INVERSE MODELING ON SOIL SOLUTION WATER TO DETERMINE SOIL CHEMICAL COMPOSITION

BRANDON MONTGOMERY

NDSU GEOCHEMISTRY 628

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OVERVIEW

Introduction

Experiment/discussion

Conclusion

Questions

RESEARCH QUESTION

Can PHREEQC be used to determine the chemical composition of soil based on soil solution water?

Controls on Soil Solution Chemistry in a Subalpine Forest in North-Central Colorado

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ABSTRACT

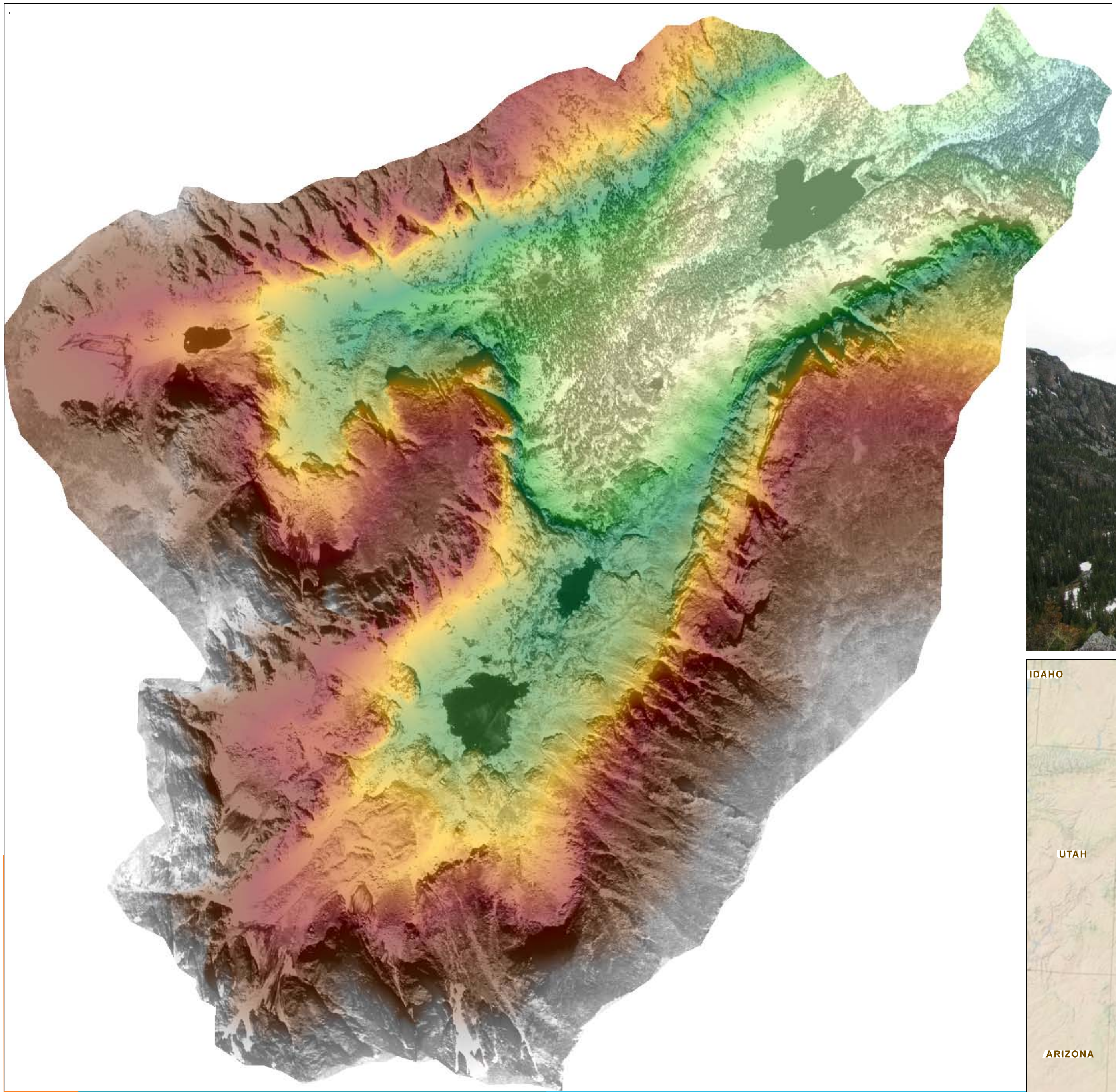
High-elevation ecosystems in the western USA are potentially susceptible to increased inputs of strong acids. A long-term research project was established to identify the processes controlling surface water chemistry and to evaluate the sensitivity of Loch Vale Watershed in Rocky Mountain National Park, Colorado, to acid precipitation. Using lysimeters, we estimated the concentration and flux of major solutes in the Oie and B horizons in an old-grown Engelmann spruce (*Picea engelmannii* Parry ex Engelm.) and subalpine fir [*Abies lasiocarpa* (Hook.) Nutt.] forest, and in an adjacent site disturbed by a snow avalanche. In the forested site, most solutes were highly concentrated in soil solutions during the initial stages of snowmelt, and concentrations declined rapidly to low levels in the first 4 to 6 wk of snowmelt. Surface water chemistry in Loch Vale Watershed is controlled principally by mineral weathering. During the early stages of snowmelt, however, the flushing of solutes, especially N, S, and C, from forest soils (which comprise only 6% of the study area) exerts an important influence. Rates of cationic denudation per unit area were 3.5 times higher in the forest (131 $\mu mol_c\ m^{-2}\ yr^{-1}$) than in the whole watershed (38 $\mu mol_c\ m^{-2}\ yr^{-1}$) probably because of H^+ exudation from roots during nutrient uptake and the generation of organic acids in the forest soils. Rates of N mineralization and nitrification as well as concentrations of NO_3 in the soil solution were higher in the second year after forest disturbance from a snow avalanche than immediately following the disturbance, indicating a delayed nitrification response. Significant amounts of NH_4 and NO_3 were temporarily stored in extractable forms in the soil during the first year after the disturbance. Although precipitation inputs and theoretical mineral weathering can explain the total annual solute flux from Loch Vale Watershed, the effects of forest soil solutes may be important during the initial stages of snowmelt and following large-scale disturbance.

