

GEOLOGY 408/508

**SOIL COLLOIDS:
SEAT OF SOIL CHEMICAL &
PHYSICAL ACTIVITY**

CHAPTER 8

Brady & Weil, Rev. 14th ed.

GENERAL PROPERTIES AND TYPES OF COLLOIDS

- **Size:**

- < 1 μm in diameter
- too small to be seen with ordinary light microscope

- **Surface area:**

- very large, > 1000 x that of same mass of sand
- 10 m^2/g : clays with only external surfaces
- 800 m^2/g : clays with external & internal surfaces

GENERAL PROPERTIES AND TYPES OF COLLOIDS

- **Surface charges:**

- may be positive or negative; most are negative
- highly variable between different colloid types
- may be affected by pH

- **Adsorption of cations & anions:**

- adsorption of cations to surfaces of negatively charged colloids is of particular significance
- concept of colloid is that of a large anion
- concentration of cations greatest nearest surface

- **Adsorption of water:**

- charges on colloids attract H₂O molecules
- H₂O molecules are strongly adsorbed
- interlayer adsorption cause swelling of some clays

SILICATE CLAY CRYSTAL & COMPLIMENT OF IONS

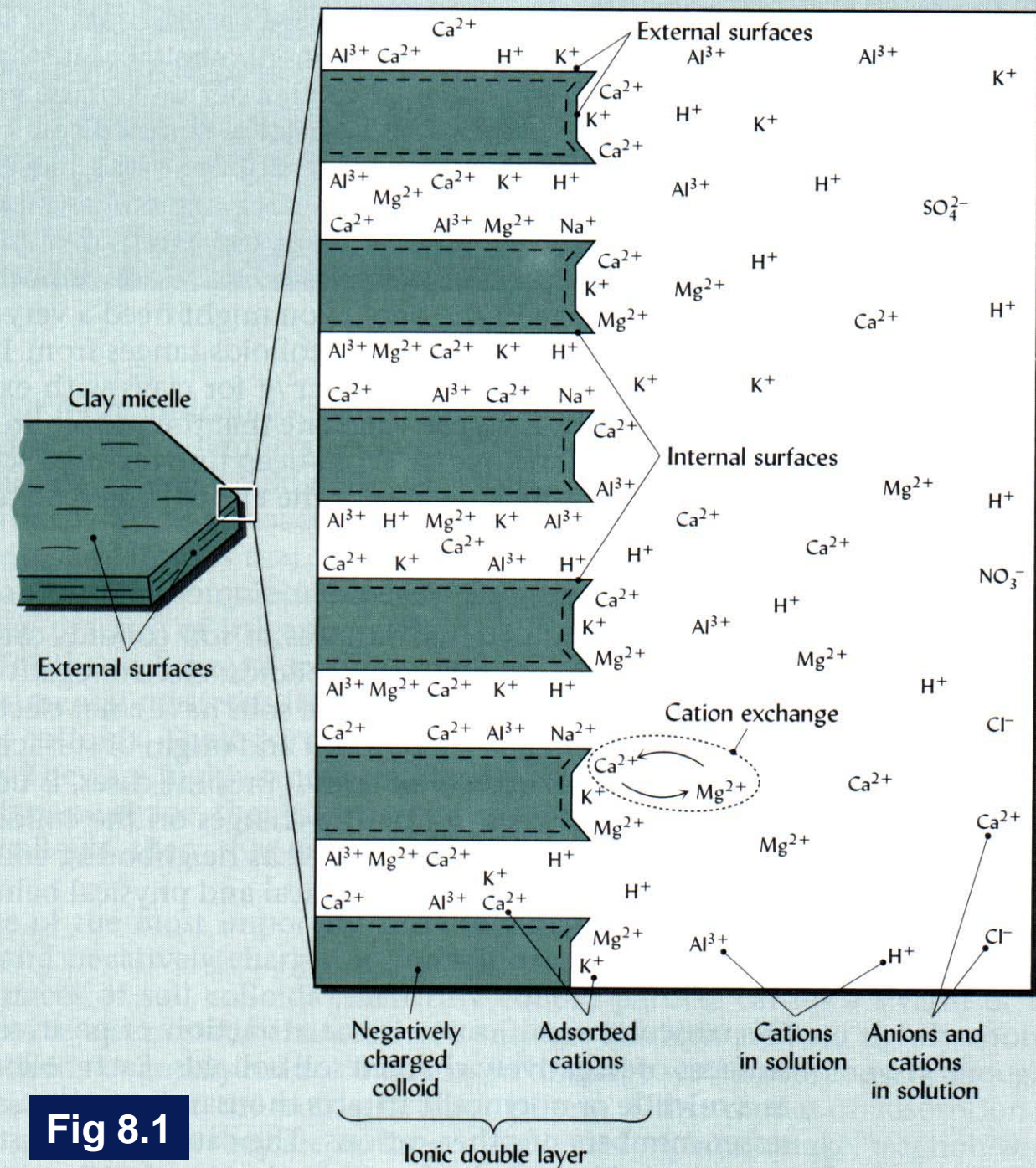


Fig 8.1

GENERAL PROPERTIES AND TYPES OF COLLOIDS

- **Types of soil colloids:**
 - **crystalline silicate clays**
 - dominant type in most soils
 - layered structure
 - variable degree of plasticity, stickiness, swelling, charge intensity
 - **noncrystalline silicate clays**
 - aluminosilicates, the two most common are allophane & imogolite
 - high amounts of both + & - charges
 - plastic when wet but not sticky

Kaolinite, a valuable mineral



Kaolinitic clay soil to be used in brick making



**Early 19th-century
English china**

GENERAL PROPERTIES AND TYPES OF COLLOIDS

- **Types of soil colloids:**

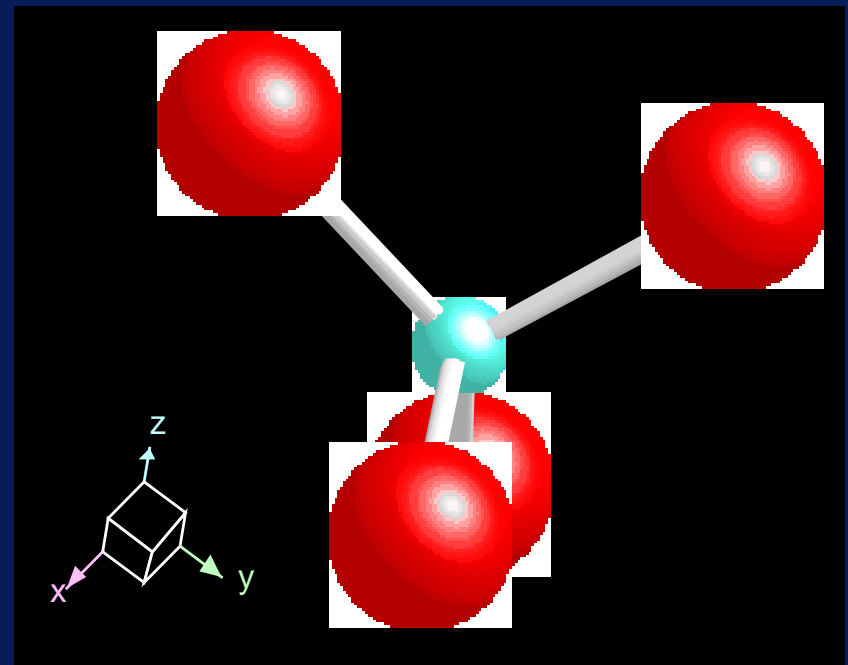
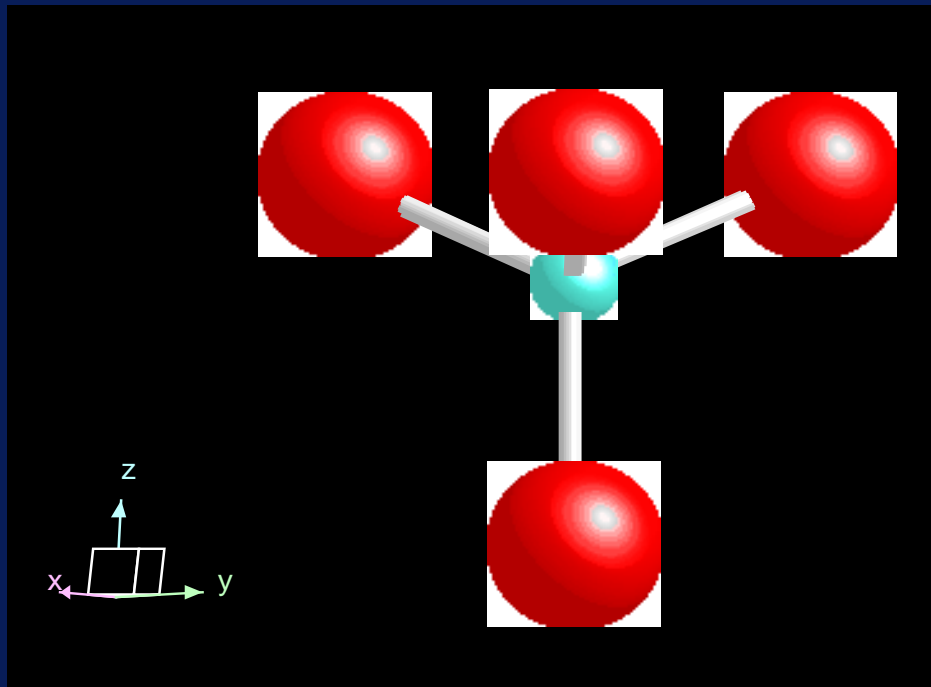
- **Fe & Al oxide clays**

- especially important in Ultisols & Oxisols
- primarily are Fe oxides or Al oxides, not Fe & Al
- some are crystalline but most are not
- may occur as coatings on other soil particles
- forms are more likely “oxy-hydroxides”

- **Organic (humus) colloids:**

- amorphous, very small in size
- both + & - charges but net negative
- have very high & pH dependent charges
- have very high capacity to adsorb water

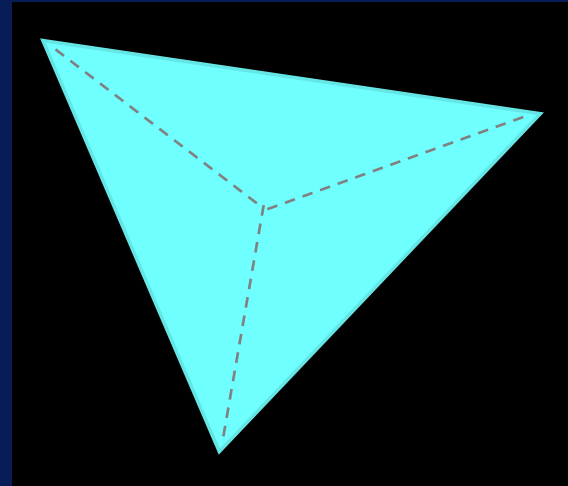
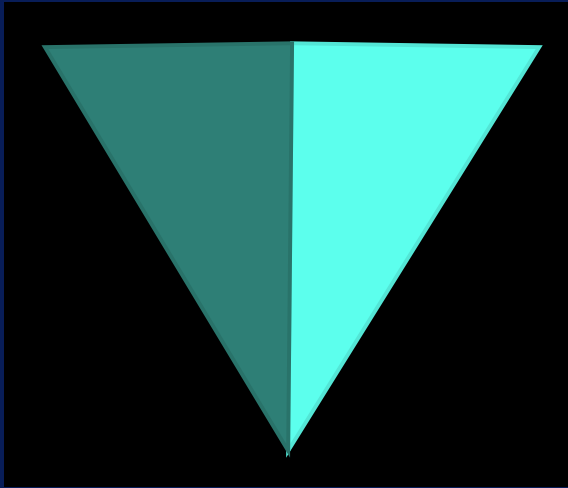
BUILDING BLOCKS OF PHYLLOSILICATES



