Plant-mediated stabilization of illitic clays in temperate soils: A potential pathway

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Clay minerals and soil potassium

- Cation exchange capacity
  - Exchangeable K (plant-available)
- K fixation
  - Nonexchangeable K
  - Strong adsorption of K by high layer-charge clays
  - e.g., vermiculite, illite

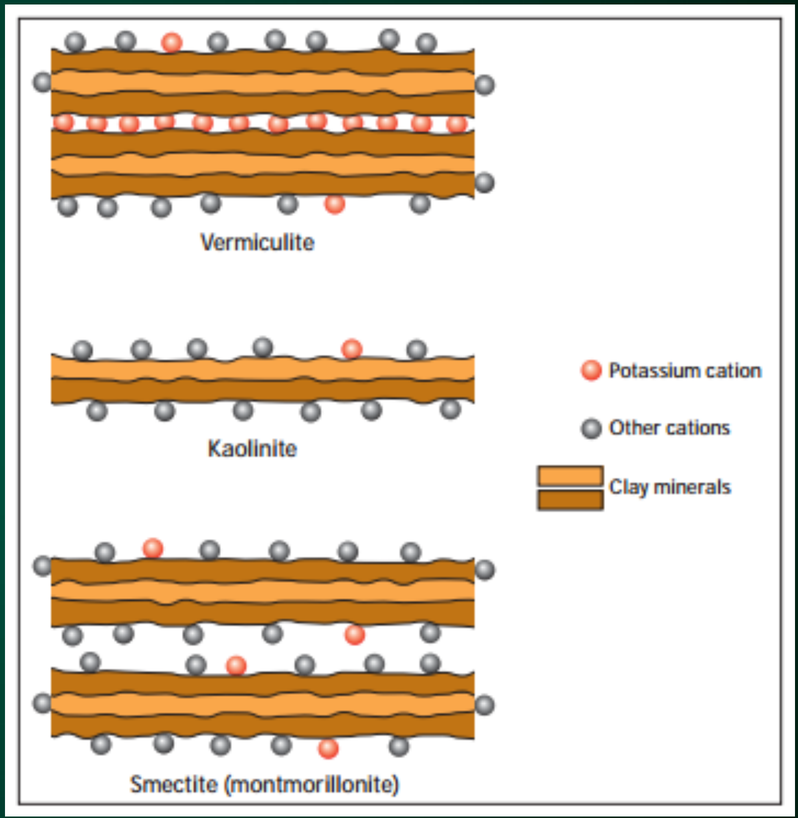

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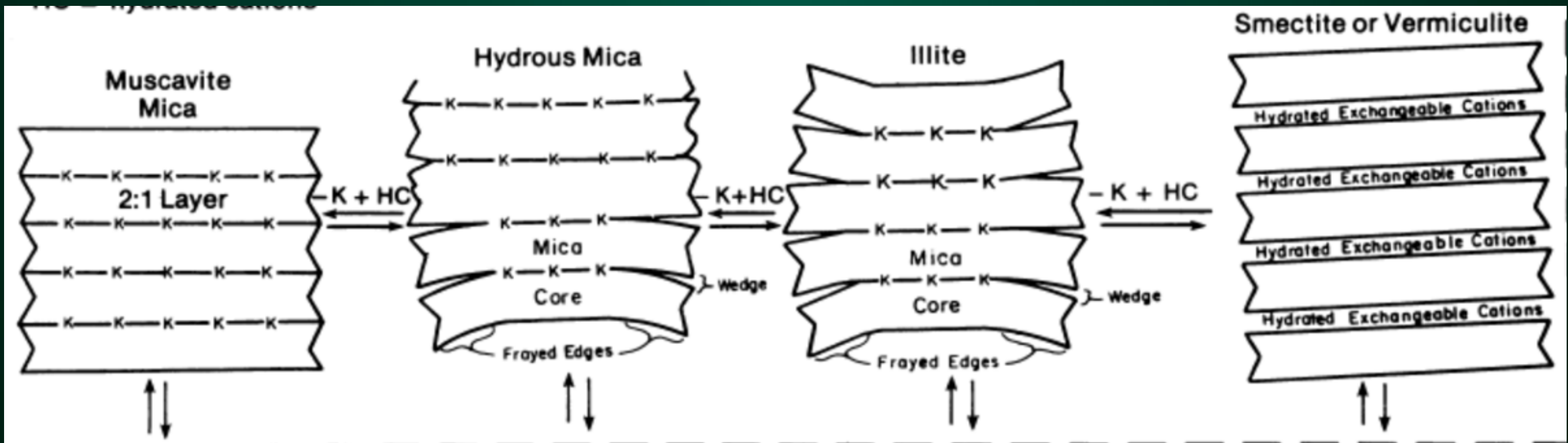
Image source
http://www.ipni.net/ppiweb/bcrops.nsf/$webindex/117C71F7BF9D1C460625795D006E55CD/$file/Page+16+BC+4+2011.pdf

Classical paradigm of mineral weathering

- Loss of Si and mobile cations (K, Ca, Mg)
  - Formation of kaolinite and gibbsite
- K loss: illite → smectite
- Si loss: 2:1 clays → kaolinite



