

Soil Colloids and Cation Exchange Capacity

Chapter 8
p. 316-362

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What should you know?

- Soil colloids - what they are, their properties
- Differences between soil clay minerals
- Properties of humic substances (active organic matter)
- Cation exchange and CEC

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Colloids

- Very small, chemically surface reactive particles
- Usually $< 1 \mu\text{m}$ diameter
- Very high surface area per unit mass (specific surface area)
- Common examples of colloidal suspensions
 - Jello
 - Milk

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Characteristics of Soil Colloids

- High surface area
 - Smectites & vermiculites: $1 \text{ g} = 800 \text{ m}^2$
 - Range: $10 - 800 \text{ m}^2 \text{ g}^{-1}$
- Electrically charged surface
 - Usually net negative surface charge
 - In low pH soils dominated by sesquioxides, allophane, imogolite, surfaces may be net positive

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Types of Soil Colloids

- Silicate clays
 - Aluminosilicate minerals
 - Crystalline and poorly crystalline types
- Humic substances
- Al and Fe oxides, hydroxides, and oxyhydroxides
 - Sesquioxides
 - Amorphous (gel-like), poorly crystalline

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What is Clay?

- Soil particle-size
 - $< 0.002 \text{ mm}$ ($< 2 \mu\text{m}$)
- Soil textural class
- A class of silicate minerals
 - The clay minerals: *phyllosilicates* or *layer silicates* or *sheet silicates*

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Origin of the Clay Minerals

- Secondary minerals formed by the:
 - Alteration of primary phyllosilicates (structure is inherited)
 - Modification of other complex silicates (e.g., feldspars, amphiboles, pyroxenes) by *neof ormation*
- They may form
 - In place: *authigenic (pedogenic)*
 - Deposited prior to soil formation: *detrital*

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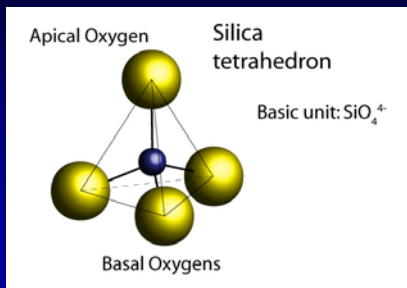
Layer Silicate Clay Minerals

- Aluminosilicate minerals
- Crystalline structure
- Structural units
 - Silicon (Si^{4+}) tetrahedral units
 - Aluminum (Al^{3+}), magnesium (Mg^{2+}), and iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$) octahedral units
 - Individual units linked into SHEETS
 - Sheets are combined in LAYERS
 - Many layers = crystal structure or CLAY MICELLE

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The Si Tetrahedron (4 sides)

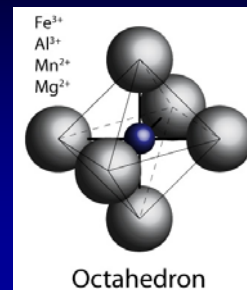
Si^{4+} coordinated with 4 O^{2-} : a net charge of -4



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The Al & Mg Octahedron (8 sides)

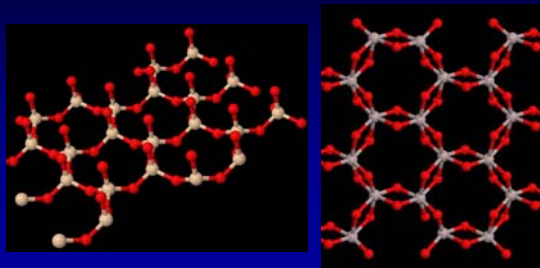
Al^{3+} (or Mg^{2+}) coordinated with 6 OH^- : a net charge of -3 (or -4)