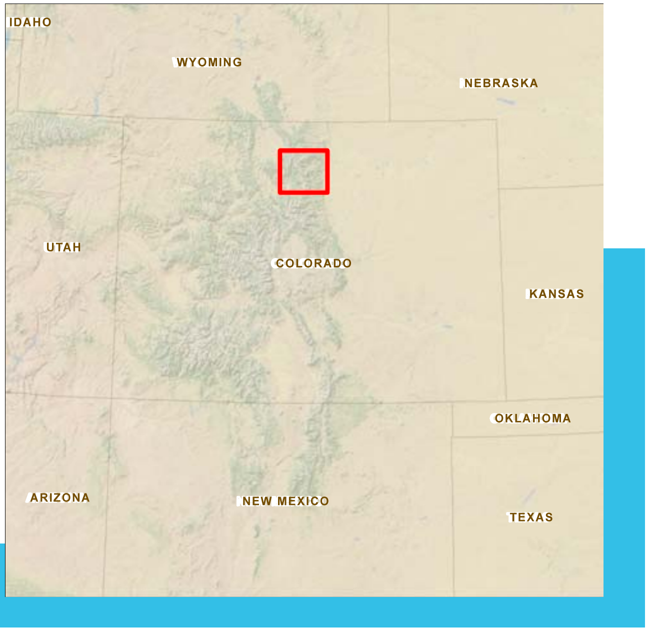
term changes in soil solution chemistry during snowmelt may also result from the flushing of byproducts of decomposition and mineral weathering (Fahey and Yavitt, 1988) that could neutralize acidity. It is likely that a combination of natural biotic and abiotic factors and anthropogenic inputs are responsible for seasonal and long-term changes in surface water chemistry.

