Clay structure and properties
Learning Objectives

• Describe the two basic kinds of clay “sheets”
• Describe isomorphous substitution (drives nutrient supply)
• Describe how and where charge imbalances occur and explain what this means for soil properties
Soil Colloids

• “Organic and inorganic matter with very small particle size and a correspondingly large surface area per unit mass” (“Soil bank”)

• Four categories:
  – Crystalline silicate clays (phyllosilicates)
  – Noncrystalline silicate clays
  – Iron and aluminum oxide clays
  – Organic matter (humus)
“Clay” is . . .

- A particle size class (<0.002 mm)
- A [mineral type](#) with specific properties and characteristics ([secondary mineral](#))
Relative Size Comparison of Soil Particles

Sand
0.05 to 2mm
feels gritty

Silt
0.002 to 0.05 mm
feels smooth

Clay
less than 0.002 mm
feels sticky

“Big” → smaller → really small
Sand → silt → clay
Fundamentals of clay mineralogy

• 2 basic building blocks: the silica (Si) tetrahedron and the aluminum (Al) octahedron

• These building blocks form sheets: “silicate layer clays”
Shape of silicon tetrahedron and aluminum octahedron

Source: Kohnke, 1968
Isomorphous substitution

~ equal shape/size (ionic radii)

- The replacement of one ion for another of similar size within the crystalline structure of the clay

- This changes the total charge and location of the charge on the mineral (greatly affecting the properties of the clay)

This takes eons!!!
It doesn’t change rapidly
Isomorphic Substitution in tetrahedral sheet

\[ (+4) \times 2 = +8 \]
\[ (-2) \times 4 = -8 \]

Net negative charge

\[ (+4) + (+3) = +7 \]

\[ +8 \]

neutral

\[ Si_2O_4 \]

\[ SiAlO_4 \]

Tetrahedral sheet
Isomorphic Substitution in octahedral sheet

\[
\begin{align*}
(OH)_2Al_2O_2 & \quad \text{neutral} \\
\text{(Column)} & \quad \text{net negative charge}
\end{align*}
\]
Ionic Radii of elements in silicate clays – Tetrahedral & Octahedral sheets

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius, nm&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Found in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>0.042</td>
<td>Tetrahedral sheet</td>
</tr>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.051</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.064</td>
<td></td>
</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.066</td>
<td>Octahedral sheet</td>
</tr>
<tr>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.070</td>
<td>Exchange sites</td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.097</td>
<td></td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.099</td>
<td></td>
</tr>
<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.133</td>
<td></td>
</tr>
<tr>
<td>O&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>0.140</td>
<td>Both sheets</td>
</tr>
<tr>
<td>OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.155</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> 1 nm = 10<sup>-9</sup>m.

Note that Al, Fe, O, and OH can fit in either.
Types of clay minerals

- Based on **numbers and combinations of structural units** (tetrahedral and octahedral sheets)
- Number of **cations** in octahedral sheet
- Size and **location of layer charge** (due to isomorphic substitution)
- Absence or presence of **interlayer cations**
- Two general categories: **1:1, 2:1**
Clay minerals

1:1 clays
(one tetrahedral sheet for each octahedral sheet)
- Kaolinite
  - Nacrite, dickite, halloysite, etc.

2:1 clays
(two tetrahedral sheets for each octahedral sheet)
- Montmorillonite, beidellite, saponite, etc.
- Illite, muscovite, biotite, etc.
- Tri- or di-vermiculite
- Cookeite, chamosite ETC

Weird-o, not truly 2:1
Visual comparison of common silicate clays

1:1 clays

- Tetrahedral sheet
- Octahedral sheet
- Tetrahedral sheet
- Octahedral sheet

Kaolinite

1:1

Kaolinite (1:1) Nonexpanding (no swelling)
1:1 Silicate Clays

- Layers composed of one tetrahedral sheet bound to one octahedral sheet
- Kaolinite: one of the most widespread clay minerals in soils; most abundant in warm moist climates
- Stable at low pH, the most weathered of the silicate clays
- Synthesized under equal concentrations of Al$^{3+}$ and Si$^{4+}$
Kaolinite

• A 1:1 clay
• **Little or no isomorphous substitution**
• “nutrient poor”
• No shrink-swell (stable because of H-bonding between adjacent layers)
• A product of acid weathering (low pH, common in soils of the SE USA)
Structure of Kaolinite

NO ISOMORPHOUS SUBSTITUTION!!

