K fixation has been studied for decades

- Vermiculite fixes K
- Sites in wedges and at frayed edges of “micas” are selective for K
- Hydroxy-interlayered vermiculite fixes K
J. Stucki and colleagues:
Reduction of Fe in smectite crystals increases layer charge


Intimate mixtures of clay and organic matter

Image by ML Thompson

Clay

Clay-protected OM

Humified OM

500 nm
Exchangeable K – Why Is It so Darn Complicated?

Michael L. Thompson
Taslima Stephen
Iowa State University
Agronomy Department
The Life of K

**Fixed K**
*Edge sites:* Dioctahedral vermiculite
*Redox sites:* Trioct. vermiculite and high-charge smectite

**STRUCTURAL K:**
- Micas
- Feldspars

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

*Exchangeable K* in organic matter

**SOLUTION K**
- KCl – Fertilizer amendments
- Root uptake
- Crop residue
- Evapotranspiration
- Leaching and lateral movement

**Harvest removal**
- Plant biomass

Leaching and lateral movement
The Life of K

**Fixed K**
- **Edge sites:** Dioctahedral vermiculite
- **Redox sites:** Trioct. vermiculite and high-charge smectite

**STRUCTURAL**
- K:
- pH, organic anions
- Micas
- Feldspars

**Exchangeable K**
- in clay minerals (smectite, verme)
- pH, site selectivity

**Exchangeable K** in organic matter

**KCl – Fertilizer amendments**

**Dissolution**

**Redox processes, pH**

**SOLUTION**
- K
- K / (Ca+Mg)

**Advection, dispersion**

**Leaching and lateral movement**

**Evapotranspiration**

**Harvest removal**

**Root uptake**

**Crop residue**

**Plant biomass**
The Life of K

Fixed K

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- K in clay minerals (smectite)
- K in organic matter

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- KCl – Fertilizer amendments

Harvest removal

Root uptake

Crop residue

Evapotranspiration

Leaching and lateral movement

Plant biomass
Mitigating Factors in Soil K Fixation by Redox Processes

• The soil may not be saturated long enough at a high enough temperature for the redox potential to get **low enough** for $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$.

• When $E_h$ **does** get low enough, Fe oxides are dissolved, opening up non-selective exchange sites and increasing the CEC.
Mitigating Factors in Soil K Fixation by Redox Processes

• Organic matter associated with soil clay may block access to the “selective” sites.

• As redox potential goes down, pH of acid soils tends to rise, increasing the CEC and the proportion of non-selective sites for K retention.
Biomass Production Cropping Systems Research Site
Treatments and Plots

- **Continuous corn** (grain and stover): with rye cover crop or no cover crop
- Multi-species **reconstructed prairie**: with annual N fertilizer or no N fertilizer
- **Corn/soybean rotation** (grain), both entry points

Four replicate blocks per treatment, no tillage
Each of the 24 plots is 27 m x 61 m
### Clarion, Nicollet, and Webster Soils

(Typic Hapludoll, Aquic Hapludoll, Typic Endoaquoll)

<table>
<thead>
<tr>
<th>Plot ID</th>
<th>Depth</th>
<th>Clay</th>
<th>pH</th>
<th>Organic C</th>
<th>CEC</th>
<th>CBD-Fe</th>
<th>AO-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td>g/kg</td>
<td>g/kg</td>
<td>cmol/kg</td>
<td></td>
<td>mg Fe / kg soil</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0-15</td>
<td>320</td>
<td>7.0</td>
<td>29.5</td>
<td>41</td>
<td>3150</td>
<td>1090</td>
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<tr>
<td>13</td>
<td>0-15</td>
<td>290</td>
<td>7.2</td>
<td>29.7</td>
<td>36</td>
<td>4046</td>
<td>1424</td>
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<tr>
<td>16</td>
<td>0-15</td>
<td>350</td>
<td>7.3</td>
<td>32.6</td>
<td>47</td>
<td>2940</td>
<td>970</td>
</tr>
<tr>
<td>21</td>
<td>0-15</td>
<td>270</td>
<td>6.3</td>
<td>21.7</td>
<td>33</td>
<td>4776</td>
<td>2171</td>
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<tr>
<td>22</td>
<td>0-15</td>
<td>240</td>
<td>6.4</td>
<td>19.9</td>
<td>29</td>
<td>6493</td>
<td>2313</td>
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<tr>
<td>24</td>
<td>0-15</td>
<td>250</td>
<td>7.3</td>
<td>25.2</td>
<td>31</td>
<td>4301</td>
<td>1474</td>
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<td>30.9</td>
<td>41</td>
<td>3551</td>
<td>1287</td>
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<tr>
<td>42</td>
<td>0-15</td>
<td>230</td>
<td>6.6</td>
<td>19.7</td>
<td>-</td>
<td>3971</td>
<td>1572</td>
</tr>
<tr>
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<td>0-15</td>
<td>220</td>
<td>6.6</td>
<td>22.7</td>
<td>28</td>
<td>4103</td>
<td>1885</td>
</tr>
</tbody>
</table>
Clay mineral suite

Dominated by *smectite*, with *vermiculite*, *clay mica*, and *kaolinite*
How much potential K-fixing capacity is present?