At Loch Vale Watershed, located in Rocky Mountain National Park, yearly average surface water pH is 6.3, but during spring snowmelt the pH of streamwater can be as low as 5.7 (Baron and Bricker, 1987). A long-term research project was established in 1983 to identify the processes controlling surface water chemistry and to evaluate the sensitivity of this watershed to acidic precipitation. Researchers have characterized the sensitivity of the soil environment to acid deposition (Walthall, 1985) and quantified rates of cationic denudation at the study area (Mast, 1989). This study of soil solution chemistry is part of a larger research project designed to quantify internal transfers of acidity and to evaluate the importance of the vegetation in influencing the geochemistry of the watershed (Arthur, 1990). The objectives of our study were to: (i) determine the importance of several mechanisms regulating soil solution fluxes, including adsorption by soil surfaces and decomposition and leaching in the forest floor, (ii) examine changes in soil solution chemistry with depth and time, and (iii) quantify element fluxes so that nutrient budgets could be calculated. Our hypotheses were that (i) concentrations of plant nutrients, especially NH, NO, and K would

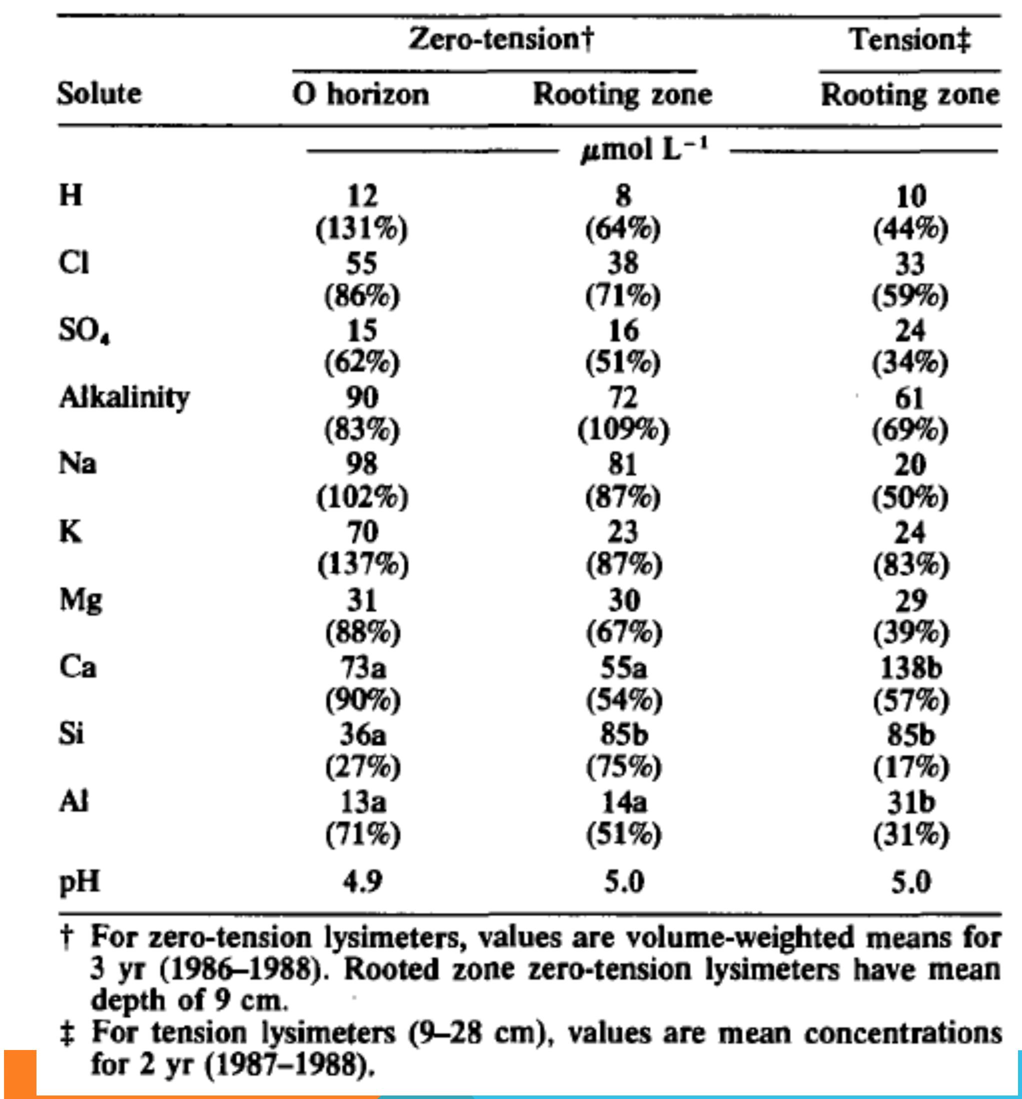
THE LOCH VALE WATERSHED

Photo Courtesy of Jake Tyson





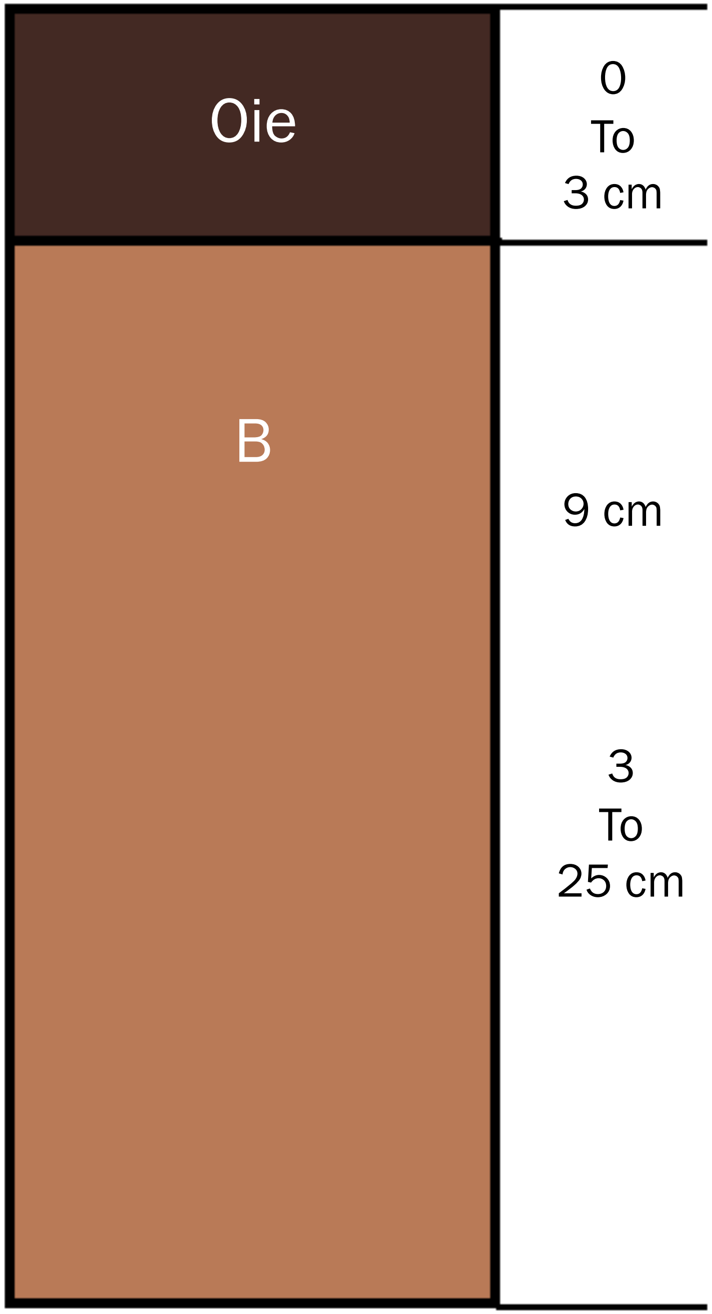
"Logistical support and/or data were provided by the USGS supported Loch Vale Watershed Long-term Ecological Research and Monitoring program and Colorado State University."