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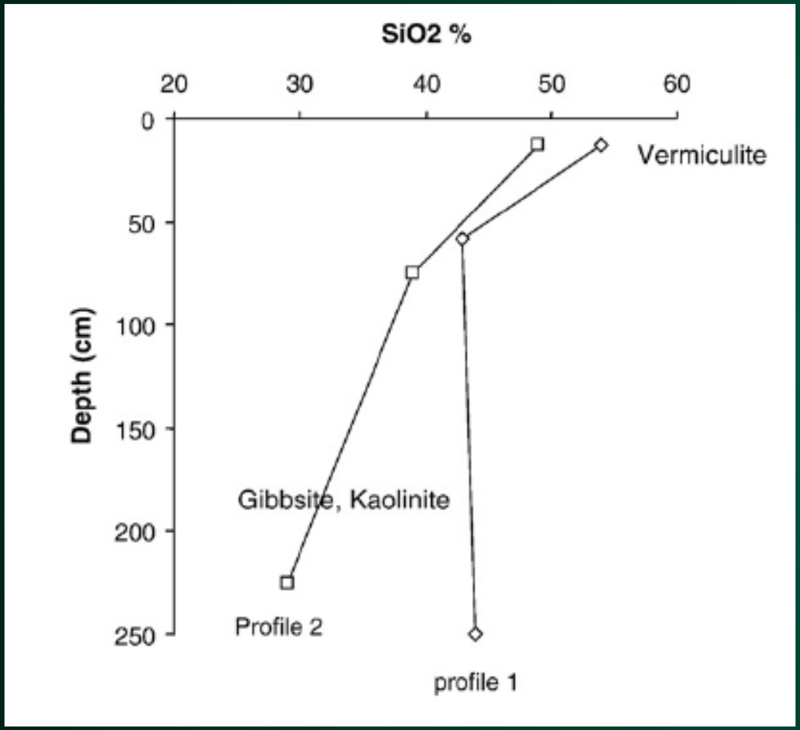
From McLean and Watson, 1985

