methods

Exchangeable ions are essential for maintaining plant nutrient levels but are not “held” strong enough to immobilize environmental pollutants

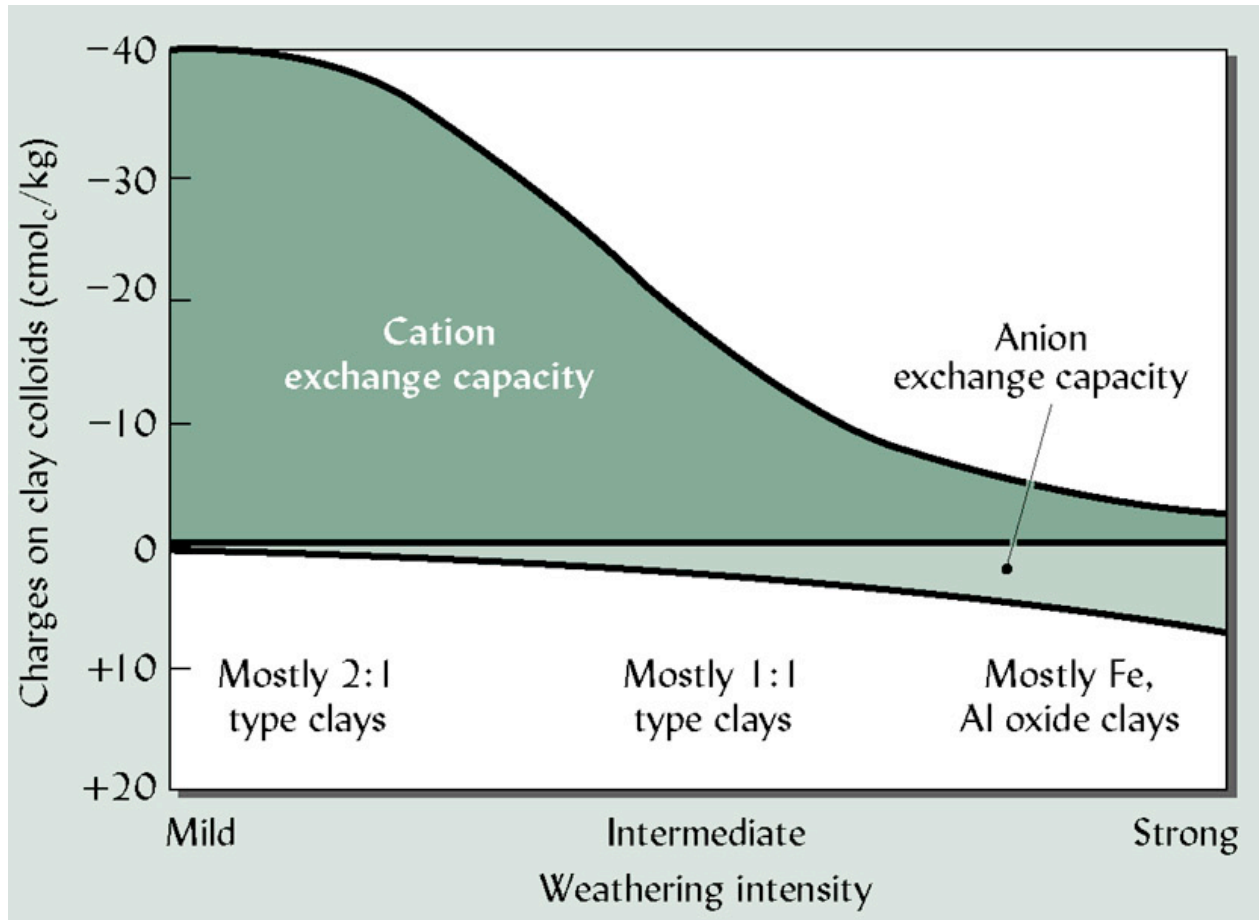
TABLE 8.7 The Average Cation Exchange Capacities (CEC) and pH Values of More Than 3000 Surface Soil Samples Representing Nine Different Soil Orders



