# Evolution of Water Chemistry from Surface Water to Aquifer

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Geochemisty 428

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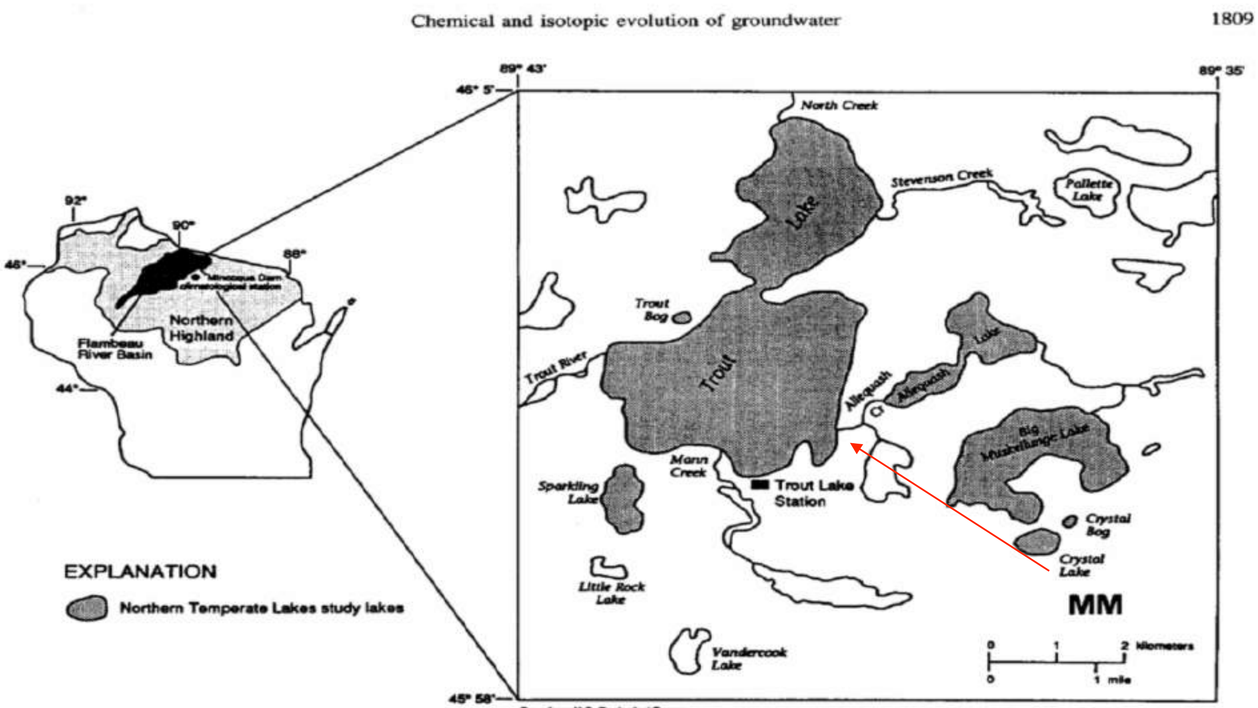
# Background

- Two studies done
  - Galen J. Kenoyer, Carl J. Bowser
  - Thomas Bullen et al
- How chemistry of water changes as it flows to an aquifer
  - Kenoyer/Bowser one flow path
  - Bullen et al two separate paths

