How Do Mineralogy and Soil Chemistry Impact How Closely Potassium Soil Test Changes Are Related To Mass Balance?

Michel D. Ransom, mdransom@ksu.edu
Angela Florence, amflorence@outlook.com
Michael Thompson, mlthomps@iastate.edu
Randal Southard, rjsouthard@ucdavis.edu
Known Facts About Soil K

• K is 7th most abundant element in earth’s crust
• K is enriched in soil during weathering
• K exists in solution, exchangeable, mineral, and fixed forms
• Soil test K values can change seasonally
• Inability to understand and predict these changes is a critical issue in nutrient management

K deficiency in soybean in Kansas, USA. Photo courtesy of D.R. Diaz, K-State Research and Extension
Objectives

- Review effects of mineralogy on K fixation
- Discuss the role in K fixation of the oxidation-reduction of Fe in structural positions of layer silicates
- Present a model of K fixation that can account for soil test results and determinations of mass balance of soil K

K deficiency in soybean in Kansas, USA. Photo courtesy of D Mengel, K-State Research and Extension
Primary minerals are minerals that crystallize from the magma of volcanic eruptions.

Those that contain K are

• **Micas** (e.g., biotite and muscovite)
• **Feldspars** (e.g., microcline and orthoclase)
What is potassium fixation?

- **Soil Solution K**
- **Structural K**
- **Fixed K**
- **Exchangeable K**

http://legacy.belmont.sd62.bc.ca/teacher/geology12/photos/minerals/K-feldspar.jpg
http://skywalker.cochise.edu/wellerr/mineral/mica/6muscovite-peel.jpg
Why is potassium fixed?

Source data:
How does clay mineralogy affect potassium fixation?

Clay mineral classification criteria
1. Layer type (1:1, 2:1, 2:1:1)

1:1

2:1

2:1:1

Building blocks
Si tetrahedron ( ▲ ) → Tetrahedral sheet ( ▲ )
Al octahedron ( ◊ ) → Octahedral sheet ( ▼ )
Weathered Micas

Images by ML Thompson
Micas are 2:1 layer silicates with $K^+$ ions occupying the ditrigonal cavities between tetrahedral and octahedral layers.

During mica weathering:
- Interlayers expand during weathering
- $K$ is released
- CEC increases

When $K$ is fixed between the layers of expanded 2:1 layer silicates:
- Interlayers contract
- $K^+$ ions are trapped in ditrigonal voids
- CEC decreases
Vermiculite is a high-charge mineral, mainly derived from biotite. 

Smectites may range in charge, but the higher the charge the more likely they are to “fix” K.
In acidic soils, *vermiculite* and *smectite* can be “pillared” with hydroxy-Al polymers. These materials are called interlayered vermiculite and smectite.
How does 2:1 clay mineralogy affect potassium fixation?

2:1 mineral classification criterion

<table>
<thead>
<tr>
<th></th>
<th>Smectite</th>
<th>Vermiculite</th>
<th>Illite/Mica</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Layer charge</strong></td>
<td>-0.2 to -0.6</td>
<td>-0.6 to -0.9</td>
<td>-0.75 to -1</td>
</tr>
<tr>
<td><em>(charge/half unit cell)</em></td>
<td><em>(de jure criterion)</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Expansibility</strong></td>
<td>High</td>
<td>Moderate</td>
<td>None</td>
</tr>
<tr>
<td><em>(de facto criterion)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Expansibility = imperfect proxy for layer charge

Expansibility = \( f(\text{layer charge}, \text{charge distribution}) \)

TEM images composed of isolated 2:1 layer silicates (smectite-group phases) and packets of discrete illite from Vali et al. (1994).

How should structural iron redox state affect potassium fixation?

\[
Fe^{3+} + e^- \rightarrow Fe^{2+}
\]

↑ negative layer charge
↑ layer contraction
↑ fixation

Relationship between Fe reduction and ↑ fixation well established for smectites containing octahedral Fe.

Reductions of structural Fe in smectites and vermiculites causes an increase in layer charge and an increase in K fixation.

Soil Redox Effects on Soil Test K

• Soil mineralogical characteristics are not dynamic during growing season.