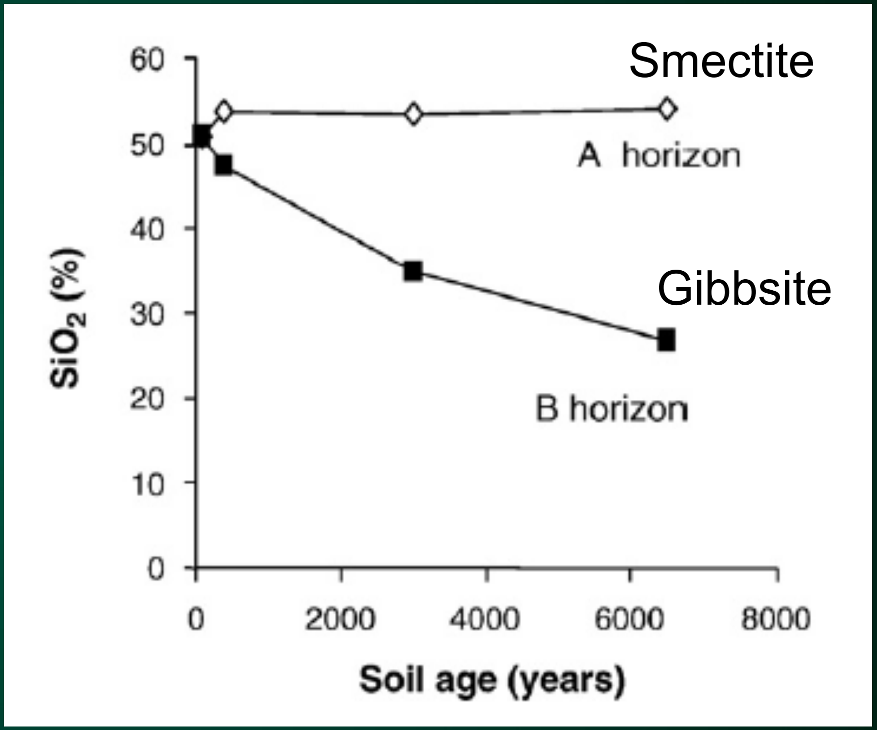
A horizons remain SiO_2 rich

Mississippi coastal plain, USA



Surface horizons higher in silica

Glacial moraine, Switzerland



No loss of silica in surface horizon over time

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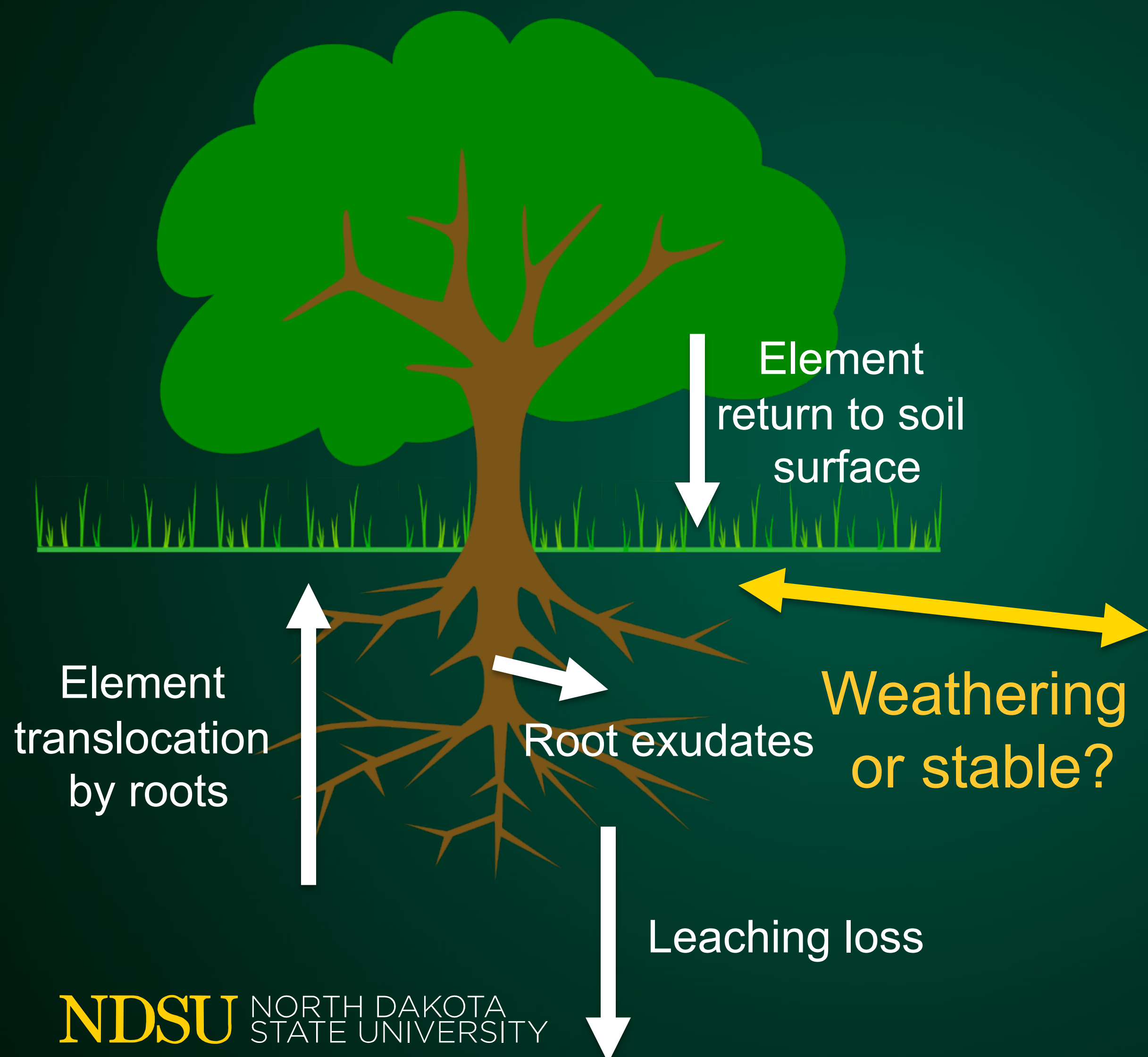
From Barré et al., 2009

Plant interactions and nutrient uplift



Positive effect on Si, K, Ca, Mg mass balance and mineral formation?

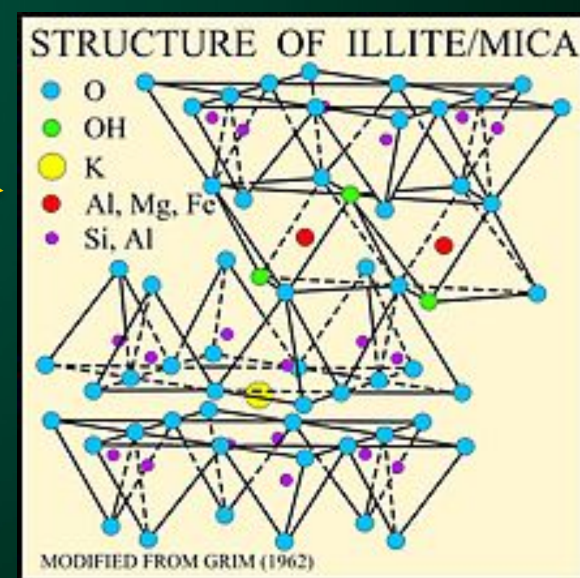


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Image source
https://openclipart.org/detail/90025/tree-branches-and-root-01r
https://commons.wikimedia.org/wiki/File:Illstruc.jpg

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

How element translocation by plants may stabilize illitic clays in the surface of temperate soils