Solute	Zero-tension† O horizon	Zero-tension† Rooting zone	Tension‡ Rooting zone
	µmol L⁻¹		
H	12 (131%)	8 (64%)	10 (44%)
Cl	55 (86%)	38 (71%)	33 (59%)
SO_4	15 (62%)	16 (51%)	24 (34%)
Alkalinity	90 (83%)	72 (109%)	61 (69%)
Na	98 (102%)	81 (87%)	20 (50%)
K	70 (137%)	23 (87%)	24 (83%)
Mg	31 (88%)	30 (67%)	29 (39%)
Ca	73a (90%)	55a (54%)	138b (57%)
Si	36a (27%)	85b (75%)	85b (17%)
Al	13a (71%)	14a (51%)	31b (31%)
pH	4.9	5.0	5.0

† For zero-tension lysimeters, values are volume-weighted means for 3 yr (1986–1988). Rooted zone zero-tension lysimeters have mean depth of 9 cm.

‡ For tension lysimeters (9–28 cm), values are mean concentrations for 2 yr (1987–1988).



Lysimeter- used to collect leachate in soils, or provide measurements for evapotranspiration.

Snowpack Melt and Precipitation Percolating through the Oie Horizon

Input Waters

```
SOLUTION 1
    temp         1
    pH           5.38
    pe           4
    redox        pe
    units        mg/kgw
    density      1
    Ca           0.2842
    Mg           0.04
    Na           0.1828
    K            0.08
    S(6)         0.5157
    Cl           0.1585
    Si           0.60667
    Al           10.2 ug/kgw
    -water       1 # kg


SOLUTION 3
    temp         5
    pH           5.48
    pe           4
    redox        pe
    units        mg/kgw
    density      1
    Ca           0.29
    Mg           0.031
    K            0.02
    Na           0.061
    Cl           0.09
    S(6)         0.81
    -water       1 # kg
```

Output Water

```
SOLUTION 2
    temp         5
    pH           4.9
    pe           4
    redox        pe
    units        umol/kgw
    density      1
    Cl           55
    S(6)         15
    Alkalinity 90
    Na           98
    K            70
    Mg           31
    Ca           73
    Si           36
    Al           13
    -water       1 # kg
```

Modeling Set-up

```
INVERSE_MODELING 1
    -solutions          1        3        2
    -uncertainty        0.75     0.75     0.75
    -phases
        CO2(g)          force dis
        CaX2
        H2(g)
        H2O(g)          force dis
        MgX2
        NH4X
        NaX
        O2(g)           force dis
        AlX3
        KX
        N2(g)
    -balances
        Al              0.75     0.75     0.75
        Alkalinity      0.75     0.75     0.75
        Ca              0.75     0.75     0.75
        Mg              0.75     0.75     0.75
        Na              0.75     0.75     0.75
        Si              0.75     0.75     0.75
        S(6)            0.75     0.75     0.75
        Cl              1        1        1
        H(0)            0.75     0.75     0.75
        K               0.75     0.75     0.75
    -range                 1000
    -minimal
    -tolerance             1e-010
    -force_solutions       false true false
    -mineral_water         true
    -multiple_precision         true
    -mp_tolerance 1e-012
    -censor_mp 1e-020
```

```
Solution 2:

                  Input          Delta     Input+Delta
          pH  4.900e+000 +  0.000e+000 =  4.900e+000
          Al  1.300e-005 +  0.000e+000 =  1.300e-005
  Alkalinity  9.000e-005 +  1.974e-005 =  1.097e-004
       C(-4)  0.000e+000 +  0.000e+000 =  0.000e+000
        C(4)  4.161e-003 +  8.152e-004 =  4.976e-003
          Ca  7.300e-005 + -5.475e-005 =  1.825e-005
          Cl  5.500e-005 + -5.053e-005 =  4.471e-006
        H(0)  0.000e+000 +  0.000e+000 =  0.000e+000
           K  7.000e-005 + -5.250e-005 =  1.750e-005
          Mg  3.100e-005 + -2.325e-005 =  7.750e-006
       N(-3)  0.000e+000 +  0.000e+000 =  0.000e+000
        N(0)  0.000e+000 +  0.000e+000 =  0.000e+000
        N(3)  0.000e+000 +  0.000e+000 =  0.000e+000
        N(5)  0.000e+000 +  0.000e+000 =  0.000e+000
          Na  9.800e-005 + -7.350e-005 =  2.450e-005
        O(0)  0.000e+000 +  0.000e+000 =  0.000e+000
       S(-2)  0.000e+000 +  0.000e+000 =  0.000e+000
        S(6)  1.500e-005 + -5.605e-006 =  9.395e-006
          Si  3.600e-005 + -2.590e-005 =  1.010e-005
           X  0.000e+000 +  0.000e+000 =  0.000e+000
```