SiO_4 Tetrahedron

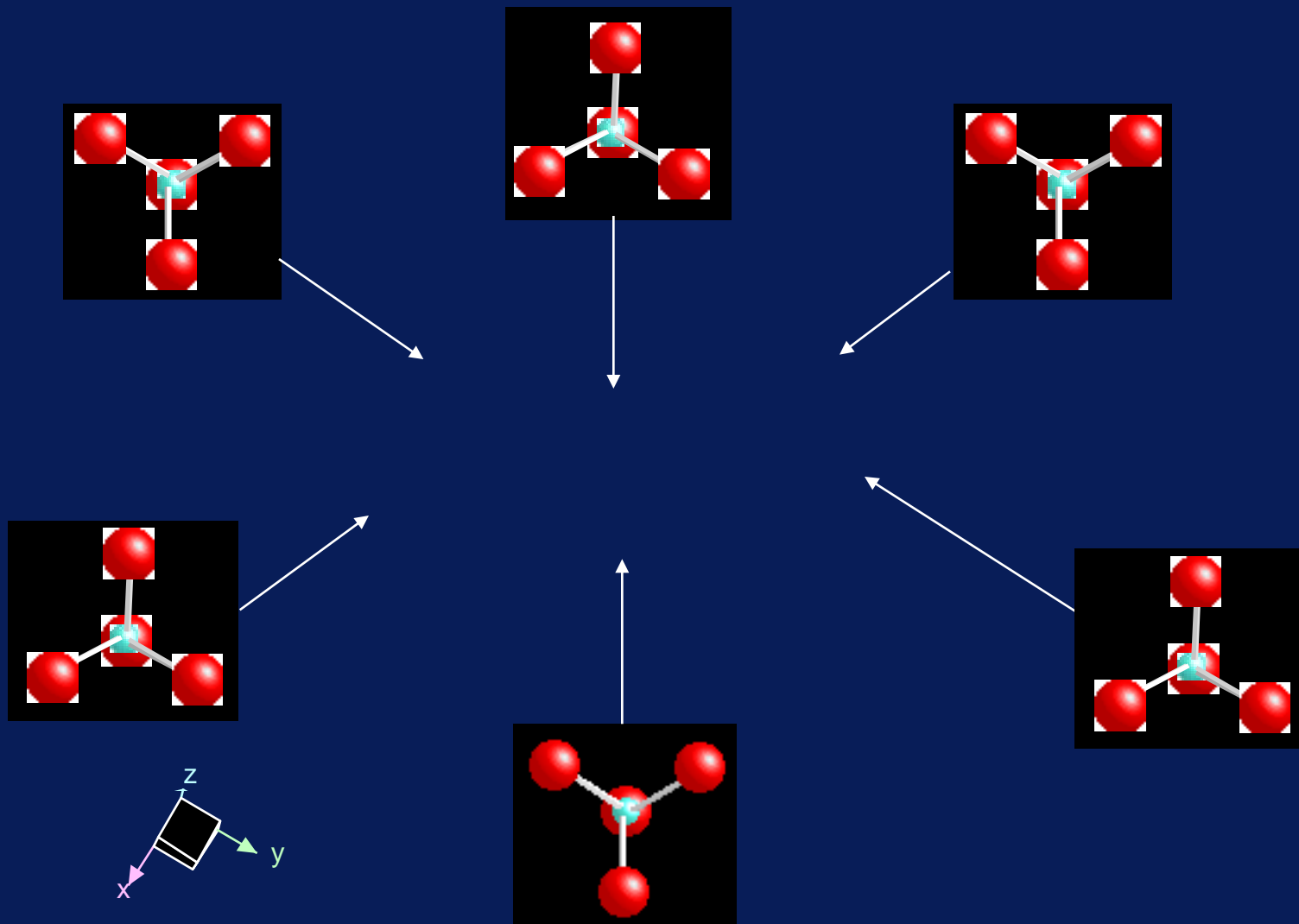
BUILDING BLOCKS OF PHYLLOSILICATES

SiO_4 Tetrahedron

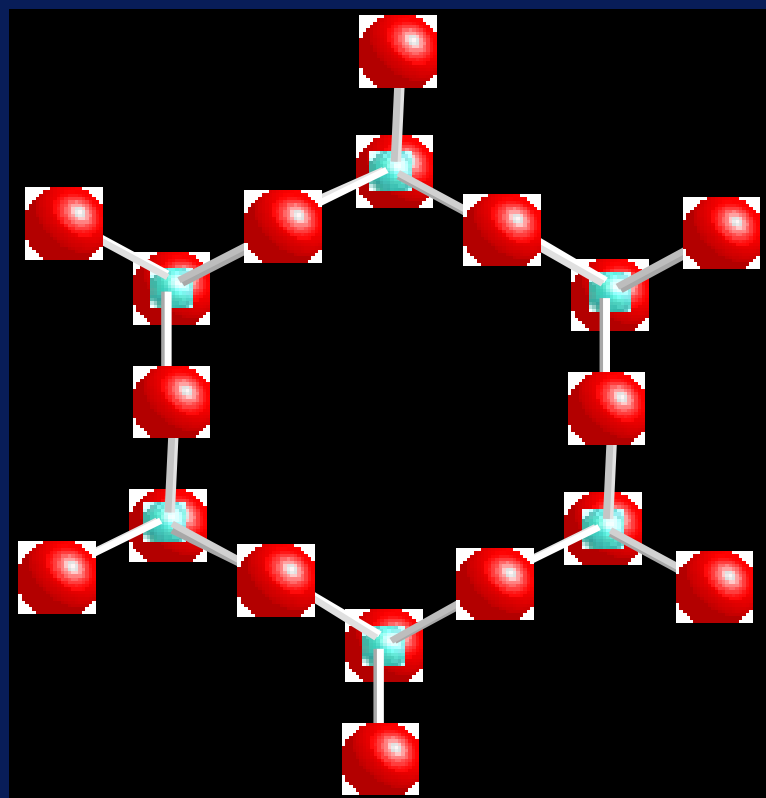


Polyhedral View

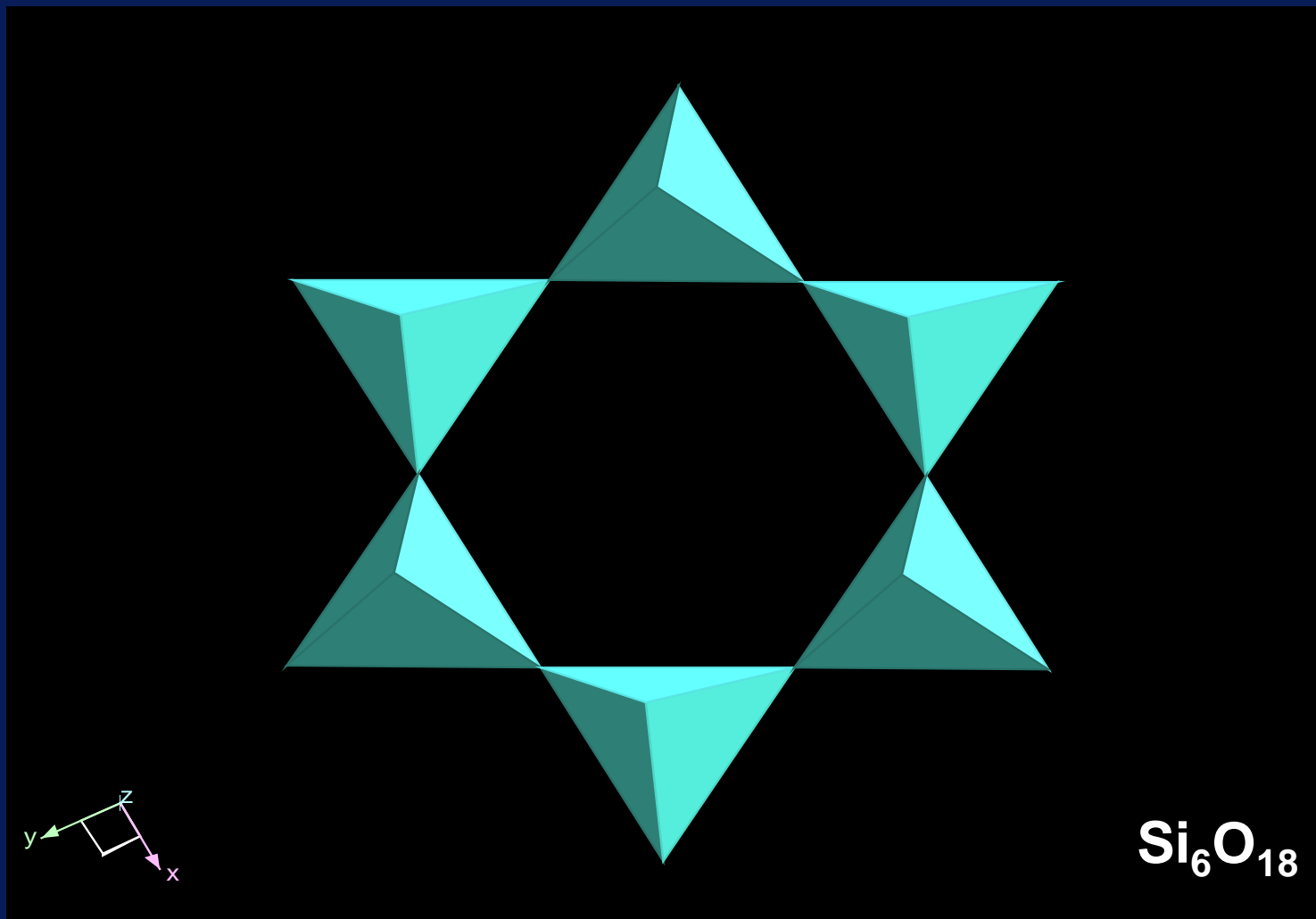
CONNECT THE TETRAHEDRA



SILICA TETRAHEDRAL RING



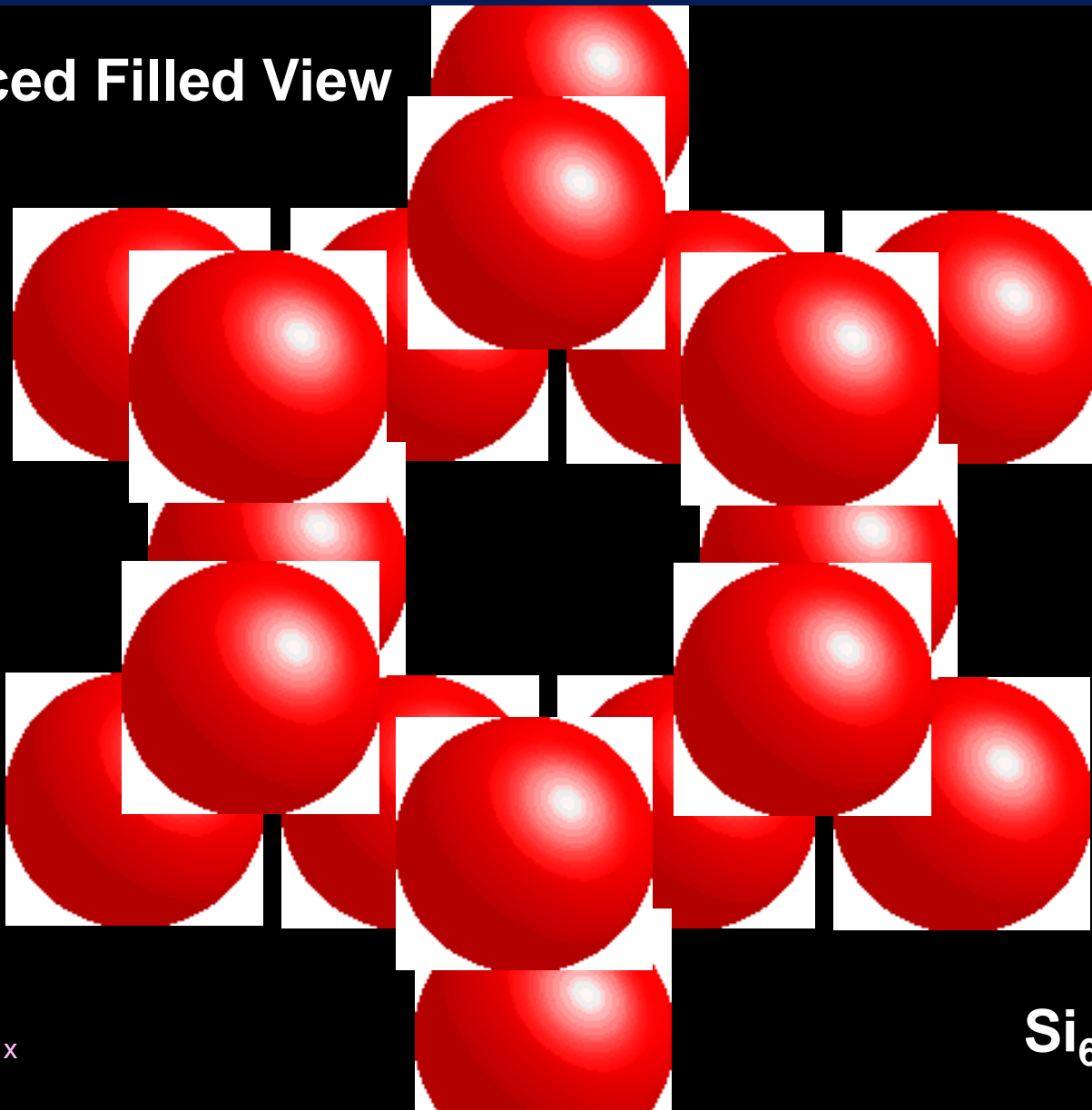
SILICA TETRAHEDRAL RING



Polyhedral View

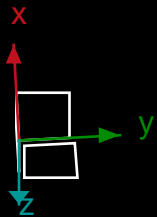
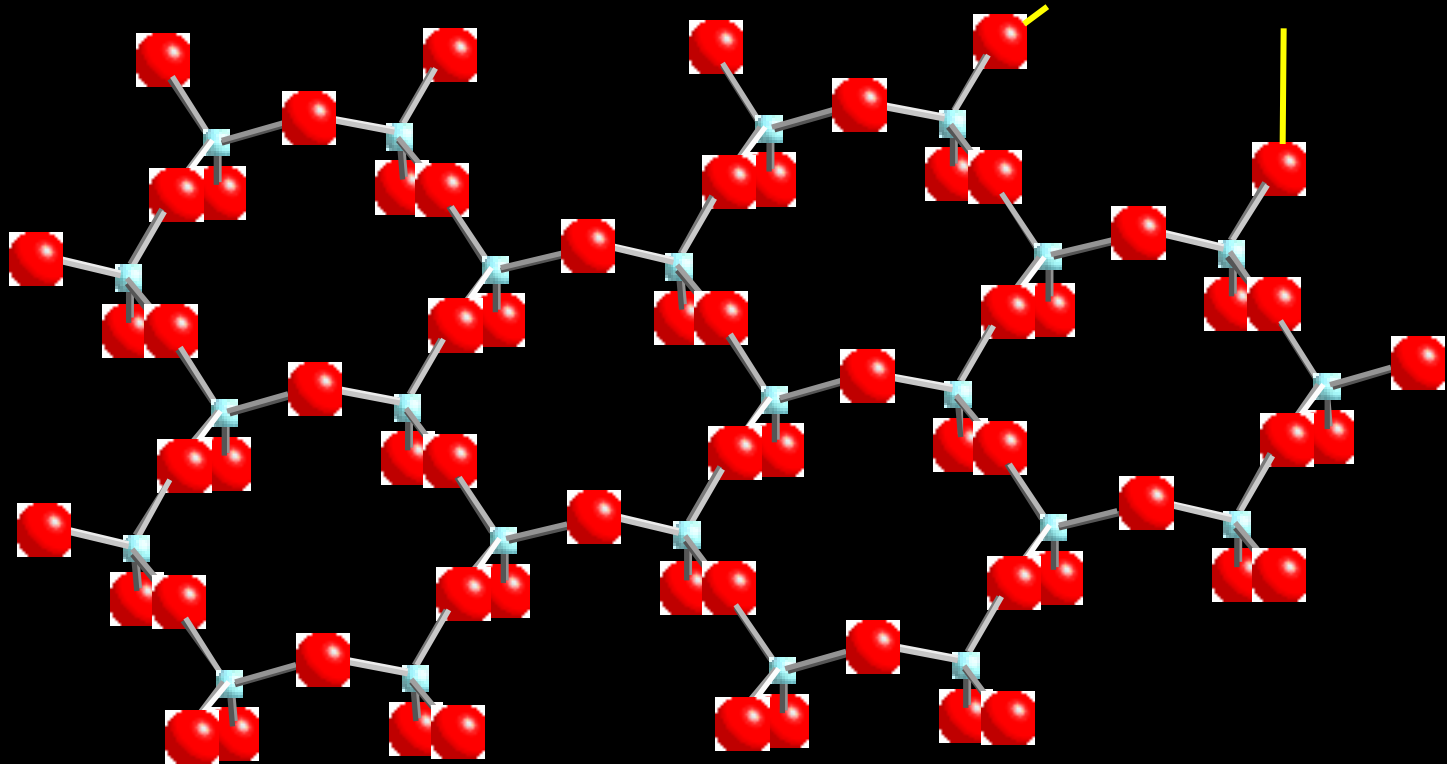
SILICA TETRAHEDRAL RING