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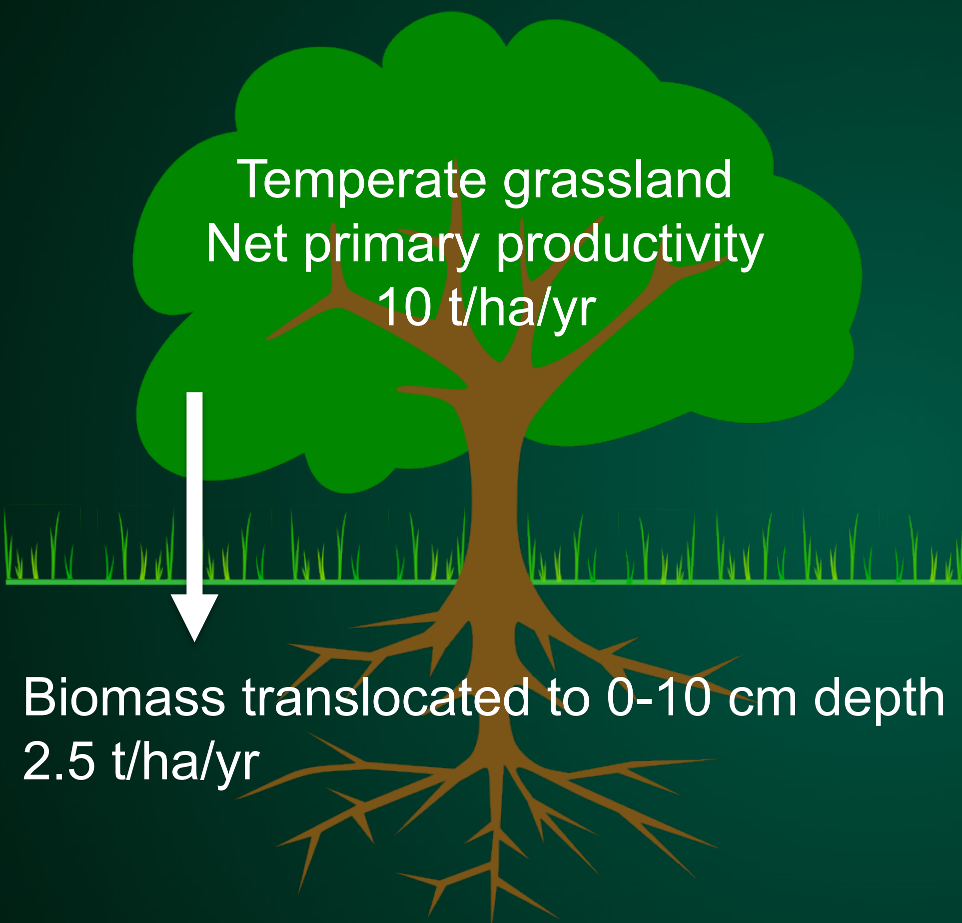
PHREEQC model

- Addition of Si, K, Ca, Mg, oxalic acid by plants
- Weathering by rainfall
- Changes in clay mineral composition

System inputs: Generic grassland



Element addition (t/ha/yr)	
K	0.125
Si	0.01875
Ca	0.025
Mg	0.01
Oxalate	0.5

Rainfall and element addition divided into 12 monthly batch-reaction events

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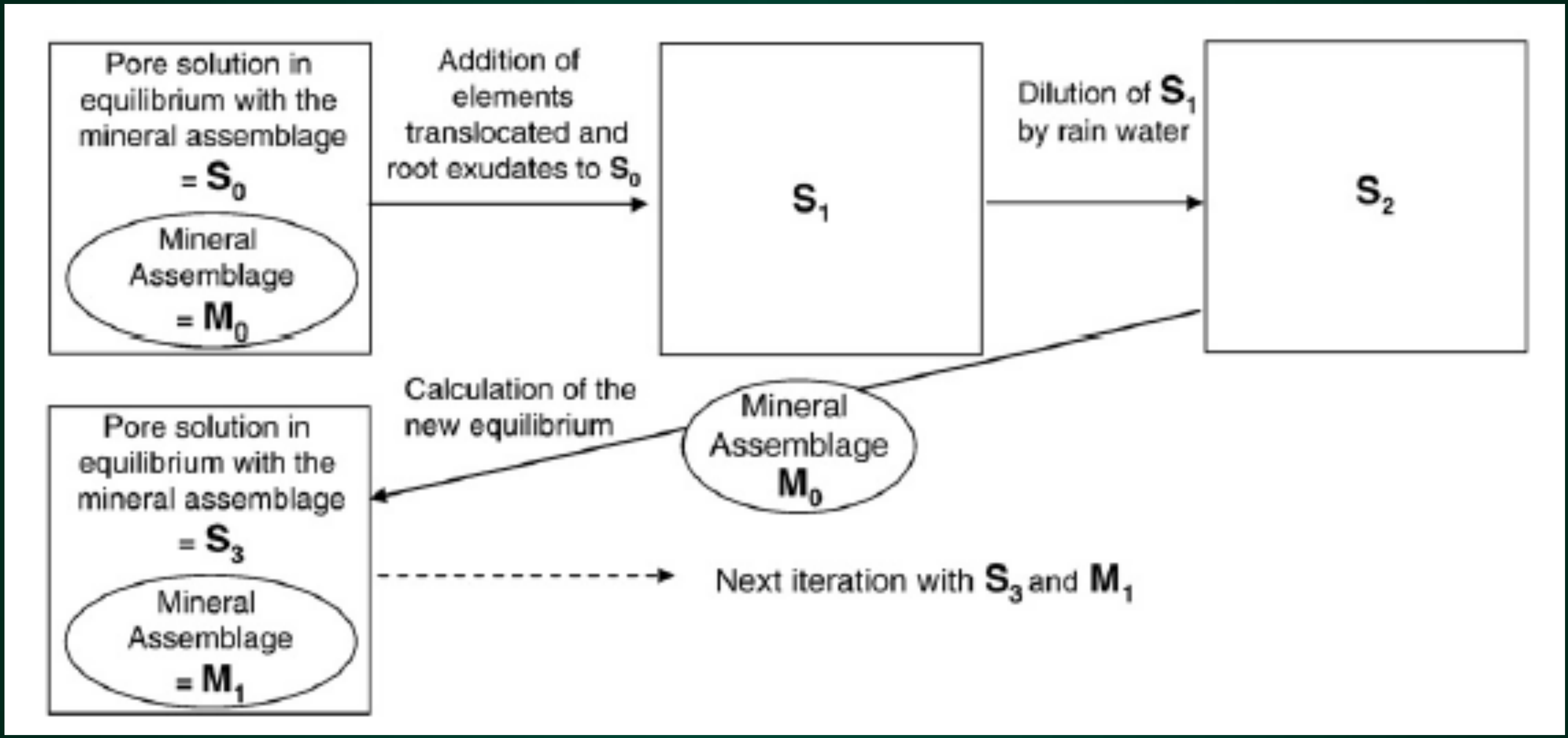
Image source
https://openclipart.org/detail/90025/tree-branches-and-root-01r
https://openclipart.org/detail/22004/weather-symbols-rain