Delta- Any adjustments to the original data (must fall within the uncertainty limits)

```
Solution fractions:                            Minimum        Maximum
   Solution   1      1.000e+000      5.093e-001     1.000e+000
   Solution   3      0.000e+000      0.000e+000     4.908e-001
   Solution   2      1.000e+000      1.000e+000     1.000e+000

Phase mole transfers:                          Minimum        Maximum
            CO2(g)      4.976e-003      2.904e-003     7.281e-003   CO2
              CaX2      1.586e-005      6.797e-006     5.722e-005   CaX2
             H2(g)      1.707e-004      1.139e-004     2.724e+001   H2
            H2O(g)      0.000e+000      0.000e+000     2.724e+001   H2O
              MgX2      6.105e-006      4.870e-006     4.981e-005   MgX2
              NH4X     -1.138e-004     -1.621e-004    -7.591e-005   NH4X
               NaX      1.655e-005      1.058e-005     1.080e-004   NaX
             O2(g)      0.000e+000      0.000e+000     1.362e+001   O2
              AlX3      1.262e-005      2.588e-006     2.270e-005   AlX3
                KX      1.545e-005      1.392e-005     1.020e-004   KX
             N2(g)      5.690e-005      3.795e-005     8.103e-005   N2

Redox mole transfers:
              H(0)      3.414e-004
             N(-3)     -1.138e-004
              N(0)      1.138e-004

Sum of residuals (epsilons in documentation):         8.814e+000
Sum of delta/uncertainty limit:                       8.813e+000
Maximum fractional error in element concentration:    9.187e-001
```

- Precipitation of Ammonium
- Immobilization
- C:N Ratio

Gravity Dependent Soil Solution Water Moving through the Mineral Horizon

Modeling Set-up

Input

```
SOLUTION 2
    temp      5
    pH        4.9
    pe        4
    redox     pe
    units     umol/kgw
    density   1
    Cl        55
    S(6)      15
    Alkalinity 90
    Na        98
    K         70
    Mg        31
    Ca        73
    Si        36
    Al        13
    -water    1 # kg
```