Spaced Filled View

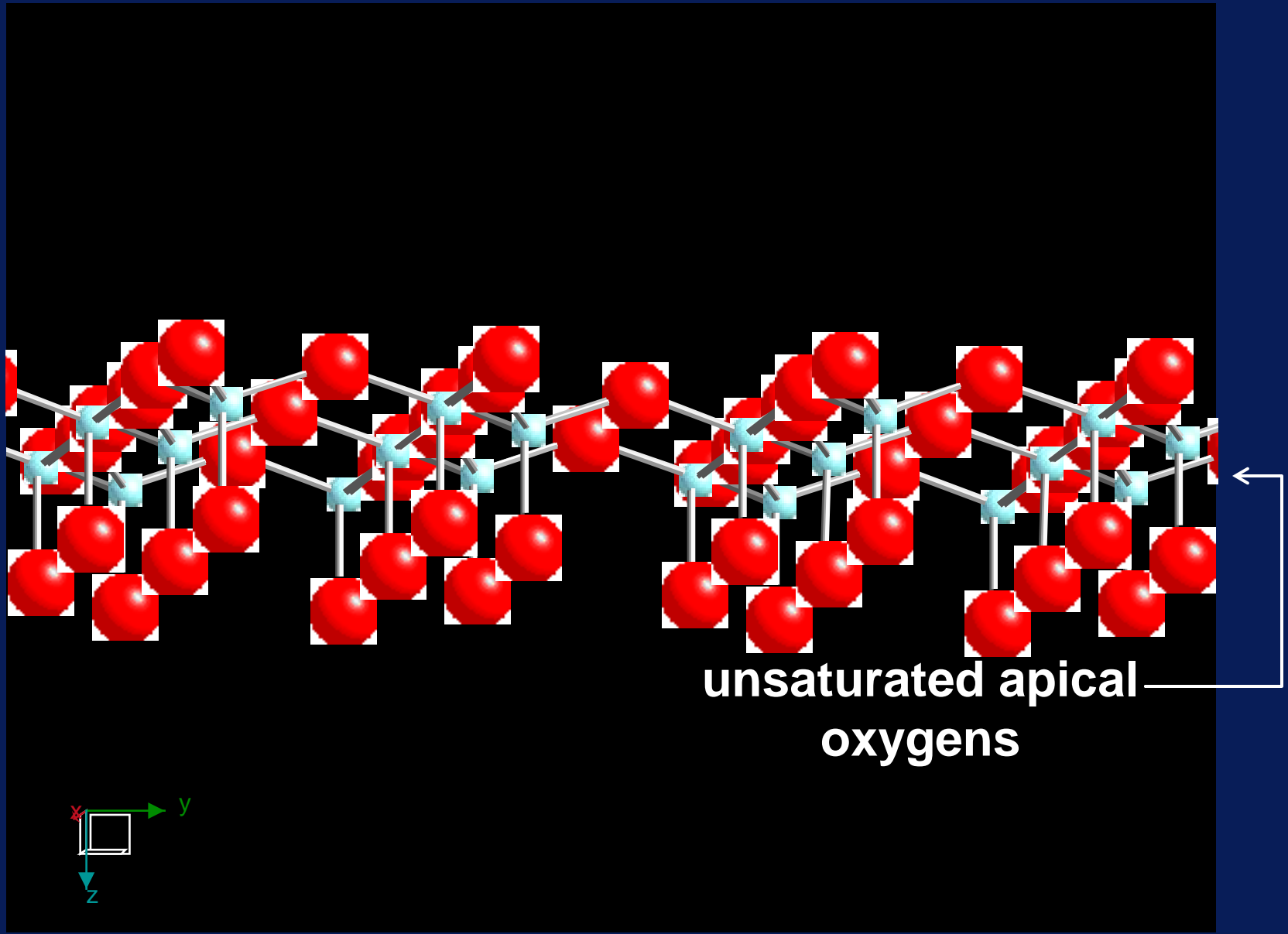


TETRAHEDRAL SHEET

unsaturated 'edge' sites

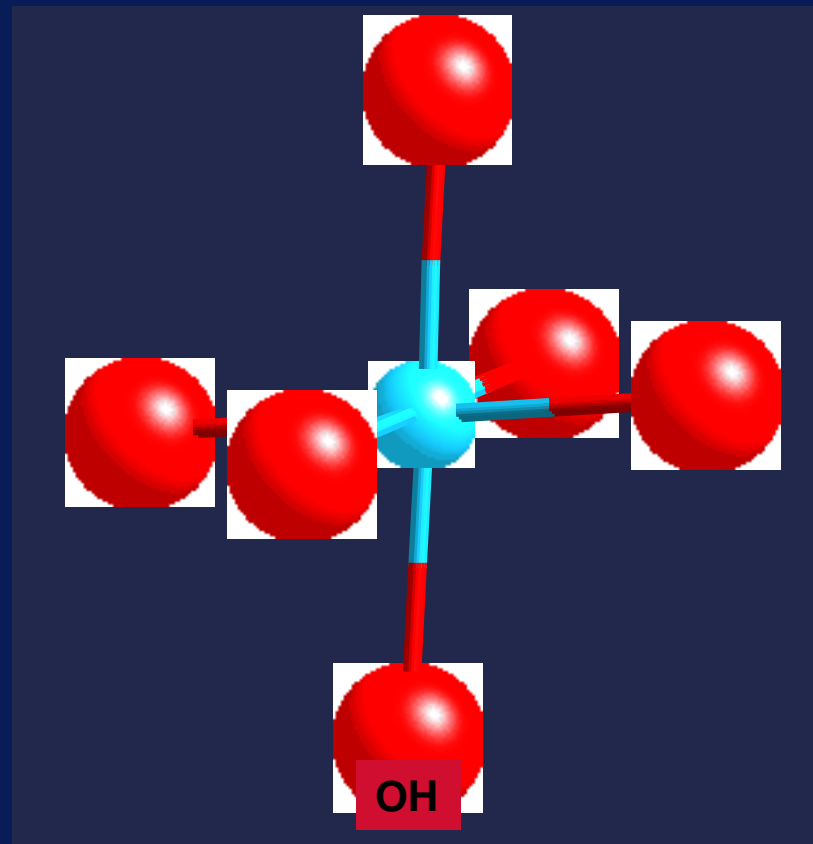


TETRAHEDRAL SHEET

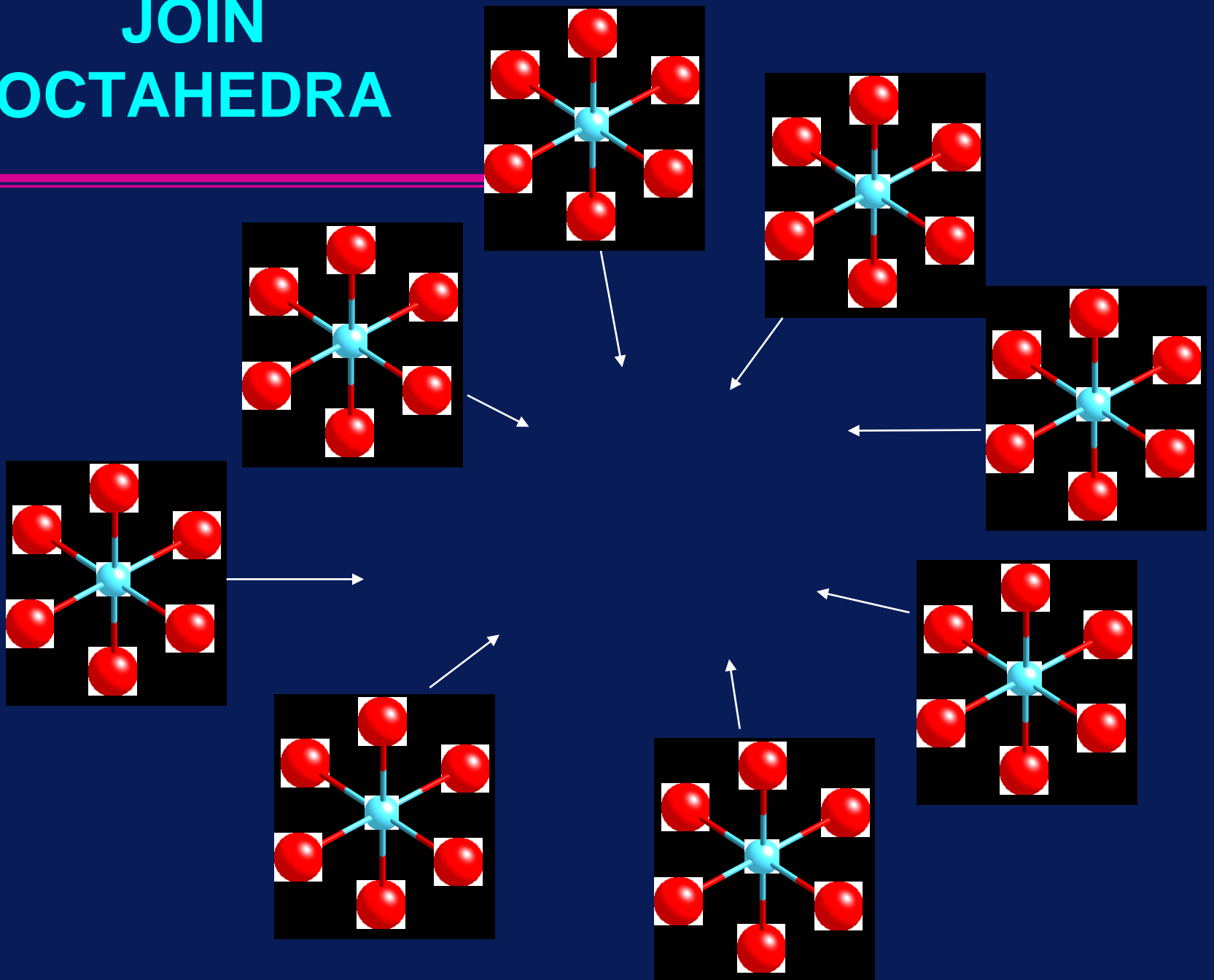


BUILDING OF OCTAHEDRAL SHEETS

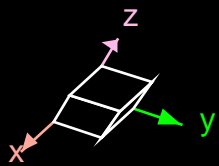
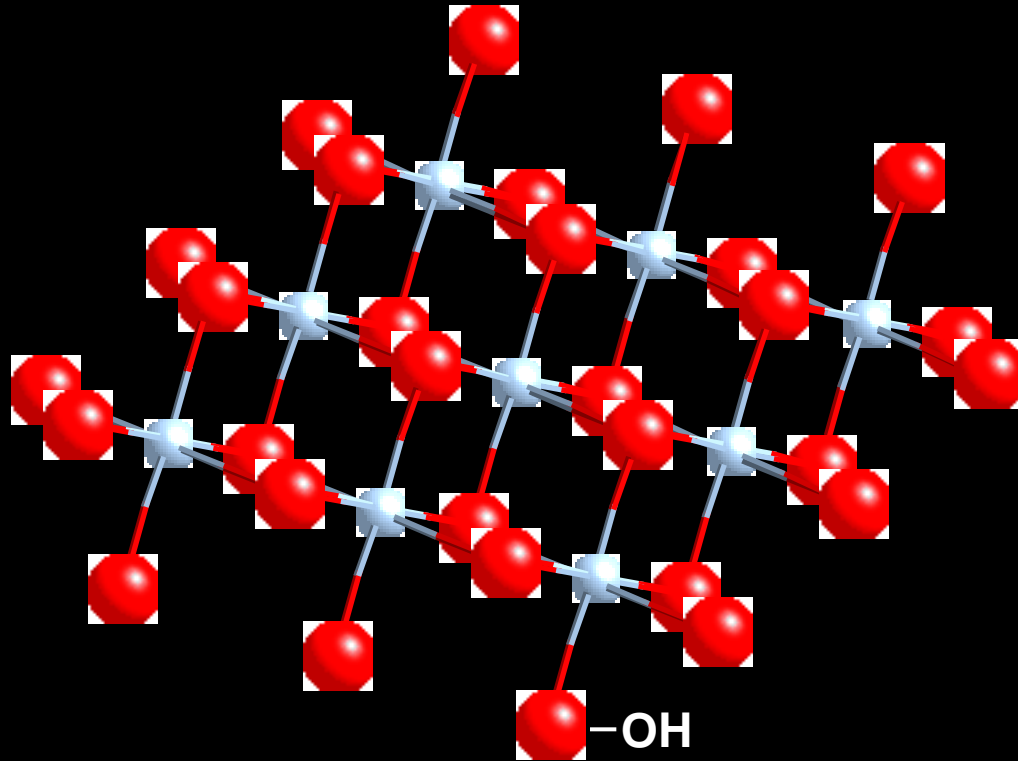
$\text{Al}(\text{OH})_6$ or $\text{Mg}(\text{OH})_6$ Octahedra



JOIN OCTAHEDRA

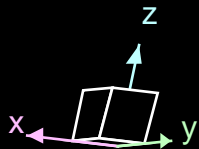
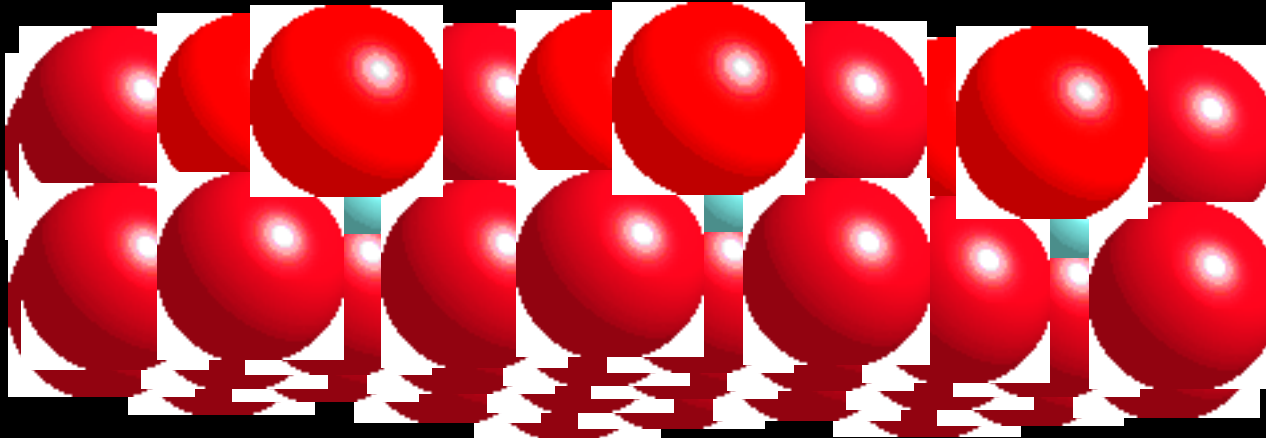


OCTAHEDRAL SHEET



OCTAHEDRAL SHEET

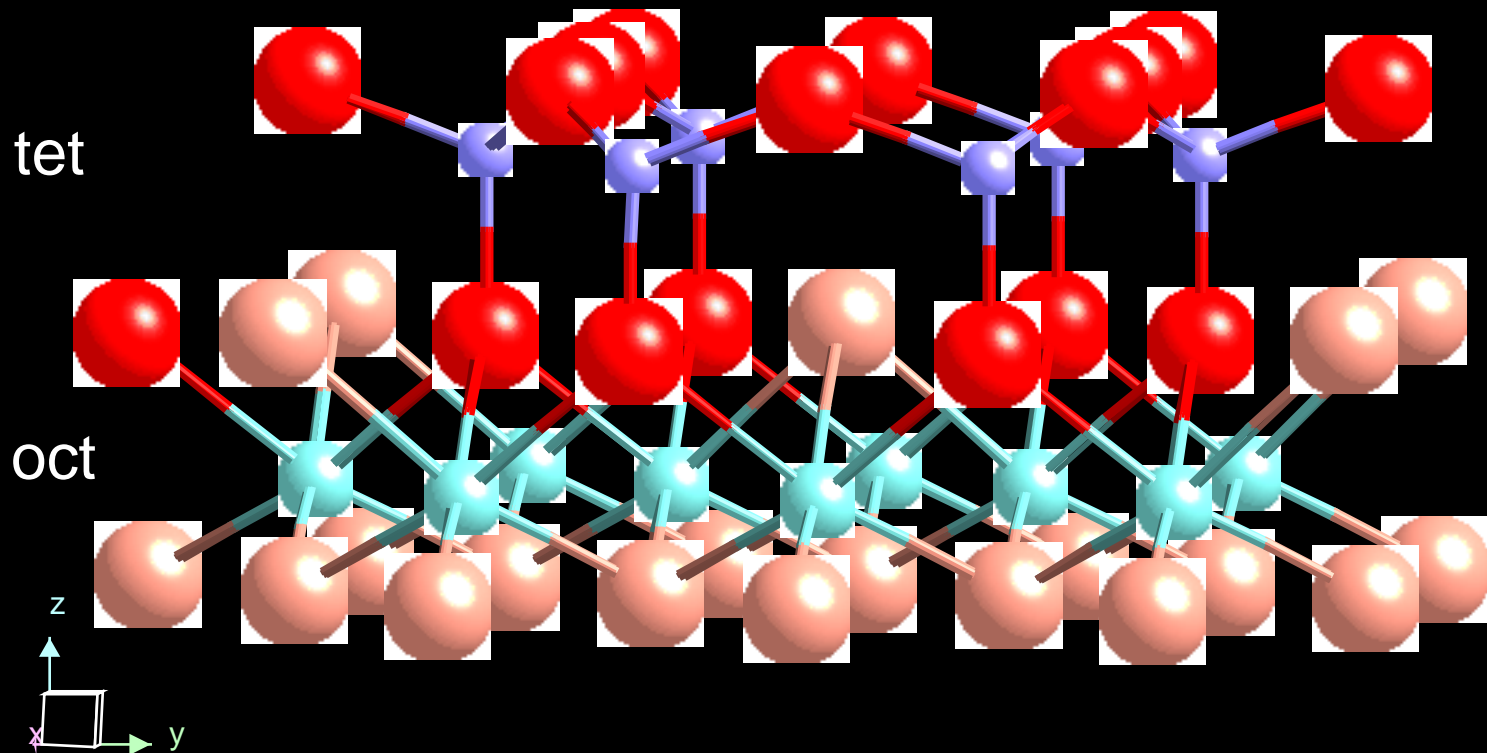
(di)OCTAHEDRAL SITE FILLING
Complete Dioctahedral Sheet