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Si and Al Sheets

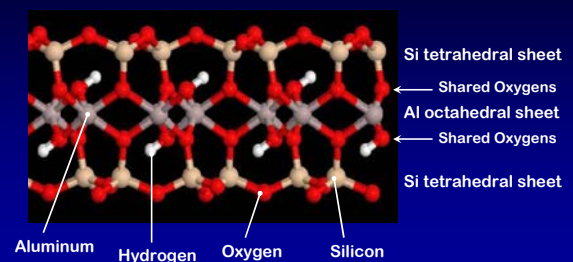
Individual tetrahedral and octahedral units are linked to form *sheets*



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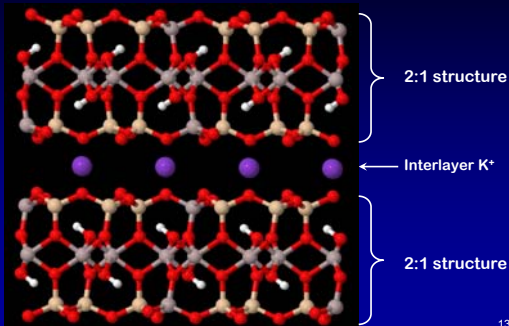
Al & Si sheets are Linked to Form *Layers*

Example: 2:1



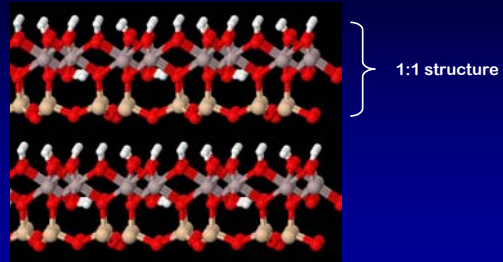
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Layers are Linked to Form **2:1 Minerals** Muscovite Mica



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Layers are Linked to Form **1:1 Minerals** Kaolinite



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Sources of Charge on Clay Minerals

pH dependent charge (charge is a function of solution chemistry)

- Dissociable -OH groups (weak acids)
- As pH increases, deprotonation increases
- Occurs at crystal edges
 - $\equiv\text{SiOH}^0 \rightarrow \equiv\text{SiO}^- + \text{H}^+$
 - $\equiv\text{AlOH}^0 \rightarrow \equiv\text{AlO}^- + \text{H}^+$
 - $\equiv\text{AlOH}^0 + \text{H}^+ \rightarrow \equiv\text{AlOH}_2^+$
- Surfaces that develop pH-dependent charge are called **amphoteric** if they can be either + or - depending on pH

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Source of Charge on Clay Minerals

- Permanent (structural) charge: from **isomorphous substitution**
- Occurs in 2:1 minerals **when they form**
- One element substitutes for another of similar size
 - Al³⁺ substitutes for Si⁴⁺ in the tetrahedral layer
 - Fe²⁺ or Mg²⁺ substitutes for Al³⁺ in the octahedral layer
- Because the substituting ion has lesser charge than the true charge-neutralizing ion, there is charge imbalance

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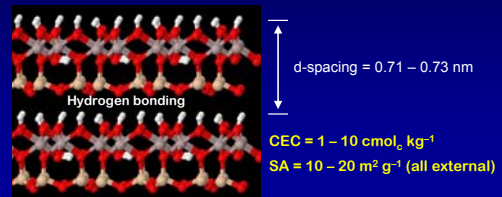
Classes of Silicate Clay Minerals

- Many different types: differentiation generally based on tetra:octa layer ratio and extent of isomorphous substitution (layer charge)
- 1:1 clays (no layer charge)
 - Kaolinites
- 2:1 non-expanding clays (high layer charge)
 - Micas (muscovite and biotite)
 - Illite
 - Chlorites
- 2:1 expanding clays
 - Intermediate layer charge: vermiculites
 - Low layer charge: smectites

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1:1 Phyllosilicates (Secondary)

- Ratio of Si to Al sheets is 1:1
- 1:1 layer attached to adjacent 1:1 layers by H-bonds (non-expansive)
 - No H₂O in the interlayer: **kaolinite**, Al₂Si₂O₅(OH)₄
 - H₂O in the interlayer: **halloysite**, Al₂Si₂O₅(OH)₄ • 2H₂O