**Ca-EC / K-EC Method**
(Coffman and Fanning (1974), ML Jackson)
K fixation is the difference between the exchange capacity determined with a Ca-saturated sample and that determined with a K-saturated sample that was heated to 110 deg C overnight.

<table>
<thead>
<tr>
<th>Ca-EC</th>
<th>K fixation capacity</th>
<th>Fraction of CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>------</td>
<td>cmol/kg</td>
<td>%</td>
</tr>
<tr>
<td>41</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>36</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>47</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>33</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>29</td>
<td>3</td>
<td>9</td>
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<tr>
<td>31</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>41</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>28</td>
<td>3</td>
<td>12</td>
</tr>
</tbody>
</table>
Will reducing conditions increase the K buffering capacity of the soil?

Wang et al., 2004

- K adsorption isotherms
- 2.5 g soil + 25 mL solution
- 0.0, 0.5, 1.0, 1.5, 2.0, 3.5, 5.0 mM KCl in 0.01 M CaCl₂
- Shake, then equilibrate
- Determine K, Ca, Mg in solution
- Determine NH₄OAc exchangeable K at end

Treatments
- *Aerobic*, no amendment, no incubation, 18 h equilibration
- *Anaerobic, no amendment*, incubation for **14 days**
- *Anaerobic, glucose amendment*, incubation for **14 days**
Potassium Exchange Isotherms

**Aerobic Sample 31**

- Change in Total K: $y = 53x - 0.04$, $R^2 = 0.99$
- Change in Exch K: $y = 45x - 0.04$, $R^2 = 0.99$
- Change in NonEx K: $y = 7x$, $R^2 = 0.96$

**Glucose: 14-day incubation Sample 16**

- Change in Total K: $y = 100x - 0.03$, $R^2 = 0.99$
- Change in Exch K: $y = 32x$, $R^2 = 0.96$
- Change in NonEx K: $y = 68x - 0.02$, $R^2 = 0.99$

Slope = buffer capacity
Change in NonExchangeable Buffer Capacity

Oneway Analysis of NExBC By Treatment

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Ratio</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatmen</td>
<td>2</td>
<td>1712.2963</td>
<td>856.148</td>
<td>7.3818</td>
<td>0.0032 *</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td>2783.5556</td>
<td>115.981</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C. Total</td>
<td>26</td>
<td>4495.8519</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Change in Total Buffer Capacity

Oneway Analysis of PBC By Treatment

Total Buffer Capacity

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Ratio</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatmen</td>
<td>2</td>
<td>8722.493</td>
<td>4361.25</td>
<td>14.3777</td>
<td>&lt;.0001 *</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td>7280.010</td>
<td>303.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C. Total</td>
<td>26</td>
<td>16002.503</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Potassium Buffering Capacity

<table>
<thead>
<tr>
<th>Condition</th>
<th>NON-EXCHANGEABLE</th>
<th>EXCHANGEABLE</th>
<th>TOTAL</th>
<th>Non Exch fraction of total PBC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[ΔNEX-K] [K/(Ca + Mg)^{1/2}]</td>
<td>[ΔEX-K] [K/(Ca + Mg)^{1/2}]</td>
<td>[ΔK] [K/(Ca + Mg)^{1/2}]</td>
<td></td>
</tr>
<tr>
<td>Aerobic</td>
<td>5</td>
<td>23</td>
<td>45</td>
<td>0.11</td>
</tr>
<tr>
<td>Anaerobic, no glucose</td>
<td>22</td>
<td>34</td>
<td>72</td>
<td>0.31</td>
</tr>
<tr>
<td>Anaerobic, with glucose</td>
<td>21</td>
<td>68</td>
<td>88</td>
<td>0.24</td>
</tr>
</tbody>
</table>
What does the change in buffer capacity correlate with?

NonExBC vs. Eh
\[ r = -0.41 \]

ExchBC vs. Eh
\[ r = -0.73 \]
Conclusion
Conclusion

It’s complicated.
Conclusions

• Reducing conditions increased the capacity of the soil to buffer added K at both exchangeable and non-exchangeable sites of the soil.

• We speculate that the increase in sites holding non-exchangeable K was due to changes in the oxidation state of Fe and subsequent K “fixation” in interlayer sites.

• We speculate that the increase in sites holding exchangeable K was due to increases in CEC as Fe oxides dissolved and opened up more clay mineral surfaces.
Exchangeable K – A beautiful mystery?

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Acknowledgments

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- Llewin Froome

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