Sheets of **silicon tetrahedra** and **aluminum octahedra** linked by **shared oxygen atoms**.
**Kaolinite under low pH**

\[ \text{Al–OH} + \text{H}^+ \leftrightarrow \text{Al–OH}_2^+ \]

No charge  positive charge
Visual comparison of common silicate clays

- Smectite
- Kaolinite
- Vermiculite
- Fine-grained mica
- Chlorite

1:1 clays
2:1 clays
2:1 Silicate Clays

- Two silica tetrahedral sheets linked to one aluminum octahedral sheet

- Three key groups:
  - **Smectites** (e.g., montmorillonite)
  - Vermiculites
  - **Micas** (e.g., illite)

- And one weirdo (the **chlorites**)

Clay minerals

1:1 clays (one tetrahedral sheet for each octahedral sheet)
- Kaolinite, nacrite, dickite, halloysite, etc.
- Montmorillonite, beidellite, saponite, etc.
- Pyrophyllite only one with no substitution

2:1 clays (two tetrahedral sheets for each octahedral sheet)
- Smectites
- Micas
- Vermiculites
- Chlorites
- Illite, muscovite, biotite, etc.
- Tri- or di-vermiculite
- Cookeite, chamosite ETC

Weirdo, not truly 2:1
Visual comparison of common silicate clays

- **Smectite**: Expanding (max. swelling)
- **Vermiculite**: Expanding (some swelling)
- **Fine-grained mica**: Nonexpanding (min. swelling)
- **Chlorite**: Nonexpanding (min. swelling)

### 2:1 clays

- Tetrahedral sheet
- Octahedral sheet
- Water molecules, Mg$^{2+}$ and other ions
- Water molecules, miscellaneous cations

### 1:1 clays

- Tetrahedral sheet
- Octahedral sheet
- Tetrahedral sheet

### Fine-grained mica

- Tetrahedral sheet
- Octahedral sheet
- Tetrahedral sheet
- Hydroxide sheet

### Chlorite

- Tetrahedral sheet
- Octahedral sheet
- Tetrahedral sheet
Smectite (2:1, Montmorillonite)

- Layer charge originates from the substitution of $\text{Mg}^{2+}$ for $\text{Al}^{3+}$ in the octahedral sheet
- Unstable (weathers to something else) under low pH and high moisture
- Most swelling of all clays
- “Nutrient rich”
Structure of basic Smectite (Montmorillonite)

- Structure of montmorillonite (a smectite): it is built of two sheets of silicon tetrahedra and one sheet of aluminum octahedra, linked by shared oxygen atoms.
Structure of basic Smectite
(Montmorillonite)

Causes cations to move into the interlayer space, where they can be replaced by other cations.

Isomorphous substitution in the octahedral sheet

= Mg (this slide only)
Visual comparison of common silicate clays

2:1 clays

Smectite
Expanding (max. swelling)

Vermiculite
Expanding (some swelling)

Fine-grained mica
Nonexpanding (min. swelling)

Chlorite
Nonexpanding (min. swelling)
Vermiculites (2:1)

- Alteration product of micas (rock form)
- Formed from loss of $K^+$
- Interlayer $K^+$ of mica replaced with $Mg^{2+}$
- Limited shrink-swell …
- High layer charges: Isomorphich substitution in BOTH tetrahedral & octahedral sheets
- “nutrient rich!” (the most)
- Stable under moderate to low soil pH, high Mg, Fe
Structure of Vermiculite

Lots of charge imbalance, both sheets:

High nutrient supply capacity

- **Al** (this slide only!) = red circle
- **Fe** = orange circle
- **Mg** (this slide only!) = black circle
Visual comparison of common silicate clays

- **Smectite**: Expanding (max. swelling)
- **Vermiculite**: Expanding (some swelling)
- **Chlorite**: Nonexpanding (min. swelling)

**2:1 clays**

- **Vermiculite**: Fine-grained mica
- **Chlorite**
(2:1, Fine-grained Mica: Illite)