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1:1 Characteristics

- Low surface area: 10 to 20 m² g⁻¹
- Low water holding capacity
- Pedogenic and common to moist, warm, weathered soils (kaolinite is present in almost all soils; halloysite present in volcanic soils)
- Low negative charge
 - Mostly pH dependent
 - Very little isomorphic substitution
 - < 10 cmol_c kg⁻¹

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2:1 Non-Expanding (Primary)

- Organization
 - Ratio of Si to Al sheets is 2:1
 - 2:1 layer attached to adjacent 2:1 layers by electrostatic forces (bridging cations)
 - K⁺ ions in the interlayer: *mica* minerals (& *illite*): *muscovite*, KAl₂(Si₃Al)O₁₀(OH)₂; *biotite*, K(Mg,Fe^{II})₃(Si₃Al)O₁₀(OH)₂
 - Mineral sheets in the interlayer: *chlorite* minerals, (LiAl₂)(OH)₆•Al₂(Si₃Al)O₁₀(OH)₂

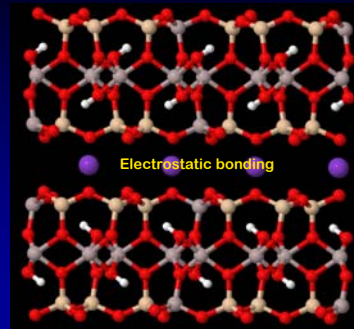
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2:1 Non-Expanding (Primary)

- Characteristics
 - Micaceous primary minerals; illite is secondary; chlorites may be primary or secondary
 - Moderate surface area, 70 to 150 m² g⁻¹
 - Low water holding capacity, non-swelling
 - Extensive isomorphic substitution, but minerals are non-expansive (no access)
 - Surface charge from isomorphic substitution of Al³⁺ for Si⁴⁺ in Si-sheets and pH-dependent edge sites: 10 to 40 cmol_c kg⁻¹

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Mica Structure

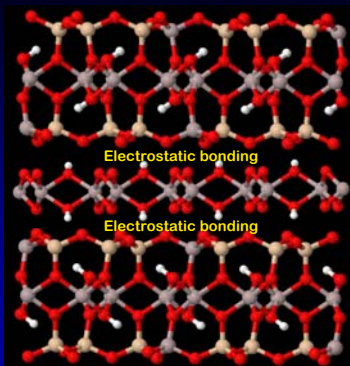


1.0 nm
d-spacing:
All mica minerals are
non-expanding

SA = 70 – 120 m² g⁻¹
(all external)
CEC = 10 – 40 cmol_c kg⁻¹

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Chlorite Structure



d-spacing = 1.44 nm

Continuous metal
hydroxide sheet holds
2:1 layers together by
electrostatic interactions

SA = 70 – 150 m² g⁻¹
(all external)
CEC = 10 – 40 cmol_c kg⁻¹

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2:1 Expanding: Vermiculites

- Organization
 - Ratio of Si to Al sheets is 2:1
 - 2:1 layer attached to adjacent 2:1 layers by electrostatic forces (bridging exchangeable hydrated cations)
 - Moderate layer charge from isomorphic substitution of Al³⁺ for Si⁴⁺ in Si-sheets (0.6 to 0.9 per formula)
 - Structure inherited from mica minerals
 - K_{0.8}(Al, Mg, Fe)₂(Si_{3.2}Al_{0.8})O₁₀(OH)₂
 - Most species are high in Mg & Fe

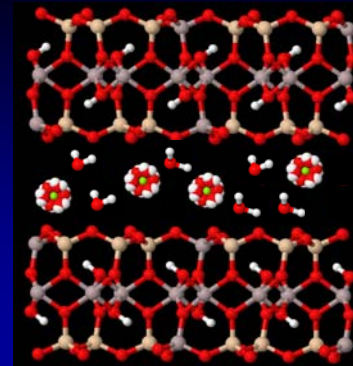
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2:1 Expanding: Vermiculites