Batch-reaction pathway



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From Barré et al., 2009

Model parameters

From Barré et al., 2009

Table 2
Selected parameter values for a "reference" temperate grassland ecosystem.

Parameter	Values
Soil horizon	0–10 cm
Bulk density	1.2 g/cm^3
Clay mineral content	25%
porosity	25%
Initial mineral phases	Illite, Ca montmorillonite, kaolinite, calcite
pCO_2	$10^{-3.5}$ ppm
Rain water	750 mm/year
Net primary production (NPP)	10 t/ha/year
ANPP	0.5*NPP
Roots in the top 10 cm	50%
Translocation	0.5*ANPP
ANPP K content	5%
ANPP Si content	0.75%
ANPP Ca content	1%
ANPP Mg content	0.4%
Root exudation	0.1*NPP
Oxalate introduced in the top 10 cm	0.5 (0.1*NPP)
Rain water interacting with pore solution (*A*)	25%
Temperature	25 °C

E14 fx

	A	B	C	D	E
1					
2		Annual	Monthly		
3	Depth (cm)	10			
4	Rain (mm/yr)	750			
5	NPP (t/ha/yr)	10			
6	Aboveground NPP	5			
7	Translocated NPP	2.5			
8					
9	ANPP K content	0.05			
10	ANPP Si content	0.0075			
11	ANPP Ca content	0.01			
12	ANPP Mg content	0.004			
13					
14	K addition	0.125	0.01042	(t/ha/mo)	
15	Si addition	0.01875	0.00156	(t/ha/mo)	
16	Ca additon	0.025	0.00208	(t/ha/mo)	
17	Mg addition	0.01	0.00083		
18					
19	Root exudation (t/ha/yr)	1.0			
20	Oxalate produced in top 10 cm	0.5	0.04167	(t/ha/mo)	
21	Rainwater acting in pore (mm)	187.5	15.625	(kg/m^2/mo)	
22					

Solution reactants

Initial pore solution

Monthly addition:

- Root exudates/elements
- Rain water

Water/clay ratio	1 kg water / 1 kg clay			
	Mass (g/m^2)	**Molec. Wt.**	**mol**	
Initial solution	25000	18.02	1387.71	H_2O
K	1.04167	39.10	0.0266	KCl
Si	0.15625	28.09	0.0056	Chalcedony
Ca	0.20833	40.08	0.0052	$CaCl_2$
Mg	0.08333	24.31	0.0034	$MgCl_2$
Oxalate	4.16667	88.02	0.0473	Oxalic acid
Water	15625	18.02	867.32	H_2O

Clay (plus calcite) composition

	Mass clay	**Formula**	**Form. Wt**	**mol**
g/m^2	25000			
Illite	6250	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	383.90	16.280
Ca-mont	6250	$Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	366.56	17.050
Kaol	6250	$Al_2Si_2O_5(OH)_4$	258.16	24.210
Calc	6250	$CaCO_3$	100.09	62.446

Adding oxalate to the model

- Oxalate: $C_2O_4^{2-}$
  - Not defined in PHREEQC database
- Mg-, Ca-, & Al-oxalate complexes

```
SOLUTION_MASTER_SPECIES
Ox      Ox-2  0.0    Ox     88.018
SOLUTION_SPECIES
        H2Ox = H2Ox
        log_k    0.0
        HOx- = HOx-
        log_k    0.0
        Ox-2 = Ox-2
        log_k    0.0
        H+ + HOx- = H2Ox
        log_K 1.25
        H+ + Ox-2 = HOx-
        log_K 4.27
PHASES
Mg-Oxalate
        MgOx = Mg+2 + Ox-2
        log_K -3.439
Ca-Oxalate
        CaOx = Ca+2 + Ox-2
        log_K -3.000
Al-Oxalate
        Al2Ox3 = 2 Al+3 + 3 Ox-2
        log_K -7.100
```

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From Harrison and Thyne, 1992

Model structure

- SOLID_SOLUTIONS
  - Defined mass added (mol)
  - Keep track of mass
- REACTION
  - Element mass added (mol)
- EQUILIBRIUM_PHASES

- Cycle ran 12 times using previous solid solution

```
TITLE Cycle 1
SOLUTION 0 Pore solution
        temp     25.0
        -water   25.0 #kg
SOLID_SOLUTIONS 0 Mineral assemblage initial
        Clay fraction
        -comp         Illite                    16.280
        -comp         Ca-montmorillonite        17.050
        -comp         Kaolinite                 24.210
        -comp         Calcite                   62.446
USE solution 0
USE solid_solution 0
EQUILIBRIUM_PHASES 0
        CO2(g)                      -3.5
SAVE solution 1
END
USE solution 1
REACTION 1
        KCl                 0.026642
        Chalcedony          0.005563
        CaCl2               0.005198
        MgCl2               0.003429
        H2Ox                0.047339
        1.0 moles
SAVE solution 2
END
USE solution 2
REACTION 2
        H2O                 1.0
        867.3192978 moles
SAVE solution 3
END
USE solid_solution 0
USE solution 3
EQUILIBRIUM_PHASES 1
```