# Trout Lake Watershed



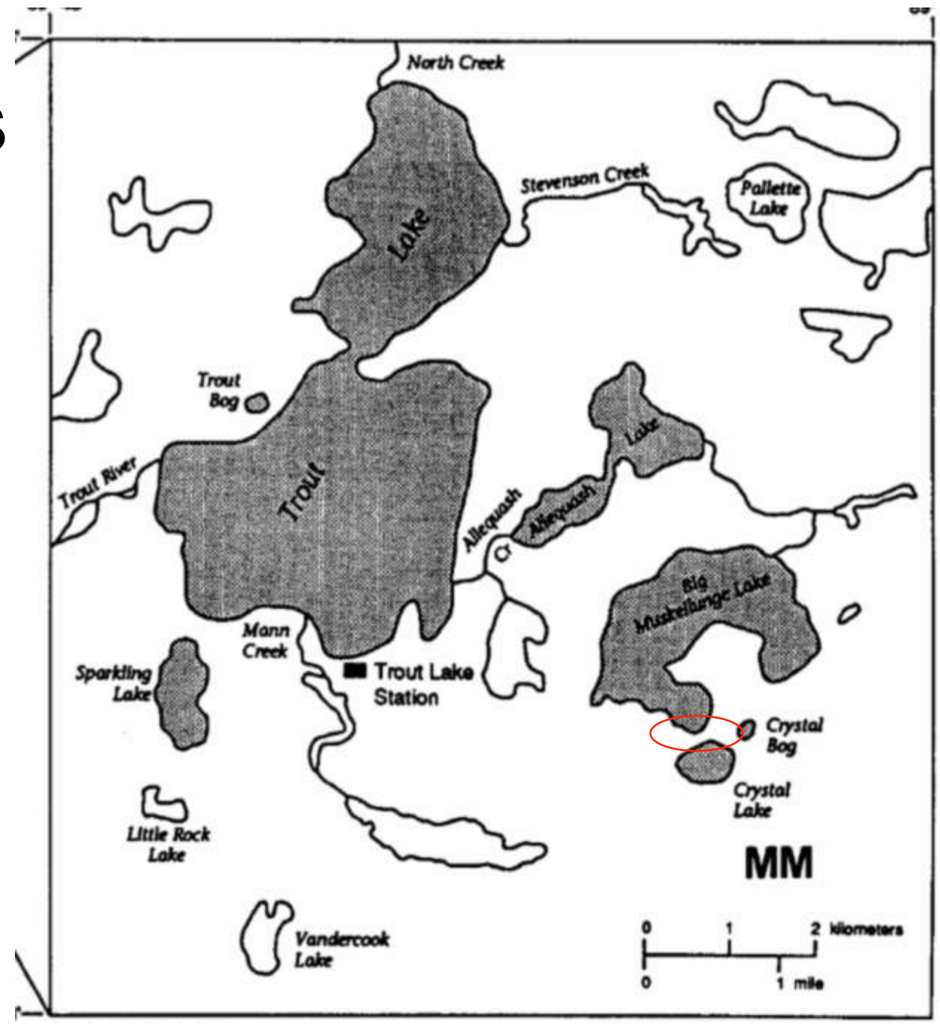

(Bullen et al, 1996)

# Geology of Aquifer

- Aquifer- 50 m sandy glacial outwash
  - Copper Falls Formation
- Overlies Precambrian Rocks
  - Gneiss, amphibolite, schist, granite, monzonites, quartzose, and feldspathic sandstones.
- Groundwater is recharged by seepage from lakes, and by precipitation that infiltrates through highlands

# Analysis of Isthmus

- Dominated by sand-sized materials
- Two extensive silt layers
- Minerals in sand fraction
  - 50-75% quartz
  - 9-15% calcic plagioclase
  - 9-15% sodic plagioclase
  - 2-10% feldspar
  - 1-2% biotite



- Clay minerals
  - 30-40% smectite
  - 30-40% illite
  - 15-30% chlorite/kaolinite
- Isthmus lies inside of state park
  - Compaction
  - Infiltration

# Kenoyer-Bowser

- Flow from Crystal Lake to aquifer
- $PCO_2$ values range from $10^{-2}$ – $10^{-2.5}$
- Age impacts saturation of minerals
- Ion exchange is assumed to be constant

(Kenoryer, Bowser, 1992)

TABLE 1. Log (IAP/Ksp) for Selected Minerals and Waters Along a Groundwater Flow Path at Crystal Lake