- Characteristics
 - Vermiculites are secondary minerals
 - Extensive surface area, 600 to 800 m² g⁻¹
 - Intermediate water holding, intermediate swelling
 - Extensive surface charge 100 to 200 cmol_c kg⁻¹

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Vermiculite Structure



Variable d-spacing:
Ca²⁺-sat: 1.44 nm
K⁺-sat: 1.0 nm

Interlayer is occupied by hydrated cations and water molecules; the ions are exchangeable

SA = 600 – 800 m² g⁻¹
(all external)
CEC = 100 – 200 cmol_c kg⁻¹

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2:1 Expanding: Smectites

- Organization
 - Ratio of Si to Al sheets is 2:1
 - 2:1 layer attached to adjacent 2:1 layers by electrostatic forces (bridging exchangeable hydrated cations)
 - Low layer charge from isomorphous substitution of Mg²⁺ for Al³⁺ in Al-sheets (0.2 to 0.6 per formula)
 - Structure inherited from illite or vermiculite, or formed pedogenically by neoformation processes

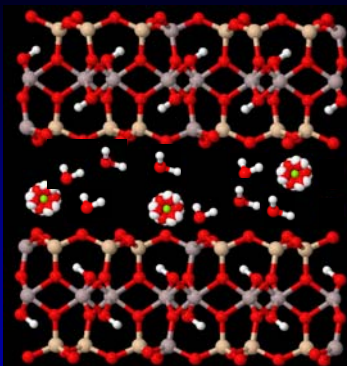
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2:1 Expanding: Smectites

- Characteristics
 - Smectites are secondary minerals
 - Smectites are a chemically and structurally complex group of minerals → numerous species
 - Common species: montmorillonite
 $\text{Ca}_{0.2}(\text{Al}_{1.6}\text{Mg}_{0.4})\text{Si}_4\text{O}_{10}(\text{OH})_2$
 - Extensive surface area, 600 to 800 m² g⁻¹
 - Large water holding, extensive swelling
 - Moderate surface charge 80 to 150 cmol_c kg⁻¹

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Montmorillonite Structure



Variable d-spacing:
large organic cations & Na⁺ (wet): ~∞
Ca²⁺-sat: 1.44 nm
K⁺- or Na⁺- sat (dry): 1.2 nm

Interlayer is occupied by hydrated cations and water molecules; the ions are exchangeable

SA = 600 – 800 m² g⁻¹
(all external)
CEC = 80 – 150 cmol_c kg⁻¹

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Allophane and Imogolite

- Mixtures of silica and alumina that are poorly-crystalline to microcrystalline
- Allophane: $\text{Al}_2\text{O}_3 \cdot (\text{SiO}_4)_{1-2} \cdot 2.5-3\text{H}_2\text{O}$
- Imogolite: $\text{Al}_2\text{SiO}_3(\text{OH})_4$
- Common in young volcanic (andic) materials
 - Insufficient weathering
 - High soluble silica concentrations
- pH dependent charge
- Exchange capacity
 - CEC: 10 to 40 cmol_c kg⁻¹ at pH 7
 - AEC: 5 to 30 cmol_c kg⁻¹ at pH 4

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Sesquioxides - Al and Fe Oxides

- As weathering continues:
 - Base cations and H_4SiO_4 are leached
 - Soils become acidic, further enhancing weathering processes
- After extensive weathering
 - Low solubility (stable minerals) sesquioxides
 - Resistant primary oxides and silicates

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Sesquioxides - Al and Fe Oxides

- Sesquioxides
 - **Gibbsite** $[Al(OH)_3]$: ubiquitous in soils, particularly those that are highly weathered (Oxisols & Ultisols) and in Al-rich soils (Andisols)
 - **Goethite** $[FeOOH]$: the most common hydrous Fe oxide (found in all soils), particularly in cool, moist climates
 - **Hematite** $[Fe_2O_3]$: found in almost all soils, favored in warm, dry climates and in the tropics and subtropics