Model output
Initial solution equilibration

-------------------------------Solid solutions-------------------------------

Solid solution	Component	Moles	Delta moles	Mole fract
Clay		1.20e+02		
	Illite	1.63e+01	-1.25e-02	1.36e-01
	Ca-montmorillonite	1.70e+01	-9.07e-02	1.41e-01
	Kaolinite	2.43e+01	1.20e-01	2.03e-01
	Calcite	6.25e+01	8.11e-03	5.20e-01

-----------------------Description of solution-----

pH = 8.265

pe = 9.684

Specific Conductance (µS/cm, 25°C) = 104

Density (g/cm³) = 0.99735

Volume (L) = 25.07403

Phase	SI**
Al(OH)3(a)	-5.15
Anorthite	-5.99
Aragonite	-0.43
Ca-Montmorillonite	-0.85
Calcite	-0.28
CH4(g)	-121.36
Chalcedony	1.28
Chlorite(14A)	-1.18
Chrysotile	0.89
CO2(g)	-3.50
Dolomite	-0.78
Gibbsite	-2.46
H2(g)	-35.95
H2O(g)	-1.50
Illite	-0.87
K-feldspar	1.45
K-mica	2.13
Kaolinite	-0.69
O2(g)	-11.39
Quartz	1.71
Sepiolite	2.51
Sepiolite(d)	-0.39
SiO2(a)	0.44
Talc	7.14

Model output
Cycle 1: Element addition & mineral re-equilibration

-------------------------------Solid solutions--------------------------------

Solid solution	Component	Moles	Delta moles	Mole fract
Clay		1.20e+02		
	Illite	1.63e+01	-8.39e-03	1.36e-01
	Ca-montmorillonite	1.70e+01	-5.02e-02	1.42e-01
	Kaolinite	2.43e+01	6.82e-02	2.02e-01
	Calcite	6.24e+01	-3.23e-02	5.20e-01

-----------------------Description of solution----

pH	=	7.960
pe	=	10.086
Specific Conductance (µS/cm, 25°C)	=	319
Density (g/cm³)	=	0.99754
Volume (L)	=	40.74688

Phase	SI**
Al(OH)3(a)	-5.16
Al-Oxalate	-38.63
Anorthite	-5.99
Aragonite	-0.43
Ca-Montmorillonite	-0.85
Ca-Oxalate	-3.12
Calcite	-0.28
CH4(g)	-122.15
Chalcedony	1.28
Chlorite(14A)	-3.39
Chrysotile	-0.44
CO2(g)	-3.50
Dolomite	-1.22
Gibbsite	-2.47
H2(g)	-36.14
H2O(g)	-1.50
Illite	-0.87
K-feldspar	1.64
K-mica	2.32
Kaolinite	-0.69
Mg-Oxalate	-3.46
O2(g)	-11.00
Quartz	1.71
Sepiolite	1.63
Sepiolite(d)	-1.27
SiO2(a)	0.44
Sylvite	-6.96
Talc	5.82

Model output
After 12 cycles

```
-------------------------------Solid solutions-------------------------------

Solid solution                 Component        Moles   Delta moles   Mole fract

Clay                                        1.20e+02
                                  Illite    1.62e+01    -9.13e-03     1.35e-01
                       Ca-montmorillonite   1.65e+01    -4.66e-02     1.38e-01
                                Kaolinite   2.50e+01     6.48e-02     2.09e-01
                                  Calcite   6.21e+01    -3.25e-02     5.18e-01
```

Cumulative change

	Initial (mol)	Final (mol)	Δmol	Relative amount (%)
Illite	16.28	16.2	-0.080	99.5
Ca-mont	17.05	16.5	-0.550	96.8
Kaolinite	24.21	25.0	0.790	103.3
Calcite	62.45	62.1	-0.346	99.4

```
Phase                  SI** l

Al(OH)3(a)            -5.13
Al-Oxalate           -38.58
Anorthite             -5.98
Aragonite             -0.43
Ca-Montmorillonite    -0.86
Ca-Oxalate            -3.12
Calcite               -0.29
CH4(g)               -21.12
Chalcedony             1.26
Chlorite(14A)         -3.33
Chrysotile            -0.44
CO2(g)                -3.50
Dolomite              -1.21
Gibbsite              -2.44
H2(g)                -10.89
H2O(g)                -1.50
Illite                -0.87
K-feldspar             1.61
K-mica                 2.34
Kaolinite             -0.68
Mg-Oxalate            -3.45
O2(g)                -61.51
Quartz                 1.69
Sepiolite              1.59
Sepiolite(d)          -1.31
SiO2(a)                0.42
Sylvite               -6.95
Talc                   5.78
```

Discrepancies with Barré et al., 2009

	Δmmol/kgw	
	Barré et al., 2009	Model attempt
Illite	0.205	-0.38
Ca-mont	-0.063	-2.59
Kaolinite	-0.182	3.72
Calcite		-1.63

- Database: PhreeqC vs. SUPCRT92
- Original clay mineral assemblage not defined

Synthesis of additional minerals?