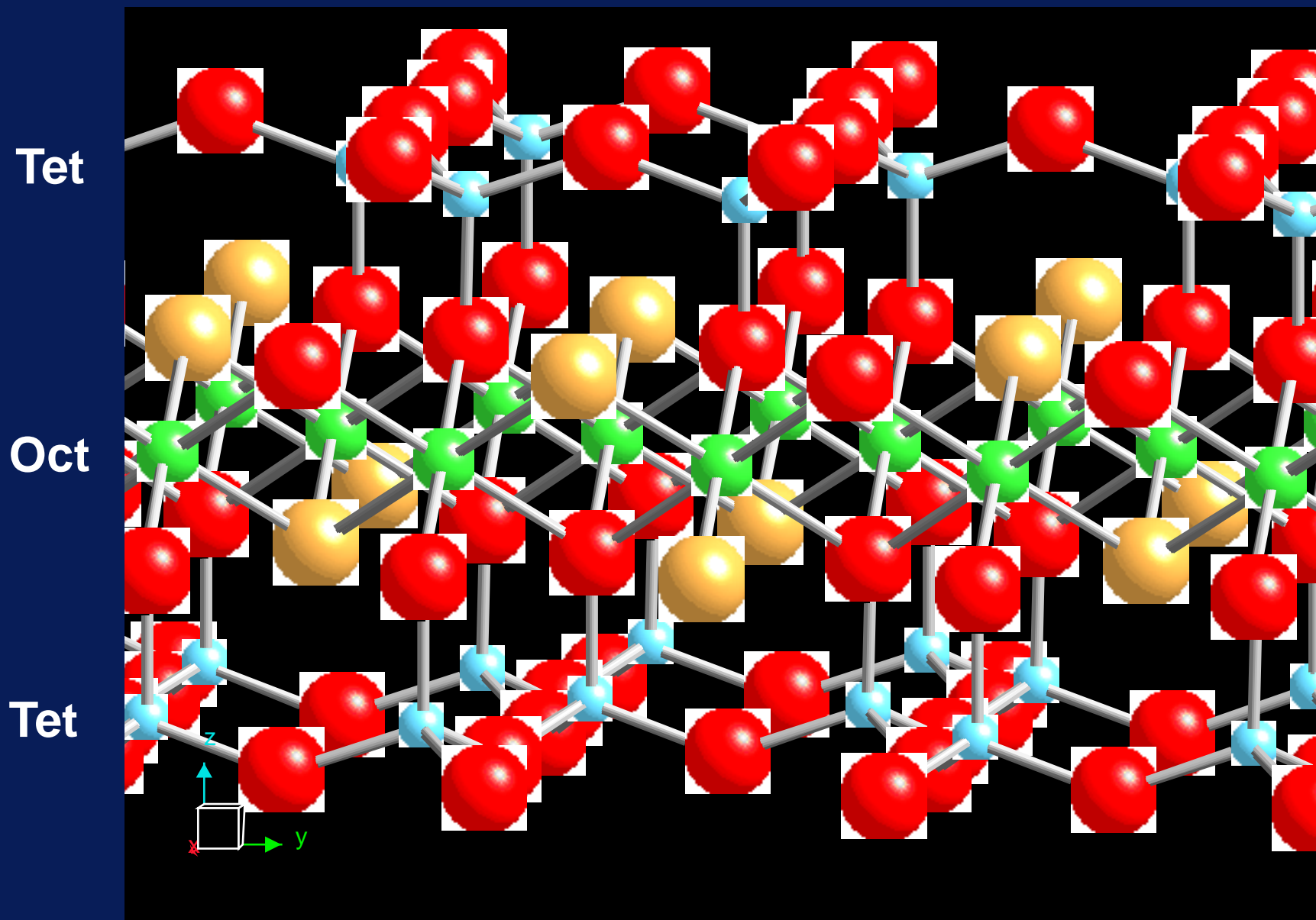
OCTAHEDRAL-TETRAHEDRAL LINKAGE

Sharing of Apical Oxygens in Tetrahedral Sheet with Hydroxyls of Octahedral Sheet

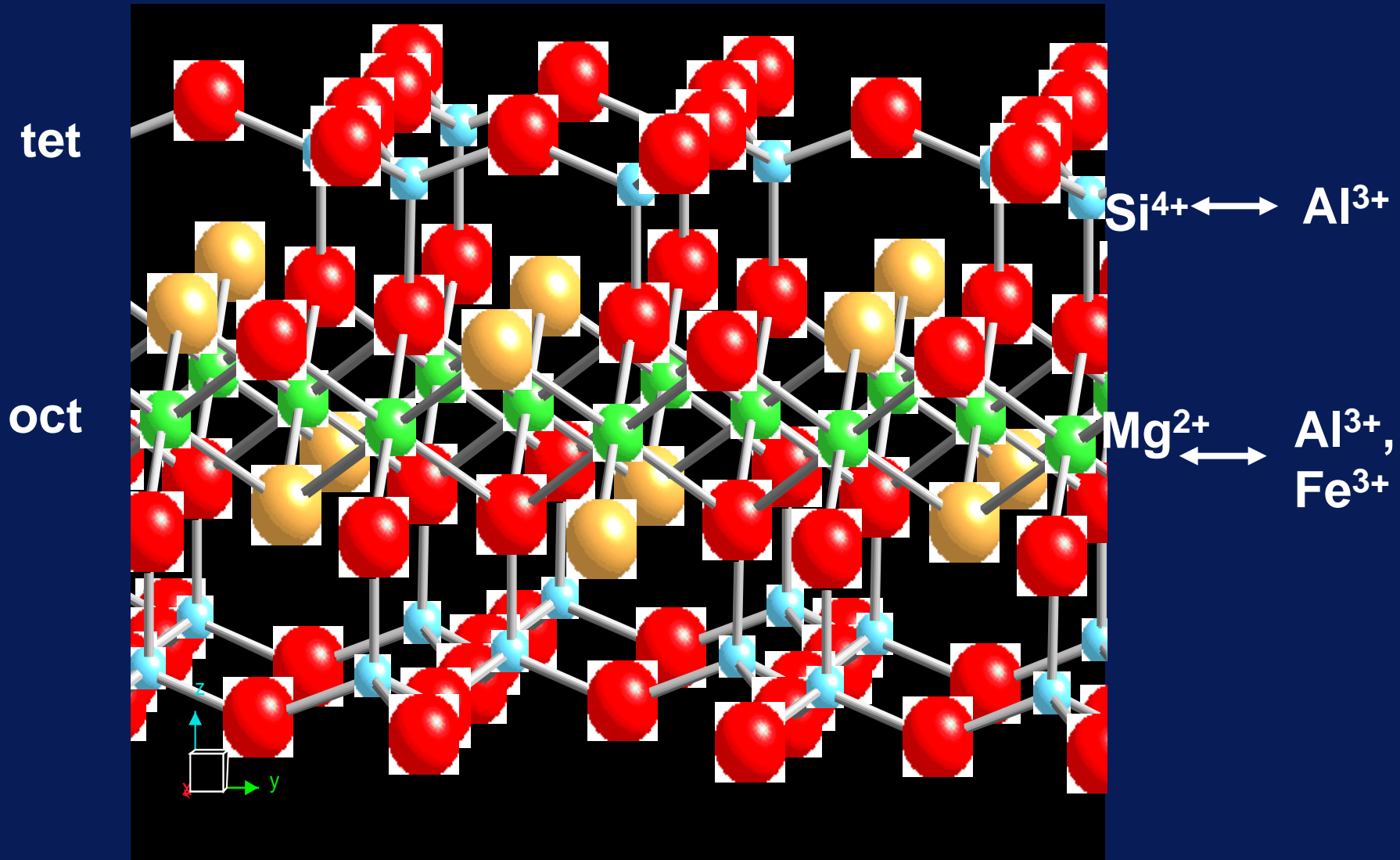
Serpentine (1:1 trioctahedral mineral)



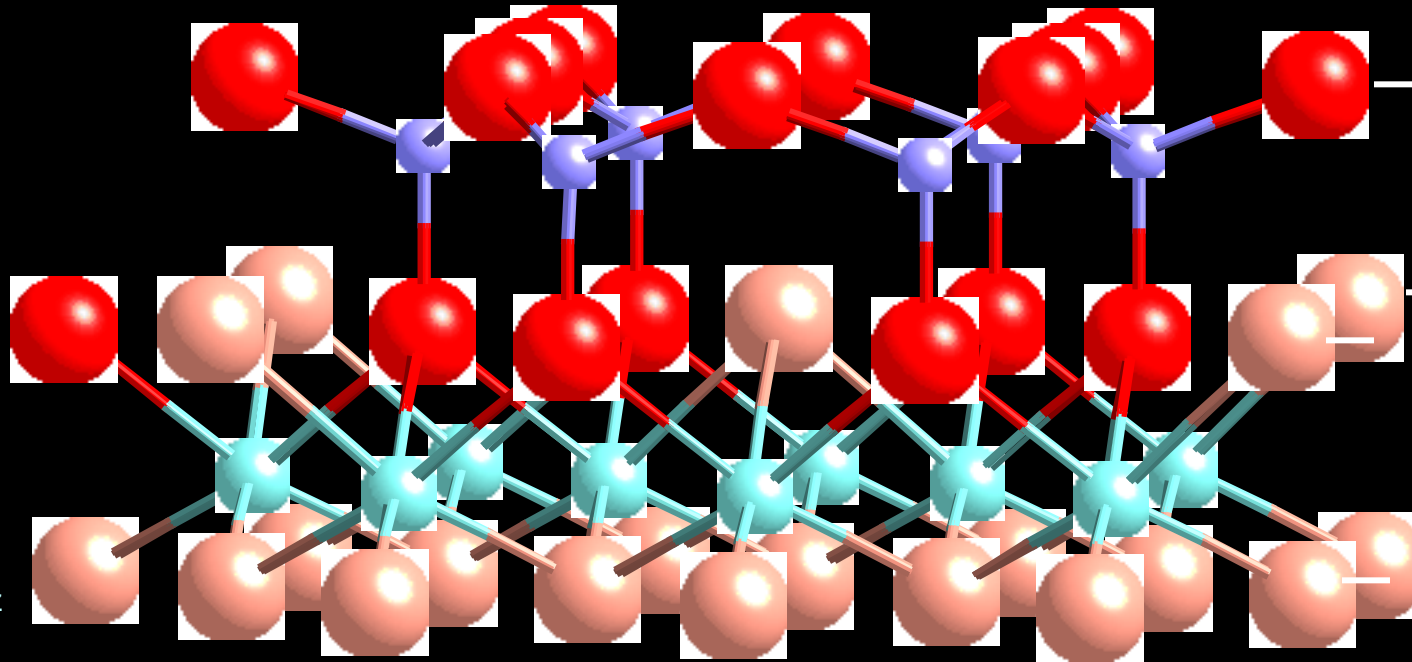
OCTAHEDRAL-TETRAHEDRAL LINKAGE



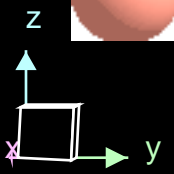
ISOMORPHIC SUBSTITUTION



SOURCE OF pH DEPENDENT CHARGES

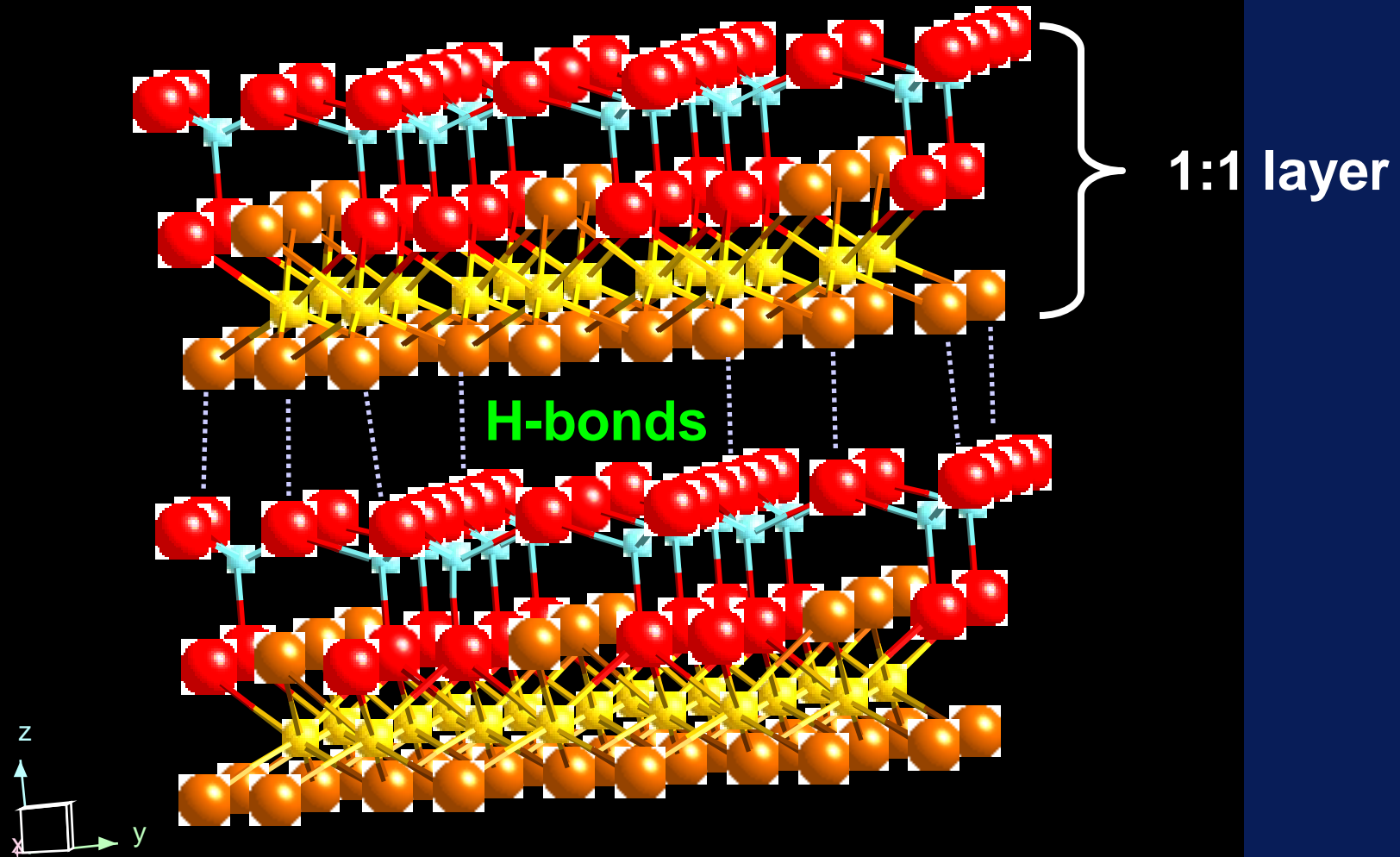


terminal
bonds



STABILITY OF 1:1 MINERALS

Serpentine (1:1 trioctahedral mineral)