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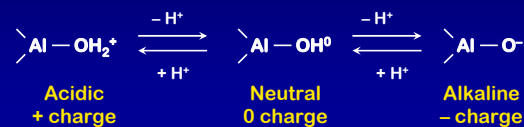
Recalcitrant (Remnant) Minerals

- Found in all soils; concentrated in highly weathered soils
 - Titanium oxides
 - Rutile $[TiO_2]$
 - Anatase $[TiO_2]$
 - Ilmenite $[FeTiO_3]$
 - Corundum $[Al_2O_3]$
 - Zircon $[ZrSiO_4]$

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Charge on Sesquioxides

- pH dependent
- In acid soils, may have positive charge
- Surface charge depends on crystallinity
 - Well-crystalline: CEC ~ 1 $cmol_c$ kg^{-1} , AEC ~ 3 $cmol_c$ kg^{-1}
 - Poorly-crystalline: CEC $\sim 10 - 100$ $cmol_c$ kg^{-1} , AEC $\sim 30 - 300$ $cmol_c$ kg^{-1}



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Weathering and Clays

- Arid to subhumid – 2:1 expanding are common (intermediate weathering stage)
- Weathering of micas forms 2:1 non-expanding illite or expanding vermiculite
- Poor drainage favors smectite formation
- Continued weathering strips out silica & bases
- High precipitation & good drainage favors decomposition of 2:1 clays and formation of 1:1 clays
- Very warm with high precipitation favors continued dissolution and formation of simple Fe and Al sesquioxides

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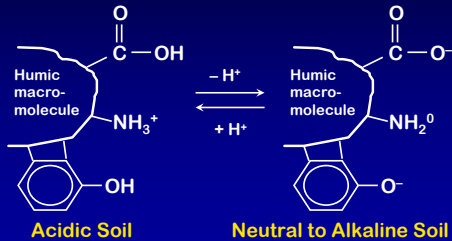
Organic Colloids – Humic Substances

- Stable organic matter left after decomposition of plant and animal detritus
- Dark brown to black, solubility in water is variable (fulvates are soluble; humins and humates not so much)
- Very high reactivity, mostly negative charge
 - pH dependent
 - CEC = 60 to 300 $cmol_c$ kg^{-1} SOM at pH 7; may account for 25 % to 90 % of the CEC of mineral soils
- High water holding capacity
- Very important relative to clays (can mask properties of clays)

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Charge on Humic Substances

- Negative charge from carboxylic acid and phenolic groups; positive from amino groups



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Cation Exchange

- Soil colloids have negative charge
 - pH dependent = variable charge
 - Isomorphic substitution = permanent charge
- Cations from the soil solution must satisfy this charge so that mineral and organic surfaces *appear* to be charge neutral

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Basic Concepts

- Cations** (\rightarrow *metals*)
 - Positively charged ions
 - Al^{3+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , H^+ , etc.
- Anions** (\rightarrow *ligands*)
 - Negatively charged ions
 - SO_4^{2-} , NO_3^- , H_2PO_4^- , HPO_4^{2-} , Cl^- , OH^- , etc.
- Cation exchange sites
 - Negatively charged sites on clay and humic colloids
 - Cations are retained at these sites by electrostatic forces

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Basic Cation Exchange Concepts

- Adsorbed cations can be replaced by other, competing cations
- Law of Mass Action and Le Châtelier's principle are obeyed (large quantity of one cation can displace different cations from sites)
- Exchange reactions are reversible, rapid, and stoichiometric with respect to charge

$$2\{\text{K}^+-\text{Soil}\} + \text{Ca}^{2+} \rightarrow 2\text{K}^+ + \text{Ca}^{2+}-\{\text{Soil}\}_2$$
- Ease of cation displacement is a function of cation size and charge