Supersaturated in:

- K-feldspar ↓
- K-mica ↑
- Talc ↓

SI after 1 cycle

Phase	SI** l
Al(OH)3(a)	-5.16
Al-Oxalate	-38.63
Anorthite	-5.99
Aragonite	-0.43
Ca-Montmorillonite	-0.85
Ca-Oxalate	-3.12
Calcite	-0.28
CH4(g)	-122.15
Chalcedony	1.28
Chlorite(14A)	-3.39
Chrysotile	-0.44
CO2(g)	-3.50
Dolomite	-1.22
Gibbsite	-2.47
H2(g)	-36.14
H2O(g)	-1.50
Illite	-0.87
K-feldspar	1.64
K-mica	2.32
Kaolinite	-0.69
Mg-Oxalate	-3.46
O2(g)	-11.00
Quartz	1.71
Sepiolite	1.63
Sepiolite(d)	-1.27
SiO2(a)	0.44
Sylvite	-6.96
Talc	5.82

SI after 12 cycles

Phase	SI** l
Al(OH)3(a)	-5.13
Al-Oxalate	-38.58
Anorthite	-5.98
Aragonite	-0.43
Ca-Montmorillonite	-0.86
Ca-Oxalate	-3.12
Calcite	-0.29
CH4(g)	-21.12
Chalcedony	1.26
Chlorite(14A)	-3.33
Chrysotile	-0.44
CO2(g)	-3.50
Dolomite	-1.21
Gibbsite	-2.44
H2(g)	-10.89
H2O(g)	-1.50
Illite	-0.87
K-feldspar	1.61
K-mica	2.34
Kaolinite	-0.68
Mg-Oxalate	-3.45
O2(g)	-61.51
Quartz	1.69
Sepiolite	1.59
Sepiolite(d)	-1.31
SiO2(a)	0.42
Sylvite	-6.95
Talc	5.78

Refitting model for K-mica, K-feldspar, talc

Initial equilibration

```
-------------Solid solutions-----------------

     Component              Moles   Delta moles

                         1.19e+02
        Illite           3.44e-02    -1.62e+01
Ca-montmorillonite       2.35e+01     6.41e+00
     Kaolinite           2.35e+01    -7.55e-01
       Calcite           6.14e+01    -1.07e+00
        K-mica           7.09e+00     7.09e+00
    K-feldspar           2.65e+00     2.65e+00
          Talc           1.35e+00     1.35e+00
```

After 12th cycle

```
-------------Solid solutions-----------------

     Component              Moles   Delta moles

                         1.19e+02
        Illite           3.46e-02     1.40e-05
Ca-montmorillonite       2.28e+01    -6.52e-02
     Kaolinite           2.37e+01     2.74e-02
       Calcite           6.07e+01    -5.21e-02
        K-mica           7.49e+00     3.51e-02
    K-feldspar           2.58e+00    -8.52e-03
          Talc           1.37e+00     1.13e-03
```

Cumulative change:
Equilibration to final

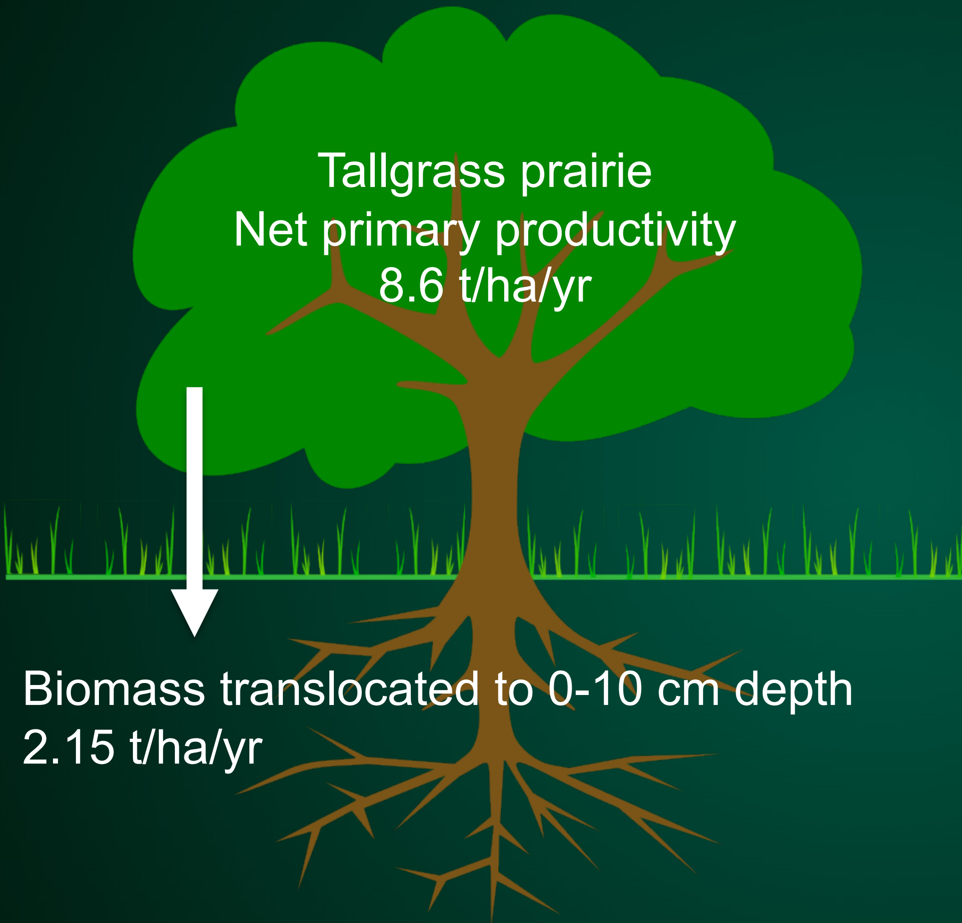
	Start (mol)	Initial equilibration (mol)	Final (mol)	Δmol final
Illite	16.28	0.0344	0.0346	0.0002
Ca-mont	17.05	23.5	22.8	-0.7
Kaolinite	24.21	23.5	23.7	0.2
Calcite	62.45	61.4	60.7	-0.7
K-mica	0.0	7.1	7.5	0.4
K-feldspar	0.0	2.7	2.6	-0.07
Talc	0.0	1.35	1.37	0.02