MODEL OF THE 2:1 TYPE CLAY MONTMORILLONITE (A SMECTITE)

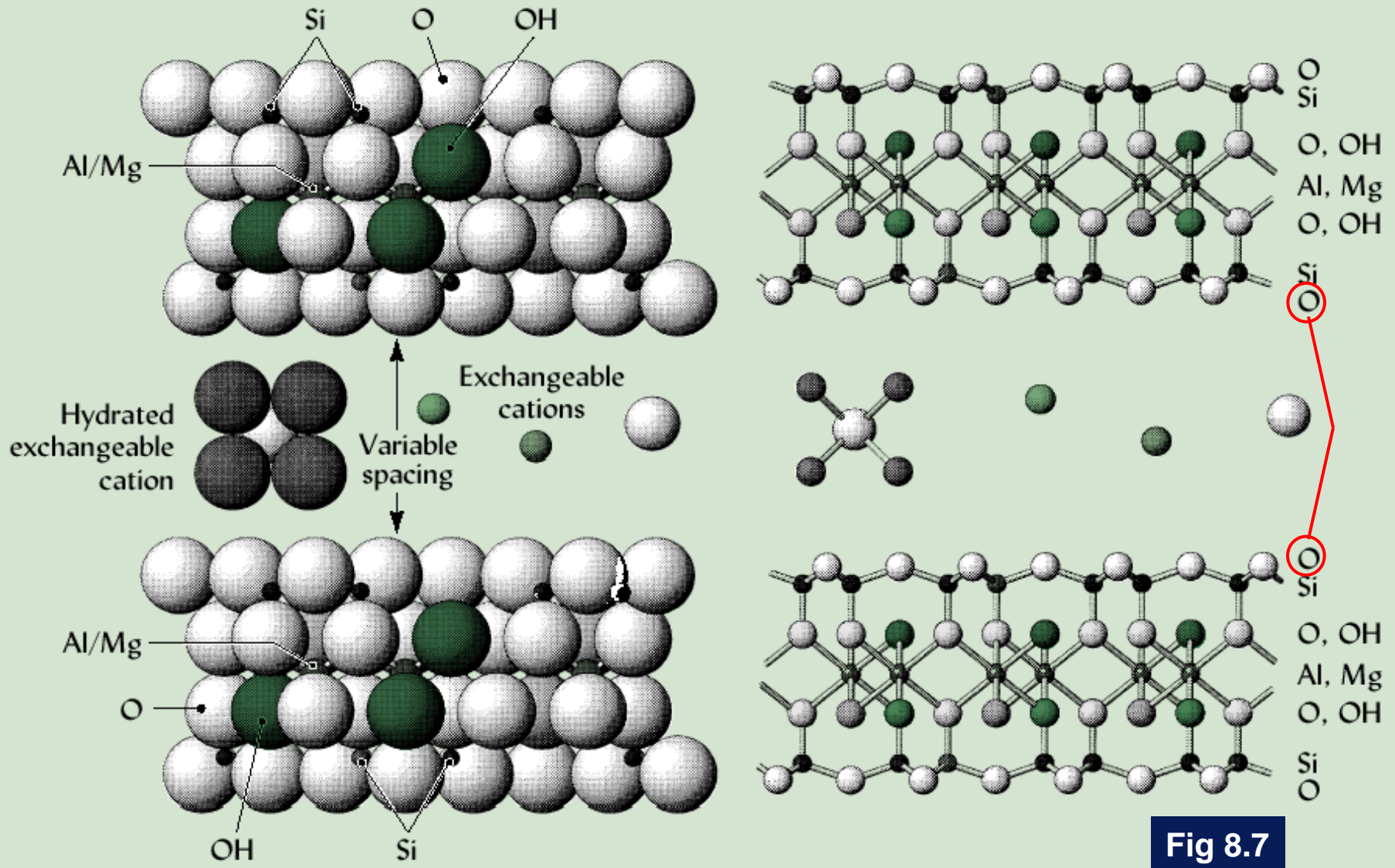


Fig 8.7

ORGANIZATION OF TETRAHEDRAL AND OCTAHEDRAL SHEETS

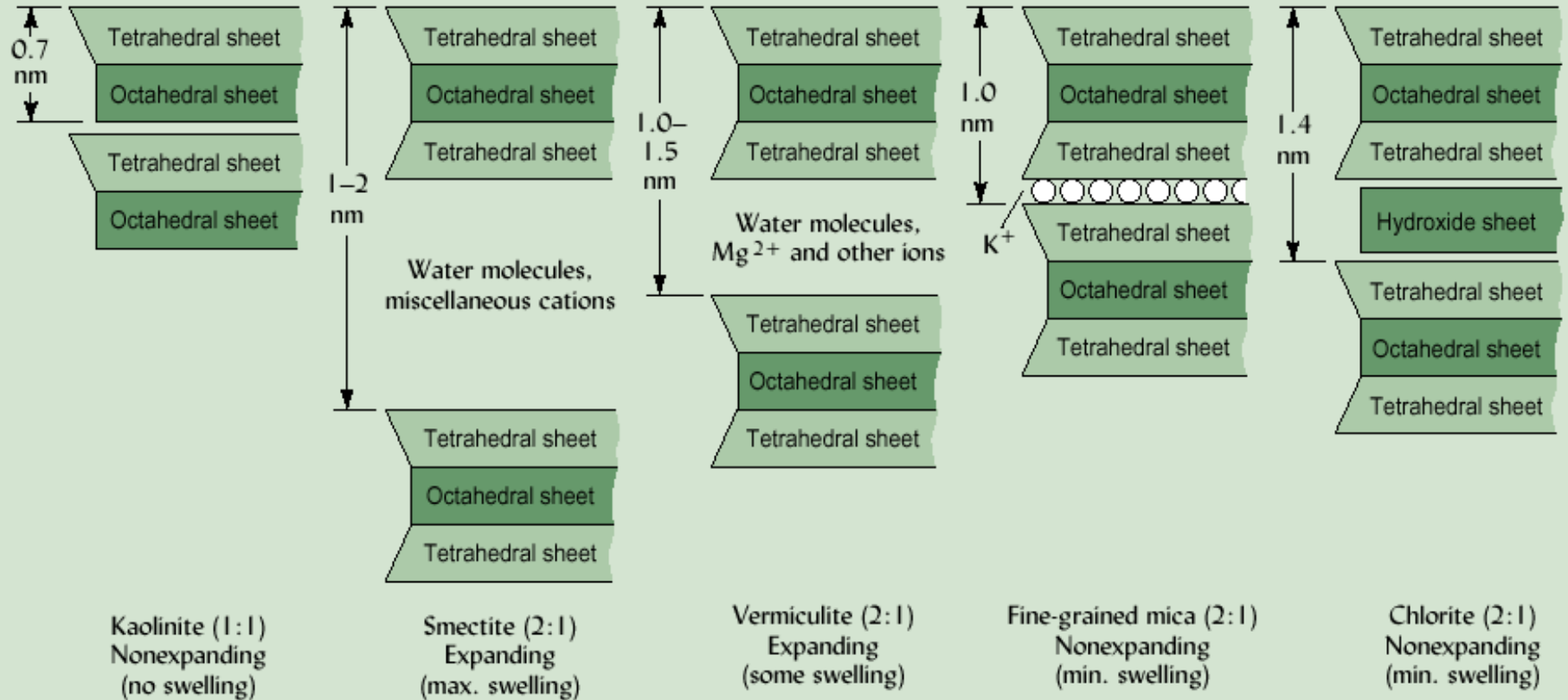
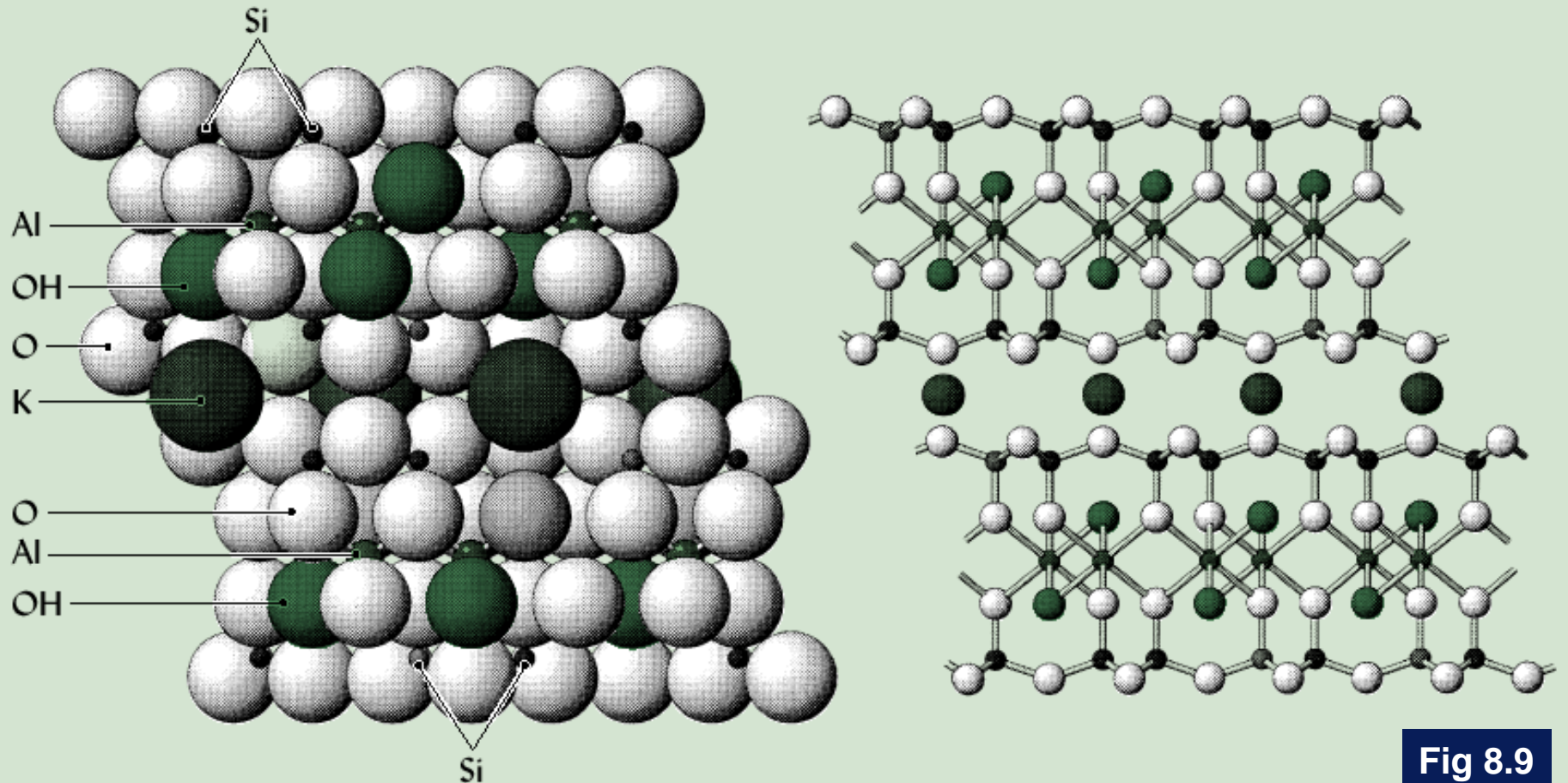


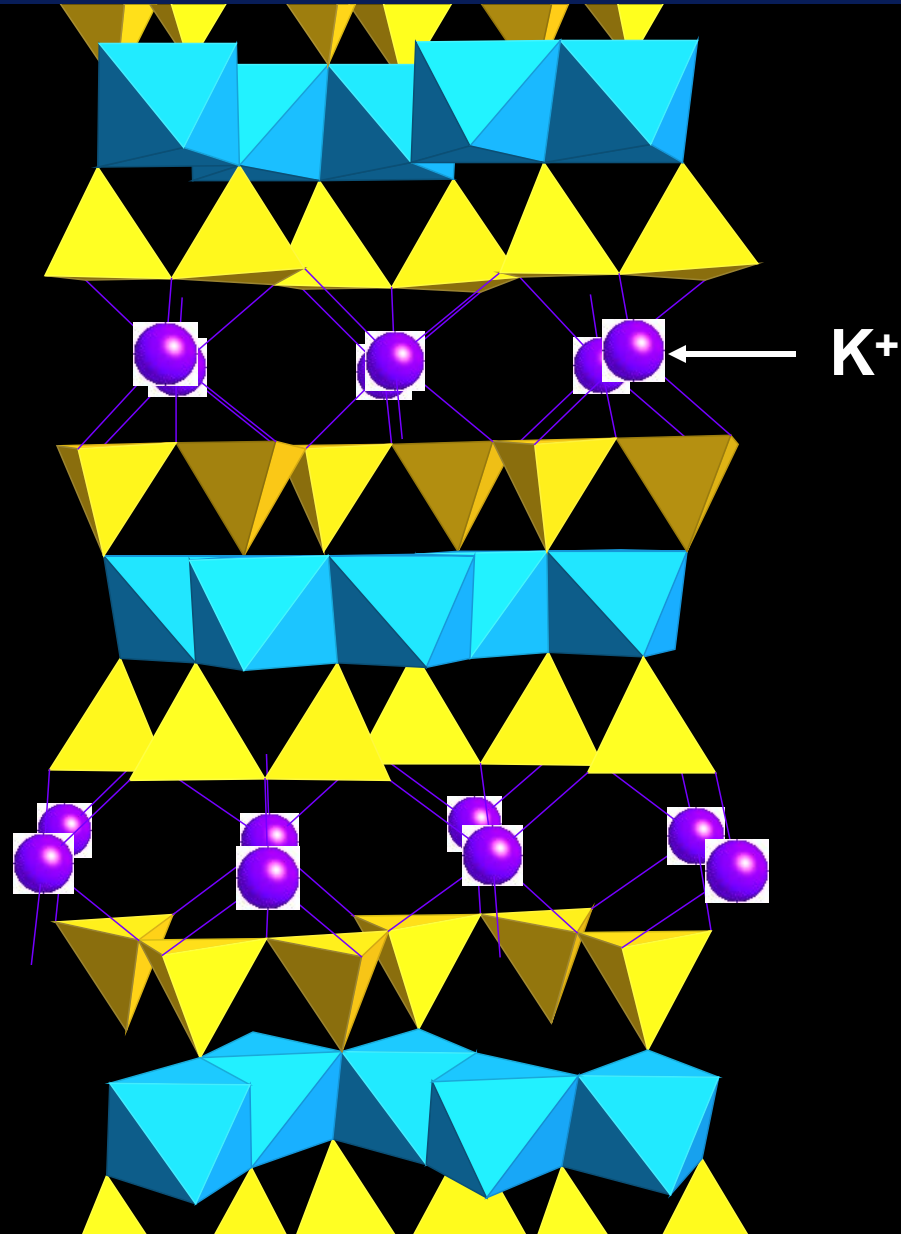
Illustration of the organization of tetrahedral and octahedral sheets in one 1:1 type and four 2:1 type clay minerals (Fig. 8.8)

POTASSIUM FIXATION



Model of a 2:1 nonexpanding lattice mineral of the fine grained mica group.