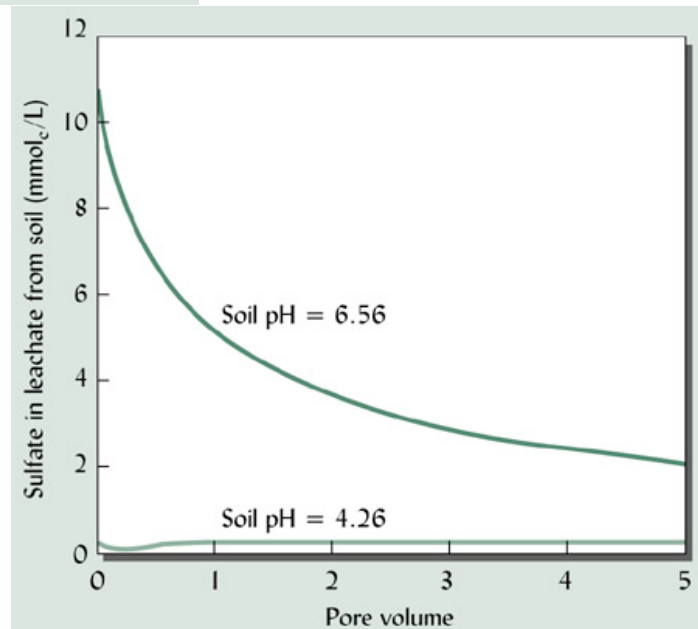
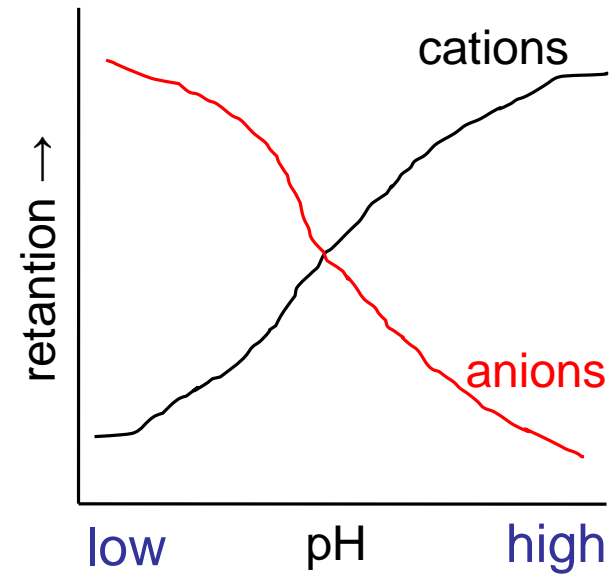
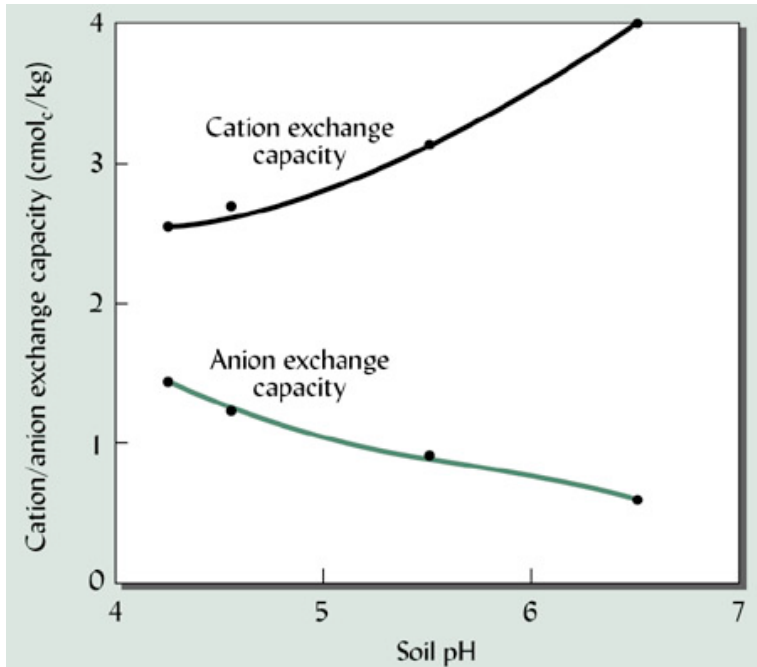
<i>Soil order</i>	<i>pH</i>	<i>CEC, cmol_c/kg</i>
Ultisols	5.60	3.5
Alfisols	6.00	9.0
Spodosols	4.93	9.3
Entisols	7.32	11.6
Inceptisols	6.08	14.6
Aridisols	7.26	15.2
Mollisols	6.51	18.7
Vertisols	6.72	35.6
Histosols	5.50	128.0

From Holmgren, et al. (1993).

Relationships: Weathering intensity, mineralogy and CEC/AEC



Relationships: Soil pH, CEC, AEC, retention/sorption of cations/anions



Base Saturation (BS) of Cation Exchange Sites

a measure of proportion of cations (compared with hydronium ions)
on exchange sites

$$\text{BS} = \frac{\text{number of exchange sites occupied by Ca + Mg + K + Na}}{\text{total number of exchange sites}} \times 100$$

high base saturation values are desirable

Soils with low CEC and/or a small base saturation value are susceptible to acidification by either natural or anthropogenic inputs

CEC Values and Major Exchangeable Cations of Selected Soils^a

SOILS	pH	CEC (mmole kg ⁻¹)	EXCHANGEABLE CATIONS (% OF TOTAL)				
			Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	H ⁺ (Al ³⁺) ^b
Average of agricultural soils (Netherlands)	7.0	383	79.0	13.0	2.0	6.0	—
Average of agricultural soils (California)	7.0	203	65.6	26.3	5.5	2.6	—
Chernozem or Mollisoll (Russia)	7.0	561	84.3	11.0	1.6	3.0	—
Sodic Merced soil (California)	10.0	189	0.0	0.0	5.0	95.0	0.0
Lanna soil, unlimed (Sweden)	4.6	173	48.0	15.7	1.8	0.9	33.6
Lanna soil, limed (Sweden)	5.9	200	69.6	11.1	1.5	0.5	17.3

^aFrom F. E. Bear (Ed.), *Chemistry of the Soil*, 2nd ed. American Chemical Society, Washington, D.C., 1964, p. 167.

^bProbably includes some titratable acidity (Chapter 8).