• Soil redox conditions can be dynamic over short time periods leading to changes in oxidation state of structural Fe in K-fixing minerals.

• Reducing conditions:
  • K fixation ↑

• Oxidizing conditions:
  • K release ↑

Photo courtesy of K-State Department of Agronomy
Interlayer potassium + (Forces of contraction > Forces of expansion) = Potassium fixation
K Fixation Model – K Mass Balance

- Correlation of soil test measurements with mass balance of K is needed for maximum K efficiency
- Difficult because K fixation varies with
  - Mineralogy of layer silicates
  - Oxidation state of Fe
  - Presence of hydroxyl Al interlayers
- Variation of K fixation caused by these factors causes spatial and temporal variations of soil test K
- For soils with K fixation, traditional soil test K measurements do not represent the seasonal and spatial variations occurring in the field
Questions and Discussion
K in Soil – A beautiful mystery

**Fixed K**
*Edge sites:* Di-vermiculite
*Redox sites:* Tri-verm and HC smectite
*Interlayer sites:* HIV and HIS

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**Exchangeable K**
in clay minerals
(smectite, vermiculite)

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**Exchangeable K**
in organic matter

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**Structural K**
Micas and Feldspars

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**pH, Eh, organic anions**

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**pH, site selectivity**

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**Redox processes, pH**

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**Evapo-transpiration**

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**Fertilizer amendments**

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**Crop residue**

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**Root uptake**

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**Harvest removal**

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**Dissolution**

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**Diffusion**

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**Leaching and lateral movement**

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**Dissolution**

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**Advection, dispersion**

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**K / \sqrt{(Ca+Mg)}**
Extrapolate Mineralogical and K-Fixation Data Using Soil Surveys

- Soil surveys are available in electronic format for virtually all of US
- Can use soil surveys to extrapolate mineralogical and K-fixation data for horizons at a specific site to other land areas by developing a procedure that does not make major changes to Soil Taxonomy or requires development of new laboratory procedures
- Requires recognition of particle size, mineralogy, and CEC classes that exhibit K fixation using data obtained with USDA-NRCS Soil Characterization Query Interface
- Particle size classes need no additional modification
  - ≥ 18% clay: loamy and clayey particle size classes (fine-loamy, fine-silty, fine, and very fine particle size subclasses)
- Existing CEC classes (superactive, active, semiactive, and subactive) need more work
  - Need to measure CEC using K as an index cation in addition to regular index cation (e.g., Ca, NH₄, or Na)
  - Determine % CEC reduction (Ransom et al., 1988) and include in database
  - Add reductive subclasses to CEC class for soils with CEC reduction > ~ 10%
Soil Properties Affecting K Fixation

- K fixation occurs with vermiculite and transitional minerals formed from weathering of mica (Hartley et al., 2014; Tran, 2012)
  - Layer charge occurs in both tetrahedral and octahedral sheets (Fe in octahedral positions)
  - Vermiculite, transitional vermiculite/smectite (TVS), and regularly interstratified mica-smectite or mica-vermiculite (RIMS/RIMV)

- Mineralogy classes need revision
  - Current classes are too broad, e.g., smectitic
  - Mineralogy of fine-loamy and fine-silty classes are based on sand and silt fraction mineralogy
  - Expand control section depth to include A

- Add new k-fixic mineralogy subclass where K-fixing minerals > ~5 – 10% in clay fraction regardless of particle-size class

- Eram series (Site 10 from Hartley, 2010)

<table>
<thead>
<tr>
<th>Layer Silicate</th>
<th>Mg-EG (Å) *</th>
<th>Mg-GLY (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Smectite</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>TVS</td>
<td>17</td>
<td>14 - 15</td>
</tr>
<tr>
<td>RIMS/RIMV (Hydrobiotite)</td>
<td>~ 24 (Mg-25)</td>
<td></td>
</tr>
</tbody>
</table>

Site 10

- Fine, mixed, active, thermic Aquic Argiudolls
- Fine, k-fixic-mixed, reductive-active, thermic Aquic Argiudolls
- K-fixing mineralogy subclass
- CEC subclass

* Indicates typical procedure done in labs