MICA SHEET WITH K^+



STRUCTURAL CHARACTERISTIC OF NONSILICATE COLLOIDS

Fe & Al oxides:

- Generally modified octahedral sheets
- Either Fe^{+3} or Al^{+3} in the cation positions
- Small amount of positive charge
- Gibbsite, $\text{Al}(\text{OH})_3$, is most common soil Al oxide
- Goethite, FeOOH , & ferrihydrite, Fe_2O_3 are common soil Fe oxides

STRUCTURAL CHARACTERISTIC OF NONSILICATE COLLOIDS

Humus:

- **Noncrystalline organic substance consisting of high MW molecules with variable composition**
- **Complex structure, major similarities of material from around the globe**
- **Generally: C = 40-60%; O = 30-50%; H = 3-7%; N = 1-5%**
- **Major component is humic acid, MW = 10,000-100,000 g/mol**
- **Large net negative charge (both + & - charges present)**
- **Contains both hydrophobic & hydrophilic sites**

GENESIS & GEOGRAPHIC DISTRIBUTION OF SOIL COLLOIDS

Silicate Clays:

Silicate clays are formed in soils by two processes:

- **Alteration:**

- minerals such as muscovite are altered by weathering processes
- resulting colloid is a 2:1 type clay

- **Recrystallization:**

- minerals are completely broken down and new minerals are formed by recrystallization of the weathering products

GENESIS & GEOGRAPHIC DISTRIBUTION OF SOIL COLLOIDS

Silicate clays (continued):

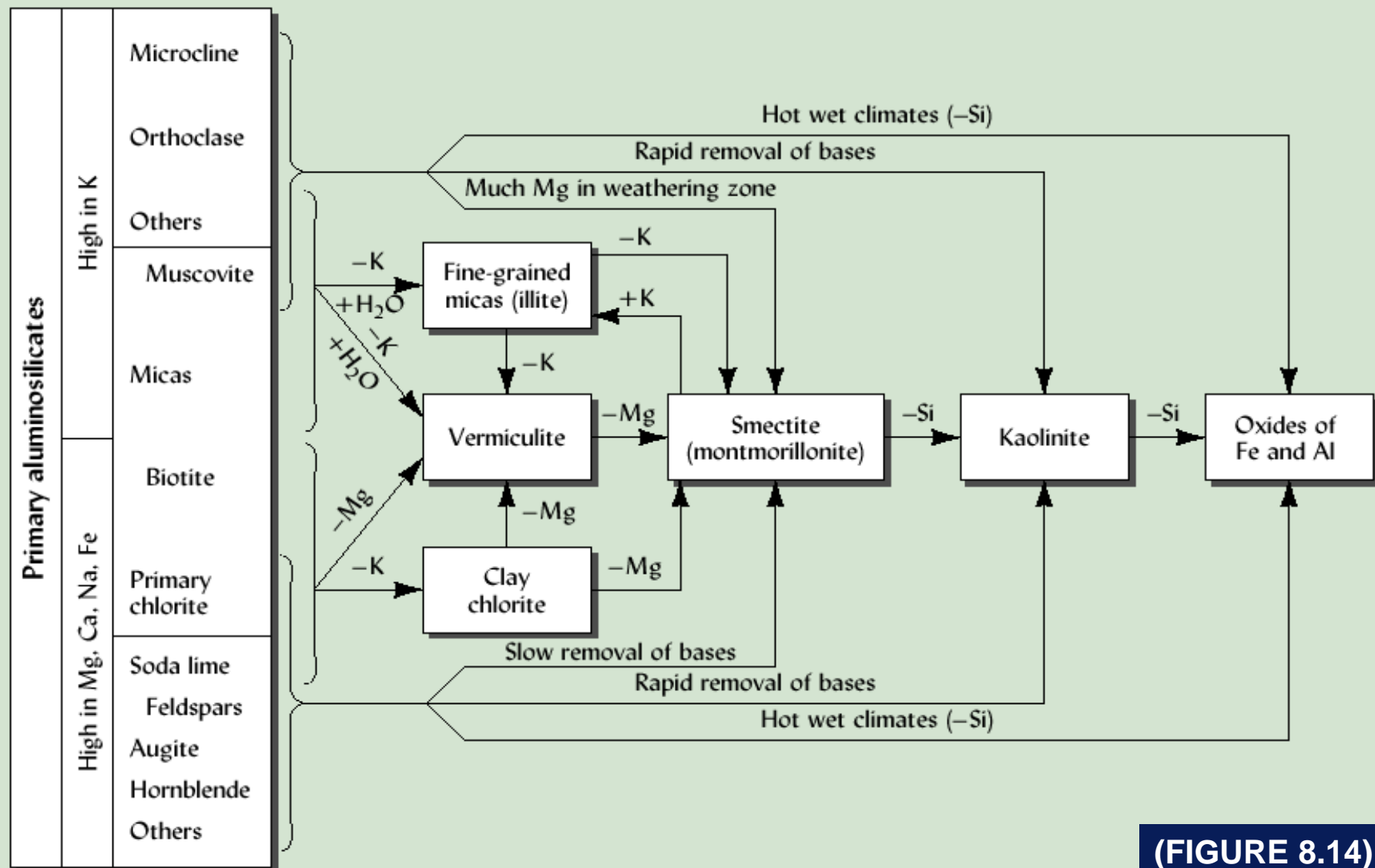
Relative stages of weathering:

- differing degrees of susceptibility to weathering of various minerals
- can identify relative degree of profile weathering by suite of minerals present (see FIGURE 8.14)

Genesis of individual silicate clays:

- muscovite, biotite \Rightarrow fine-grained micas, chlorite, vermiculite
- fine-grained micas, chlorite \Rightarrow vermiculite, smectite
- recrystallization (alkaline) \Rightarrow smectite
- recrystallization (acid) \Rightarrow kaolinite

FORMATION OF VARIOUS LAYER SILICATE CLAYS AND OXIDES OF FE & AL



(FIGURE 8.14)

GENESIS & GEOGRAPHIC DISTRIBUTION OF SOIL COLLOIDS

Mixed and interstratified layers:

- weathering is a gradual process and many partially altered products may be present
- K^+ leached from some layers may be replaced by Ca^{++} , Mg^{++} & $H_2O \Rightarrow$ mixture of properties to form a fine-grained mica-vermiculite
- others: chlorite-vermiculite; vermiculite-smectite

Iron & aluminum oxides:

- Goethite ($FeOOH$) dominant in most soils
- Hematite (Fe_2O_3) forms under drier, warmer conditions
- Gibbsite (Al_2O_3) forms where Si is removed via acid leaching

GENESIS & GEOGRAPHIC DISTRIBUTION OF SOIL COLLOIDS

Allophane and imogolite:

- Poorly crystalline materials produced from Al and Si hydroxide gels
- Significant positive charges - binds anions, OM

Geographic distribution of clays:

- Related to parent material & climate
- See FIGURE 8.16

Soil order differences:

- Related to weathering intensity reflected by soil order
- Alfisols, Mollisols, Vertisols - more 2:1 clay types
- Ultisols, Oxisols - more 1:1 clays and Al, Fe oxides

SOURCES OF CHARGES ON SOIL COLLOIDS

Constant charges: (from isomorphous substitution)

Negative charges:

- substitution of lower charged ion for higher charged ion (Mg^{+2} for Al^{+3} ; Al^{+3} for Si^{+4})

Positive charges:

- substitution of higher charged ion for lower charged ion (Al^{+3} for Mg^{+2} ; Al^{+3} for Fe^{+2})

pH-dependent charges: (associated with -OH groups)

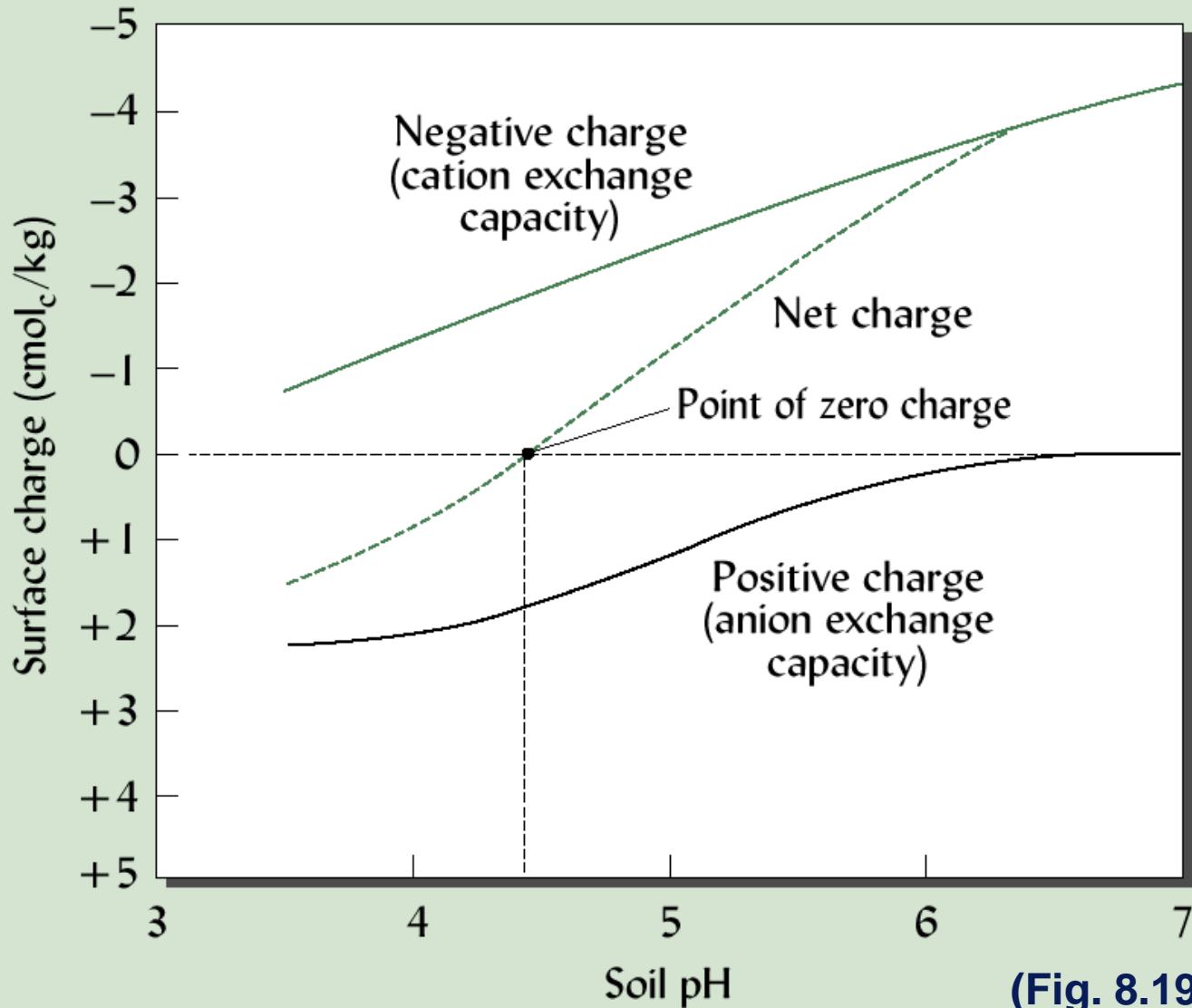
Negative charges:



Positive charges:

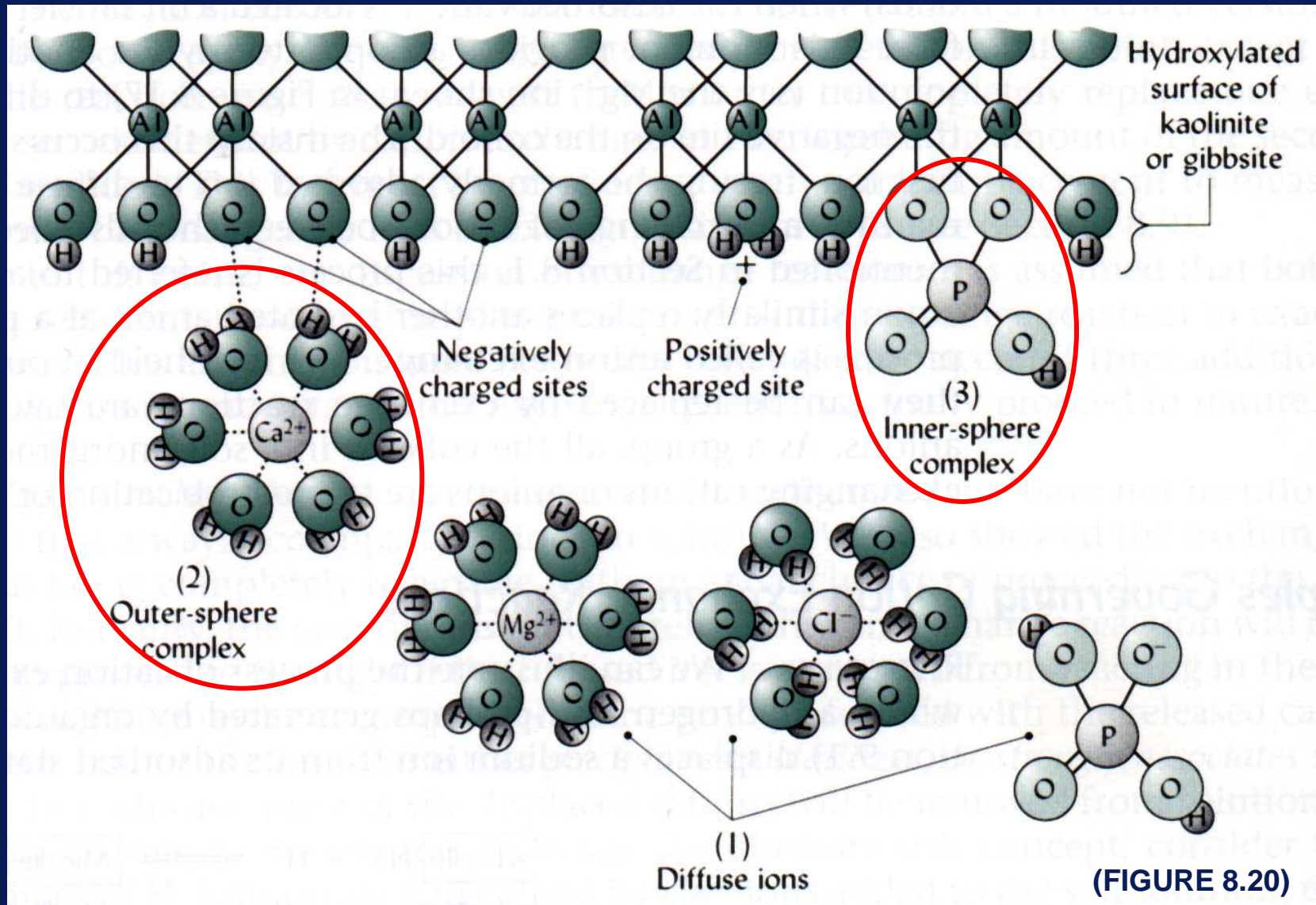


Relationship between soil pH and positive and negative charges on an Oxisol surface horizon