Temperature grassland: Model failure

- Parameters of Barré et al., 2009
  - Failure to synthesize illite
  - Synthesis of kaolinite backs up classical weathering theory
- Allowance for K-mica, K-feldspar, talc
  - Immediate re-equilibration to those minerals
  - Illite, kaolinite, K-mica, and talc synthesized
  - Kinetic considerations

System inputs: Eastern ND

From Whitman and Wali, 1975



Element addition (t/ha/yr)	
K	0.1075
Si	0.016125
Ca	0.0215
Mg	0.0086
Oxalate	0.43

Rainfall and element addition divided into
12 monthly batch-reaction events

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Image source
https://openclipart.org/detail/90025/tree-branches-and-root-01r
https://openclipart.org/detail/22004/weather-symbols-rain

Eastern ND: Model semi-success

Surface soil from Milnor, ND 2015 (0-6 inches)

	Soil analysis	Initial (mol)	Final (mol)	Δmol
	% of clay fraction			
Illite	20	12.66	12.7	0.04
Ca-mont	74	49.06	45.5	-3.56
Kaolinite	6	5.65	9.79	4.14
Calcite	2.8 (of whole soil)	6.99	7.12	0.13

Discussion

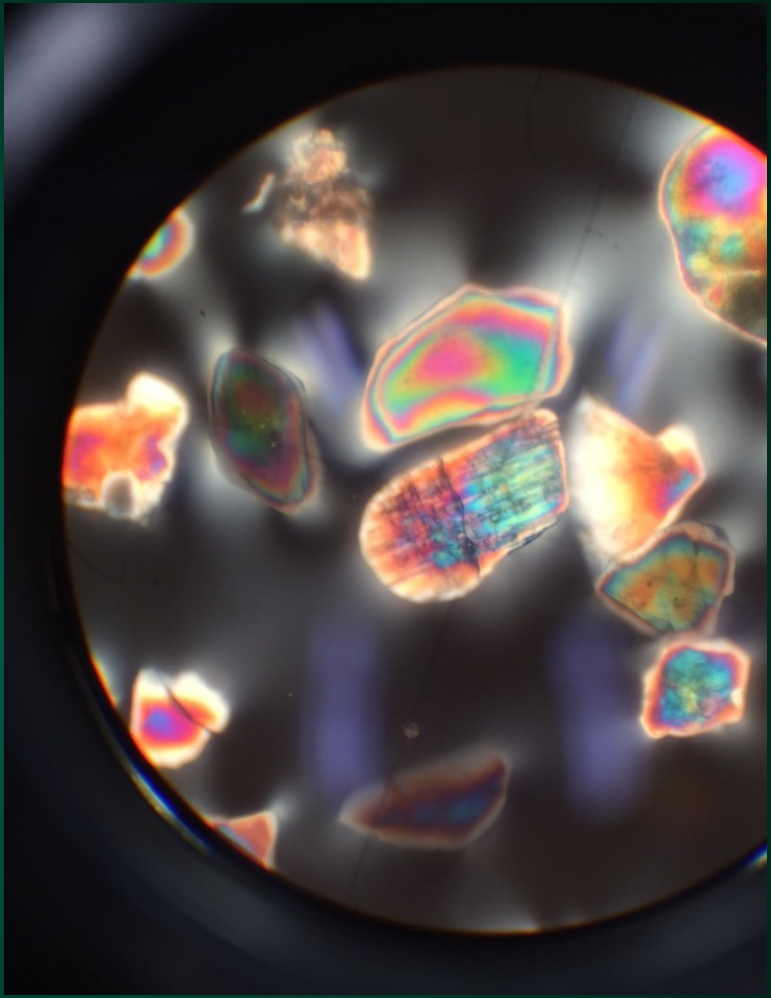
- Unable to reproduce Barré et al., 2009
  - Original clay mineral assemblage

- Neoformation of K-mica and K-feldspar?
- Nonexchangeable K release slow in soils (Sparks and Huang, 1985)
- Eastern ND soil
  - Stabilized illite and kaolinite, loss of smectite

Conclusion

- Model requires some “tinkering”
  - System and soil characteristic dependent
  - Kinetic considerations
- Possible rejection of classical weathering theory in surface soils
  - Empirical data
  - Element translocation and nutrient uplift
  - Fertilizer K additions, crop K removal

Questions?



“Tartan” twinning of microcline (K-feldspar)

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