- $\text{Al}^{3+}$ substitution for $\text{Si}^{4+}$ on the tetrahedral sheet
- Strong surface charge
- “fairly nutrient poor”
- Non-swelling, only moderately plastic
- Stable under moderate to low pH,
Structure of Illite
Structure of Illite

1. Isomorphous substitution is in the tetrahedral sheets

2. K+ comes into the interlayer space to satisfy the charge and "locks up" the structure
Visual comparison of common silicate clays

2:1 clays

Smectite
Expanding (max. swelling)

Vermiculite
Expanding (some swelling)

Fine-grained mica
Nonexpanding (min. swelling)

Chlorite
Nonexpanding (min. swelling)
Chlorites (2:1:1)

- Hydroxy sheet in the interlayer space
- Restricted swelling
- “Nutrient poor”
- Common in sedimentary rocks and the soils derived from them
- Isomorphous substitution in both tetrahedral and octahedral sheets
Structure of Chlorite

1. Iron-rich
2. “locked” structure
3. Low nutrient supply capacity

Mg-Al hydroxy sheet

- Red = Al
- Orange = Fe
- Blue = Mg
Visual comparison of common silicate clays

1:1 clays
- Kaolinite
  - 1:1
  - Nonexpanding (no swelling)
- Smectite
  - Expanding (max. swelling)
2:1 clays
- Vermiculite
  - Expanding (some swelling)
- Fine-grained mica
  - Nonexpanding (min. swelling)
- Chlorite
  - Nonexpanding (min. swelling)

- Tetrahedral sheet
- Octahedral sheet
- Water molecules, Mg$^{2+}$ and other ions
- Hydroxide sheet

0.7 nm
1.0 nm
1.4 nm
1.0–1.5 nm
1–2 nm
### Comparison of common silicate clays

<table>
<thead>
<tr>
<th>Property</th>
<th>Kaolinite</th>
<th>Smectite</th>
<th>Fine-grained mica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swelling</td>
<td>Low</td>
<td>High</td>
<td>Low to none</td>
</tr>
<tr>
<td>Bonding</td>
<td>Hydrogen (strong)</td>
<td>Van der Waal’s (weak)</td>
<td>Potassium ions (strong)</td>
</tr>
<tr>
<td>Fertility</td>
<td><strong>Low</strong>: 2-5 cmol$_c$/kg</td>
<td><strong>High</strong>: 80-120 cmol$_c$/kg</td>
<td><strong>Mod</strong>: 15-40 cmol$_c$/kg</td>
</tr>
<tr>
<td>Charge location</td>
<td>Edges only – NO isomorphous substitution</td>
<td>Octahedral sheets</td>
<td>Tetrahedral sheets</td>
</tr>
<tr>
<td>General class</td>
<td>1:1 (TO)</td>
<td>2:1 (TOT)</td>
<td>2:1 (TOT)</td>
</tr>
</tbody>
</table>

**Notes:**
- CEC = Capacity to Exchange Cations
- 1:1, 2:1 = General class of clay
- Strong and weak bonds refer to the strength of bonding interactions.
Location of internal charge imbalance

1:1 clays
- Smectite (Expanding (max. swelling))
- Kaolinite (1:1) Nonexpanding (no swelling)
- Vermiculite (Expanding (some swelling))
- Fine-grained mica (Nonexpanding (min. swelling))
- Chlorite (Nonexpanding (min. swelling))

2:1 clays
- Chlorite
- Vermiculite (Expanding (max. swelling))
- Smectite (Expanding (max. swelling))
- Kaolinite (1:1) Nonexpanding (no swelling)

No charge
- Tetrahedral
- Octahedral
Weathering pattern of clay formation

 ultisols

 oxisols

 entsols, inceptisols

 Source: Brady and Weil, 1996
Types of charge

- Permanent
due to isomorphous substitution

- pH-dependent
variable, due to edges
Permanent charge

• Due to isomorphous substitution

Octahedral sheet neutral

Net negative charge
pH-dependent charge: on edges!!!

H⁺ bound tightly, so the lower the pH, the less exchange there is (i.e., lower nutrient availability)

Espec. Important in kaolinite, humus, where no internal charge imbalance