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Chemistry concepts

- 1 mole = 6.022×10^{23} entities (e.g., atoms)
- 1 cmol = mol \div 100
- Molecular weight (MW) = mass (g) of a substance in 1 mol
 - Ca \approx 40 g mol $^{-1}$, K \approx 39 g mol $^{-1}$,
 - Al \approx 27 g mol $^{-1}$, Mg \approx 24 g mol $^{-1}$,
 - Na \approx 23 g mol $^{-1}$, H \approx 1 g mol $^{-1}$
- So, 1 mol Ca = 40 g; 1 cmol Ca = 0.4 g

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What is cmol_c?

- Units of CEC are cmol_c kg $^{-1}$: centimoles of *charge* per kilogram of soil
- 1 cmol K $^+$ = 1 cmol_c
- 1 cmol Ca $^{2+}$ = 2 cmol_c
- 1 cmol Al $^{3+}$ = 3 cmol_c
- A soil with a CEC of 10 cmol_c kg $^{-1}$ would require:
 - 10 cmol kg $^{-1}$ of K $^+$, or 5 cmol kg $^{-1}$ of Ca $^{2+}$, or 3.3 cmol kg $^{-1}$ of Al $^{3+}$
 to neutralize the soil exchange complex

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Factors Affecting Cation Adsorption

- Soil solution composition
 - The exchange complex reflects soil solution composition: Ca^{2+} dominates in soil solutions, also dominates exchange complex
- Soil pH
 - Acid soils: higher Al^{3+} and H^+ in solution and on exchange complex
 - Al is actually present as $\text{Al}(\text{OH})_2^+$
 - Neutral to alkaline (pH > 6.5): low Al^{3+} and H^+ , high Ca^{2+} , Mg^{2+} , K^+ , & Na^+

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Factors Affecting Cation Adsorption

- Strength of adsorption increases as:
 - Cation valence (z_c) increases
 - Hydrated size (R_{hyd}) decreases
 - Strength of negative charge on colloid (z_{soil}) increases
- Force of attraction of a cation to the soil exchange complex obeys Coulomb's Law:

$$F = \frac{z_c z_{\text{soil}}}{\epsilon R_{\text{hyd}}^2}$$

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Factors Affecting Cation Adsorption

- The relative replaceability of exchangeable cations (ease of removal) is described by a *lyotropic series*
- For monovalent cations:
 - $\text{Li}^+ \approx \text{Na}^+ > \text{K}^+ \approx \text{NH}_4^+ > \text{Rb}^+ > \text{Cs}^+$
- For divalent cations:
 - $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} \approx \text{Ba}^{2+}$
- Monovalent cations are not necessarily easier to displace than divalent cations

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Exchange Complex Composition

Ion	cmol _c kg ⁻¹	
	pH < 6	pH > 7
Ca^{2+}	3.80	25.18
Mg^{2+}	1.65	10.06
Na^+	0.25	1.21
K^+	0.23	0.74
Al^{3+}	8.76	0

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Importance?

- Storage of plant nutrients
 - Major source of K, Mg, Ca
- Buffering Capacity
 - Moderates change in solution pH and nutrient concentrations (high CEC requires high limestone to increase pH of acid soils)
- Adsorption of trace metals
 - Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , others
- Adsorption of cationic pesticides, other organic compounds

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Cation Exchange Capacity – CEC

- Definition: *moles of exchangeable cation charge adsorbed per unit mass of soil*
- Units: centimoles of positive charge from cations per kilogram of soil: cmol_c kg⁻¹
- Recall that ½ cmol Ca^{2+} , ⅓ cmol Al^{3+} , or 1 cmol K^+ or Na^+ will neutralize 1 cmol_c of soil charge

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CEC and Soil Orders

Order	cmol _c kg ⁻¹	Order	cmol _c kg ⁻¹
Alfisols	15.4	Mollisols	24.0
Andisols	30.9	Oxisols	7.6
Aridisols	17.8	Spodosols	26.7
Entisols	19.9	Ultisols	8.9
Inceptisols	21.1	Vertisols	50.1