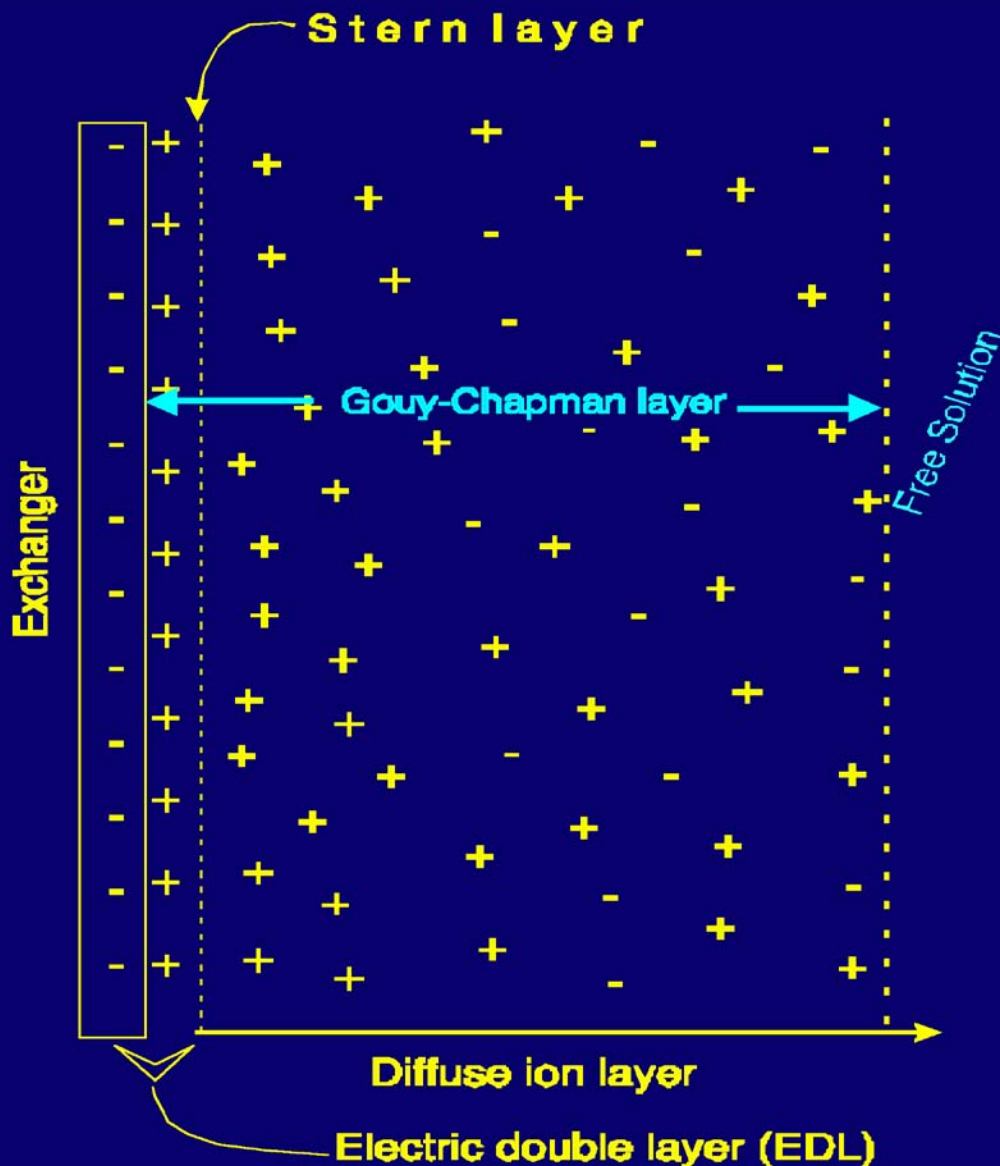
(Fig. 8.19)

ADSORPTION OF CATIONS AND ANIONS

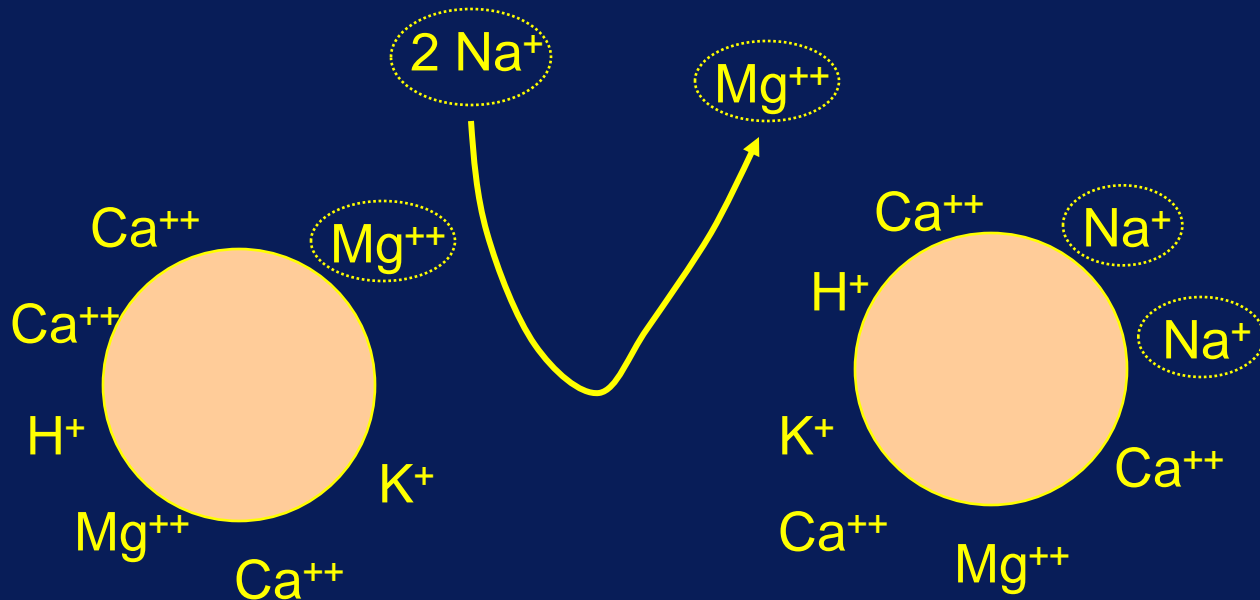


(FIGURE 8.20)

IONIC DISTRIBUTION AWAY FROM A NEGATIVELY CHARGED SURFACE



CATION EXCHANGE REACTIONS



Principle of Cation Exchange: Mg^{++} is Replaced by Na^+

CATION EXCHANGE REACTIONS

Principles governing cation exchange reactions:

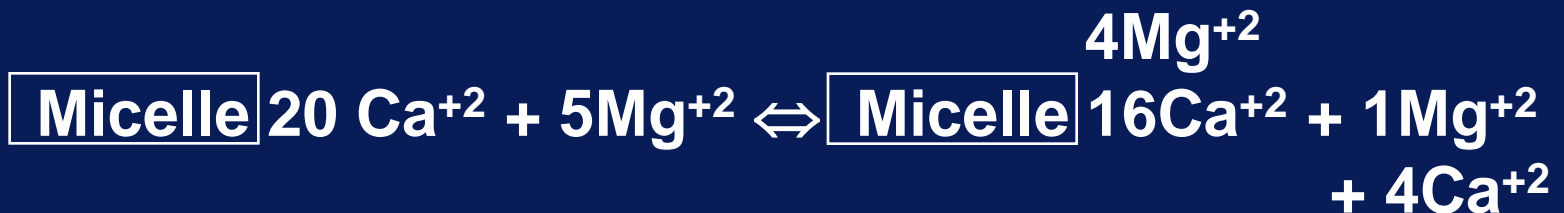
Reversibility:



Charge equivalence:



Ratio law:



Ratio: 4Ca:1Mg

CATION EXCHANGE REACTIONS

Principles governing cation exchange reactions:

Anion effects on mass action:

- an exchange reaction will be more likely to proceed to the right if released ion is prevented from reacting in the reverse direction
- processes which accomplish this are precipitation, volatilization and strong association with an anion

Cation selectivity: $\text{Al}^{+3} > \text{Ca}^{+2} > \text{Mg}^{+2} > \text{K}^{+}=\text{NH}_4^{+} > \text{Na}^{+}$

Complimentary cations:

- in complex mixture of ions, likelihood of displacement of an ion depends on strength of sorption of ion **and** neighboring ions

CATION EXCHANGE CAPACITY

Means of expression:

- the CEC is expressed as the number of moles of positive charge adsorbed per unit mass
 - units:-centimoles of charge per kilogram (cmol_c/kg)
 - milliequivalents per 100g ($\text{me}/100 \text{ g}$)
- *numerical values of these two are the same***

Methods of determining CEC:

Buffer CEC methods - NH_4OAc at $\text{pH} = 7$
(acetate solutions) - BaOAc at $\text{pH} = 8.2$

Effective CEC (unbuffered)- measure at actual soil pH , using unbuffered salt (NH_4Cl , CaCl_2)

CATION EXCHANGE CAPACITY

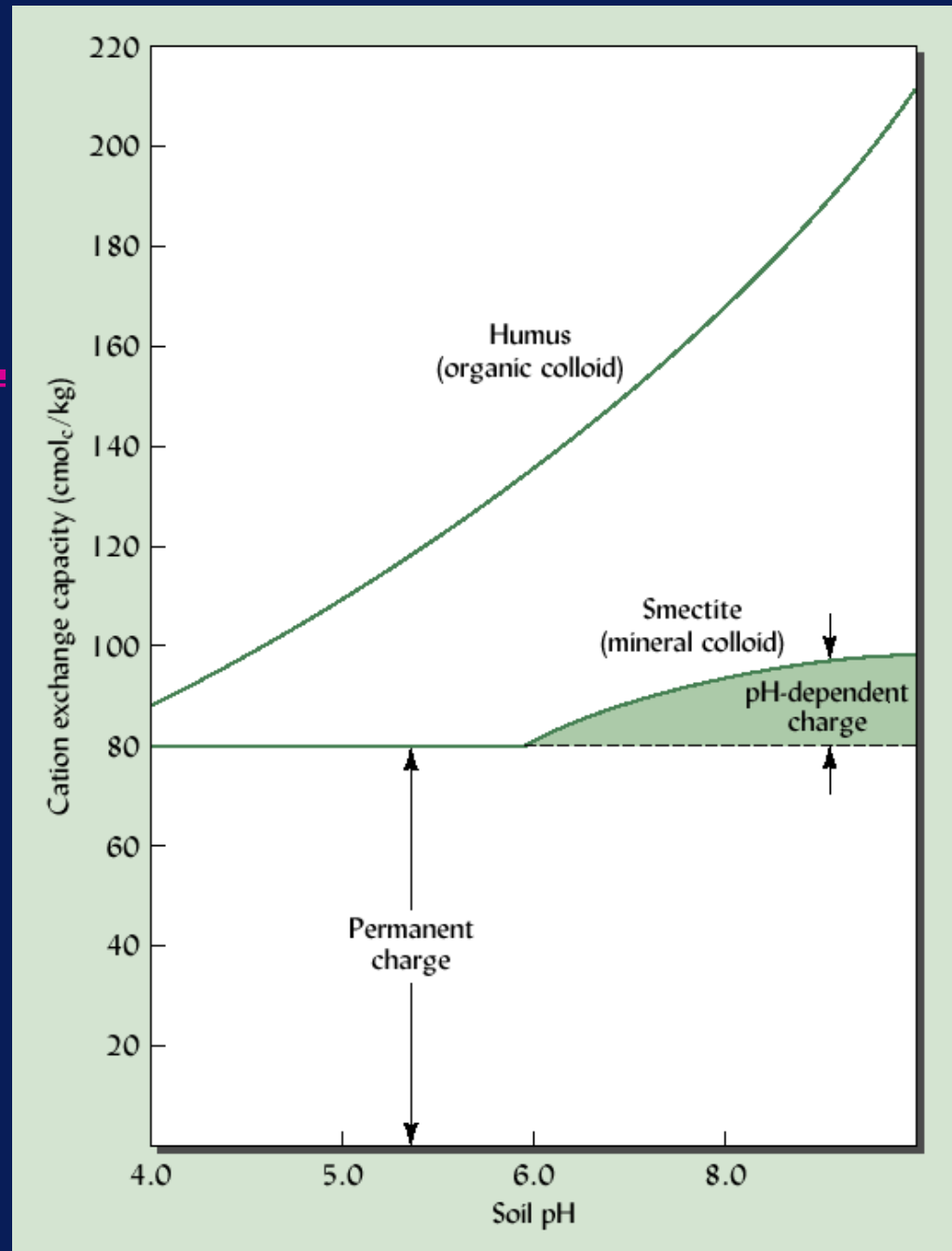
Cation exchange capacities of soils:

- CEC of a given soil is a function of the CEC of each of the colloids present
- Can generalize CECs of soil orders by evaluating types and amounts of colloids present
- See Figure 8.23 & Table 8.7
- Soil pH has strong influence on CEC (Figure 8.25)
 - low pH, low CEC
 - high pH, higher CEC

Influence of pH on the cation exchange capacity of smectite and humus.