Output

```
SOLUTION 3
    temp      5
    pH        5
    pe        4
    redox     pe
    units     umol/kgw
    density   1
    S(6)      16
    Alkalinity 72
    Na        81
    K         23
    Mg        30
    Ca        55
    Si        85
    Al        14
    Cl        38
    -water    1 # kg
```

```
INVERSE_MODELING 1
    -solutions      2       3
    -uncertainty   0.5     0.4
    -phases
        Al(OH)3(a)
        Albite                dis
        Alunite               dis
        Anhydrite
        Anorthite             dis
        Aragonite             dis
        Ca-Montmorillonite
        Calcite          force
        Chalcedony
        Chlorite(14A)
        Chrysotile
        CO2(g)           force
        Dolomite
        Gibbsite         force dis
        Gypsum           force
        H2(g)
        H2O(g)
        Halite
        Illite
        K-feldspar       force dis
        K-mica           force dis
        Kaolinite
        O2(g)                 dis
        Quartz           force dis
        Sepiolite
        Sepiolite(d)
        SiO2(a)
        Talc                  dis
    -range           1000
    -minimal
    -tolerance         1e-010
    -mineral_water     true
    -multiple_precision     true
    -mp_tolerance 1e-012
    -censor_mp 1e-020
```

```
Phase mole transfers:                 Minimum        Maximum
        Alunite     1.120e-005     0.000e+000     1.840e-005
KAl3(SO4)2(OH)6
Ca-Montmorillon    -1.807e+001    -1.807e+001    -1.807e+001
Ca0.165Al2.33Si3.67O10(OH)2
        Calcite     2.982e+000     2.981e+000     2.982e+000   CaCO3
     Chrysotile    -9.685e+000    -9.685e+000    -9.685e+000   Mg3Si2O5(OH)4
         CO2(g)    -2.978e+000    -2.978e+000    -2.978e+000   CO2
         Gypsum     0.000e+000    -1.440e-005     2.240e-005   CaSO4:2H2O
         Halite     4.860e-005     4.860e-005     5.320e-005   NaCl
         K-mica     7.200e-006     0.000e+000     1.840e-005
KAl3Si3O10(OH)2
      Kaolinite     2.105e+001     2.105e+001     2.105e+001   Al2Si2O5(OH)4
      Sepiolite     1.453e+001     1.453e+001     1.453e+001
Mg2Si3O7.5OH:3H2O

Redox mole transfers:

Sum of residuals (epsilons in documentation):        8.106e+000
Sum of delta/uncertainty limit:                      8.106e+000
Maximum fractional error in element concentration:   4.000e-001
```

```
Phase mole transfers:                 Minimum        Maximum
      Anhydrite     2.240e-005    -1.000e+003     1.000e+003   CaSO4
      Anorthite     3.826e+000     0.000e+000     1.000e+003   CaAl2Si2O8
Ca-Montmorillon    -2.321e+001    -1.000e+003     1.000e+003
Ca0.165Al2.33Si3.67O10(OH)2
        Calcite     3.576e-003    -1.000e+003     1.000e+003   CaCO3
  Chlorite(14A)    -4.784e+000    -1.000e+003     1.000e+003
Mg5Al2Si3O10(OH)8
         CO2(g)     0.000e+000    -1.000e+003     1.000e+003   CO2
       Gibbsite     0.000e+000     0.000e+000     1.000e+003   Al(OH)3
         Gypsum     0.000e+000    -1.000e+003     1.000e+003   CaSO4:2H2O
         Halite     4.860e-005     4.860e-005     5.320e-005   NaCl
         Illite     3.067e-005    -1.000e+003     3.067e-005
K0.6Mg0.25Al2.3Si3.5O10(OH)2
     K-feldspar     0.000e+000     0.000e+000     1.000e+003   KAlSi3O8
         K-mica     0.000e+000     0.000e+000     1.000e+003
KAl3Si3O10(OH)2
      Kaolinite     2.800e+001    -1.000e+003     1.000e+003   Al2Si2O5(OH)4
         Quartz     0.000e+000     0.000e+000     1.000e+003   SiO2
   Sepiolite(d)     1.196e+001    -1.000e+003     1.000e+003
Mg2Si3O7.5OH:3H2O

Redox mole transfers:

Sum of residuals (epsilons in documentation):        8.106e+000
Sum of delta/uncertainty limit:                      8.106e+000
Maximum fractional error in element concentration:   4.000e-001
```

CONCLUSIONS

Inverse modeling constraints

User constraints

Accuracy?

SOURCES

Arthur, M.A., and T.J. Fahey. 1993. Controls on Soil Solution Chemistry in a Subalpine Forest in North-Central Colorado. Soil Sci. Soc. Am. J. 57: 1122-1130.

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QUESTIONS?