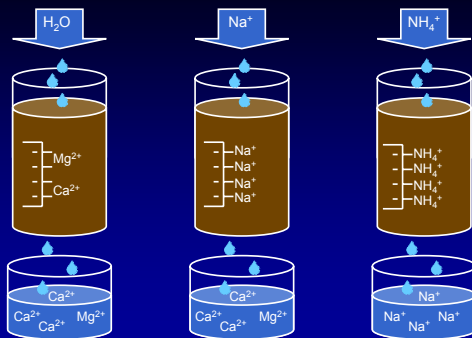
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Measuring CEC

- Soil is rinsed of **soluble** cations
- Soil exchange complex is saturated with an **index cation**, such as Na⁺
 - Na⁺ replaces native cations, which are rinsed away
- The Na⁺-saturated soil is treated with a second index cation, such as NH₄⁺
 - NH₄⁺ replaces the Na⁺
- The displaced Na⁺ is measured
- The cmol of displaced Na⁺ per kg of soil is the CEC

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Measuring CEC



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Effect of Texture on CEC

- Sands: 1 to 5 cmol_c kg⁻¹
- Sandy loams: 5 to 10 cmol_c kg⁻¹
- Loams and silt loams: 5 to 15 cmol_c kg⁻¹
- Clay loams: 15 to 30 cmol_c kg⁻¹
- Clays: > 30 cmol_c kg⁻¹
- Why differences?
- What does this mean for soil properties?

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Estimating CEC

- Measure or estimate % clay and % SOM
- Assign each component an average CEC
 - Montmorillonite = 100 cmol_c kg⁻¹
- Convert CEC of component from cmol_c kg⁻¹ to cmol_c %⁻¹
 - 1 kg mont. clay = 100 cmol_c
 - 100 % mont. clay = 100 cmol_c
 - 1 % mont. clay = 1 cmol_c, or 1 cmol_c %⁻¹ mont.
- Multiply mineral CEC/% by the actual % in soil
- Add all components

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Example

- Soil has 2 % SOM, 20 % montmorillonite, 10 % illite
- SOM = 200 cmol_c/kg = 2 cmol_c/%
- mont. = 100 cmol_c/kg = 1 cmol_c/%
- illite = 40 cmol_c/kg = 0.4 cmol_c/%
- CEC = (2% × 2 cmol_c/%) + (20% × 1 cmol_c/%) + (10% × 0.4 cmol_c/%)
- CEC = 28 cmol_c/kg soil

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CEC Calculations

- Assume soil with CEC = 20 cmol_c/kg
 - Ca-saturation = 45%
 - Mg-saturation = 20%
 - K-saturation = 10%
 - Al-saturation = 25%
- How many kg of Ca per hectare-15 cm of soil?

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CEC Calculations

- cmol_c/kg as Ca²⁺ = 20 cmol_c/kg × 0.45 = 9 cmol_c
- 9 cmol_c (Ca²⁺)/kg × 0.2 g Ca/cmol_c = 1.8 g Ca
- 1 hectare (ha)-15 cm = 2 × 10⁶ kg soil

$$\frac{\text{kg Ca}}{\text{ha} - 15\text{cm}} = \frac{9 \text{ cmol}_c \text{ Ca}}{\text{kg soil}} \times \frac{0.2 \text{ g Ca}}{\text{cmol}_c \text{ Ca}} \times \frac{2 \times 10^6 \text{ kg}}{\text{ha} - 15 \text{ cm}} \times \frac{\text{kg Ca}}{1000 \text{ g Ca}}$$

$$\frac{\text{kg Ca}}{\text{ha} - 15 \text{ cm}} = \frac{3600 \text{ kg Ca}}{\text{ha} - 15 \text{ cm}} \text{ (exchangeable Ca}^{2+} \text{ only)}$$

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