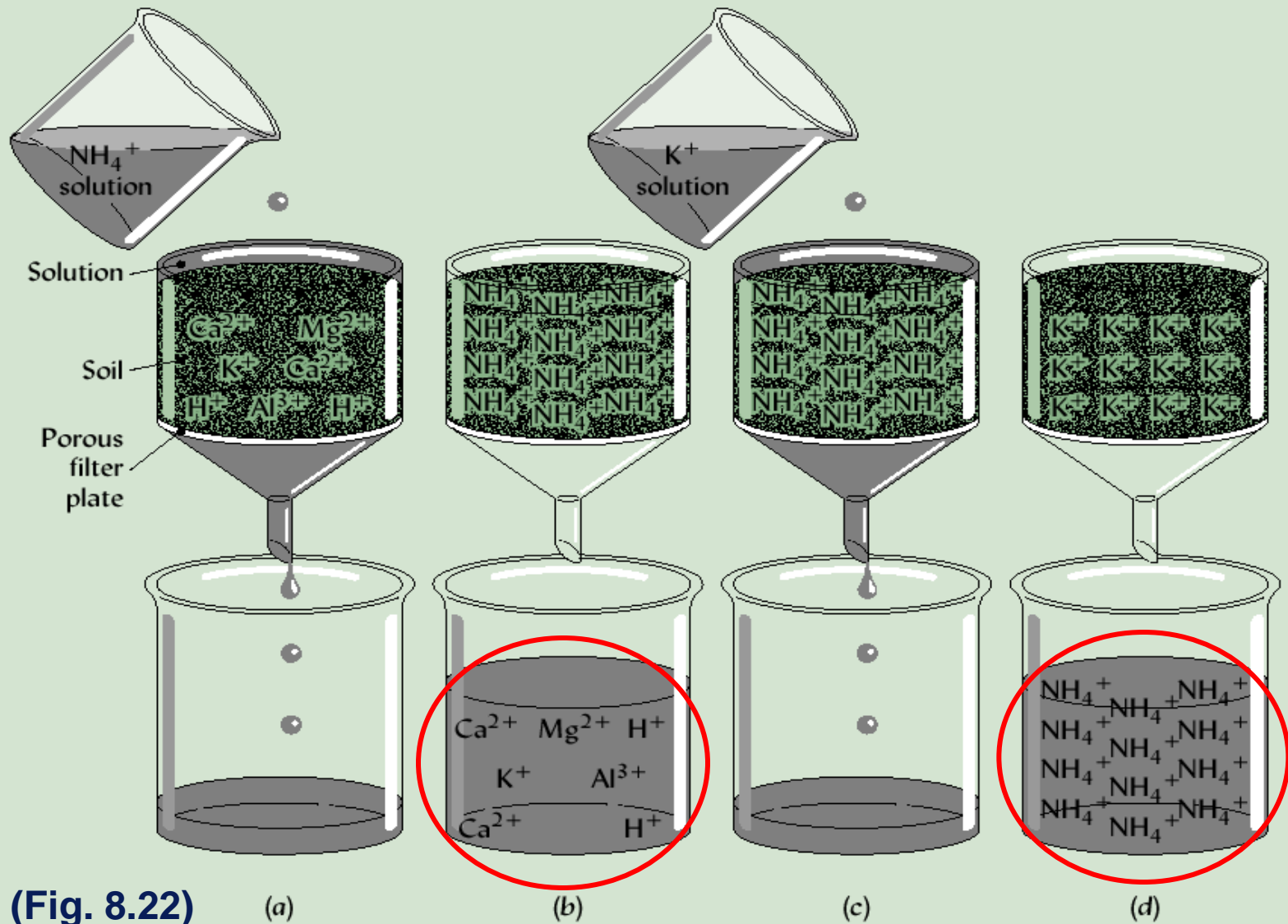
Below pH 6.0 the charge for the clay mineral is relatively constant (permanent).

A small amount of the charge on the clay and all charges on humus are pH dependent.



(Fig. 8.25)

Illustration of a method for determining cation exchange capacity of soils



(Fig. 8.22)

(a)

(b)

(c)

(d)

REPRESENTATIVE CATION EXCHANGE CAPACITIES OF COMMON MATERIALS IN SOILS (pH 7.0)

Exchanger (Soil Phase)	Cation Exchange Capacity (CEC) Cmols kg ⁻¹
Organic matter	100 - 300
Vermiculite	100 - 150
Allophane	100 - 150
Smectite (montmorillonite)	60 - 100
Chlorite	20 - 40
Illite	20 - 40
Kaolonite	2 - 16
Hydrous oxides	2 - 8

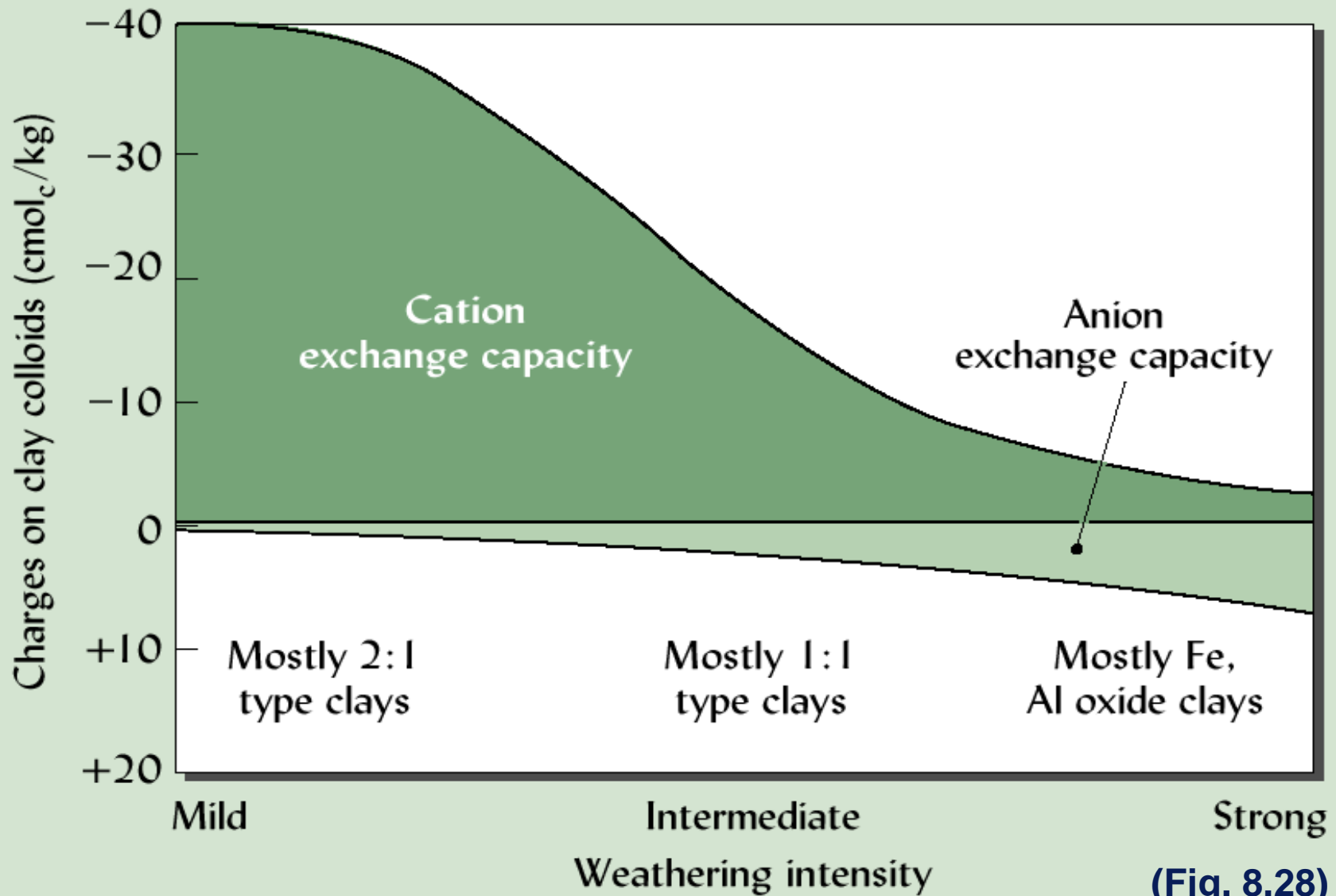
EXCHANGEABLE CATIONS IN FIELD SOILS

- **Percentage cation saturation - % of CEC sat'd by given cation**
- **Percent base saturation - % of CEC sat'd by Ca, Mg, K, Na**
- **Higher nutrient availability when % sat'n is high**
- **Complimentary cations effect availability of given cation; related to strength of sorption**
- **Type of colloid affects ease of exchange:**
 - **smectites have high charge densities and strongly bind sorbed cations; kaolinite binds less strongly**

ANION EXCHANGE

- **Anions held to colloids by two major means:**
 - **anion adsorption (parallel to cation adsorption)**
 - **formation of inner sphere complexes:**
 - **P ($-\text{PO}_4^{-3}$) attached by partial covalent bonding to colloid (see Figure 8.20)**
- **As soils weather, CEC generally decreases and AEC increases (Figure 8.28- mild vs strong weathering conditions)**

The effect of weathering intensity on the charges of clay minerals and their CECs and AECs



(Fig. 8.28)

SORPTION OF PESTICIDES & GROUNDWATER CONTAMINATION

- Pesticides are sorbed to (mostly) organic colloids by a process termed **partitioning**
- Most pesticides are hydrophobic and sorb weakly to moist silicate clays
- Can sorb large organic cations to silicate clays to form **organoclays** which will then sorb pesticides (these are used in water remediation)
- Soil distribution coefficient, K_d

$$K_d = \text{mg chem sorbed/kg soil} \div \text{mg chem/L sol'n}$$

$$K_{oc} = \text{mg chem sorbed/kg OC} \div \text{mg chem/L sol'n}$$

BINDING OF BIOMOLECULES TO CLAY & HUMUS

- **The enormous surface area & charged sites on colloids attract & bind many biologically active substances:**
 - **DNA, enzymes, proteins, toxins, viruses**
 - **binding takes place rapidly after addition**
- **Bound substances are protected from enzymatic attack**
- **Many of these substances retain their biological activity**
- **These substances may persist in soil for long periods of time**
 - **implications for persistence of short-lived toxins and genetically modified materials**

PHYSICAL IMPLICATIONS OF SWELLING-TYPE CLAYS

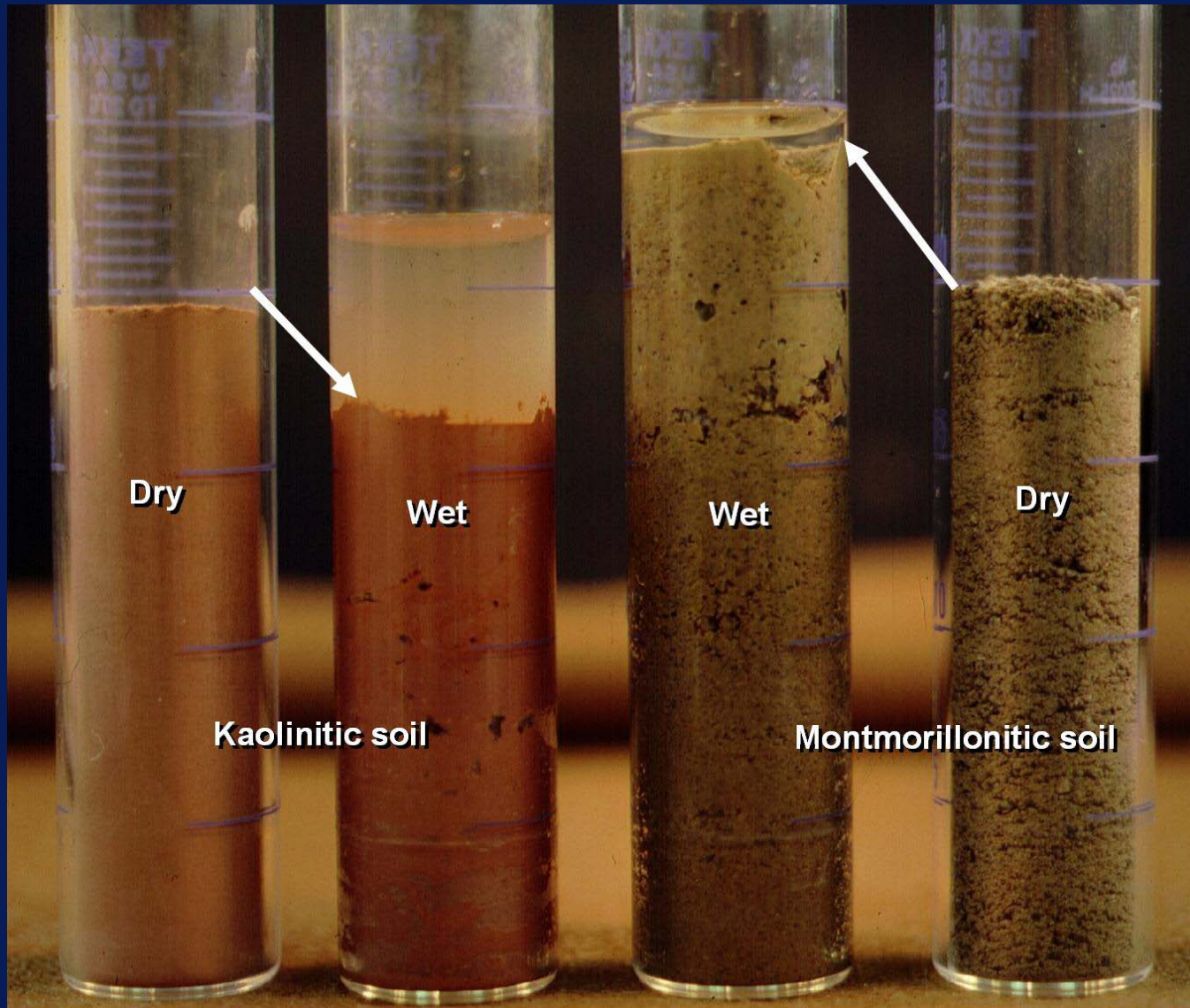
Engineering hazards:

- damage to roads, buildings, pipelines
- most problem with smectitic clays
- can move to different location; use pilings

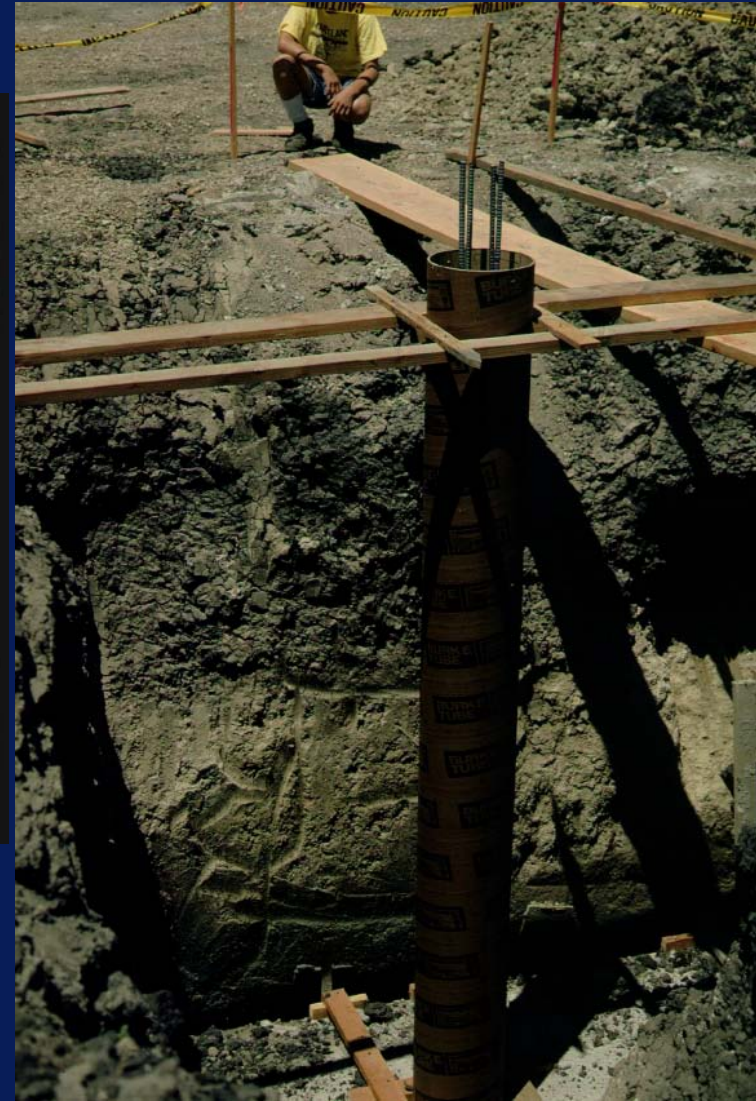
Environmental uses:

- in liners to seal ponds, lagoons, landfills
- around monitoring wells to prevent downward or upward leakage
- injected slurry wall to stop migration of contaminated groundwater
- organoclays for contaminant removal

Response of two soil types to addition of water



Support pilings for houses built on expansive soils



(Figure 8.33a, b)

Use of bentonite as seal for an environmental monitoring well