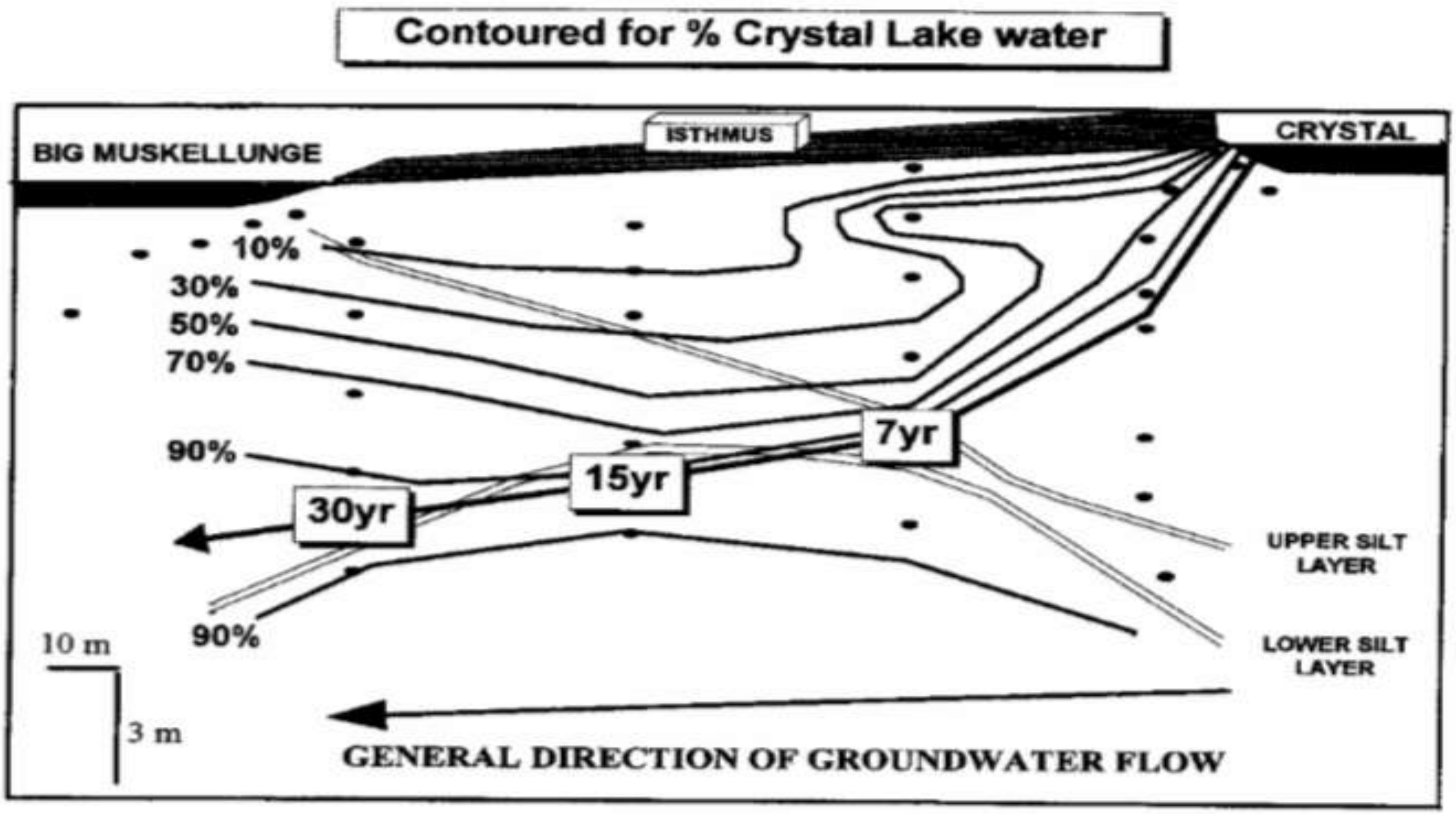
| | Well Number | | |
|---|---|---|---|
| | K86 | K68 | K75 |
| Groundwater age, years | 1.2 | 3.0 | 5.2 |
| Albite | −7.5 | −3.3 | −3.1 |
| Anorthite | −10.0 | −5.0 | −4.4 |
| Phlogopite | −31 | −25 | −23 |
| Diopside | −17 | −14 | −13 |
| Forsterite | −21 | −19 | −18 |
| Enstatite | −10 | −8.6 | 7.8 |
| Tremolite | −49 | −39 | −34 |
| Calcite | −4.9 | −4.3 | −3.7 |
| Dolomite | −10 | −9.2 | −8.0 |
| Quartz | −0.3 | 0.4 | 0.4 |
| Silica gel | −1.3 | −0.6 | −0.6 |
| Halloysite | −2.5 | 1.9 | 1.9 |
| Gibbsite | 1 | 2 | 2 |
| Kaolinite | 2 | 6 | 6 |
| Illite | −3 | 3 | 3 |
| Ca-montmorillonite | −1 | 5 | 5 |
| Montmorillonite (Belle Fourche) | −1 | 5 | 5 |
| Montmorillonite (Aberdeen) | −2 | 3 | 4 |
| Na-beidellite | −2 | 3 | 3 |

# Kenoyer-Bowser

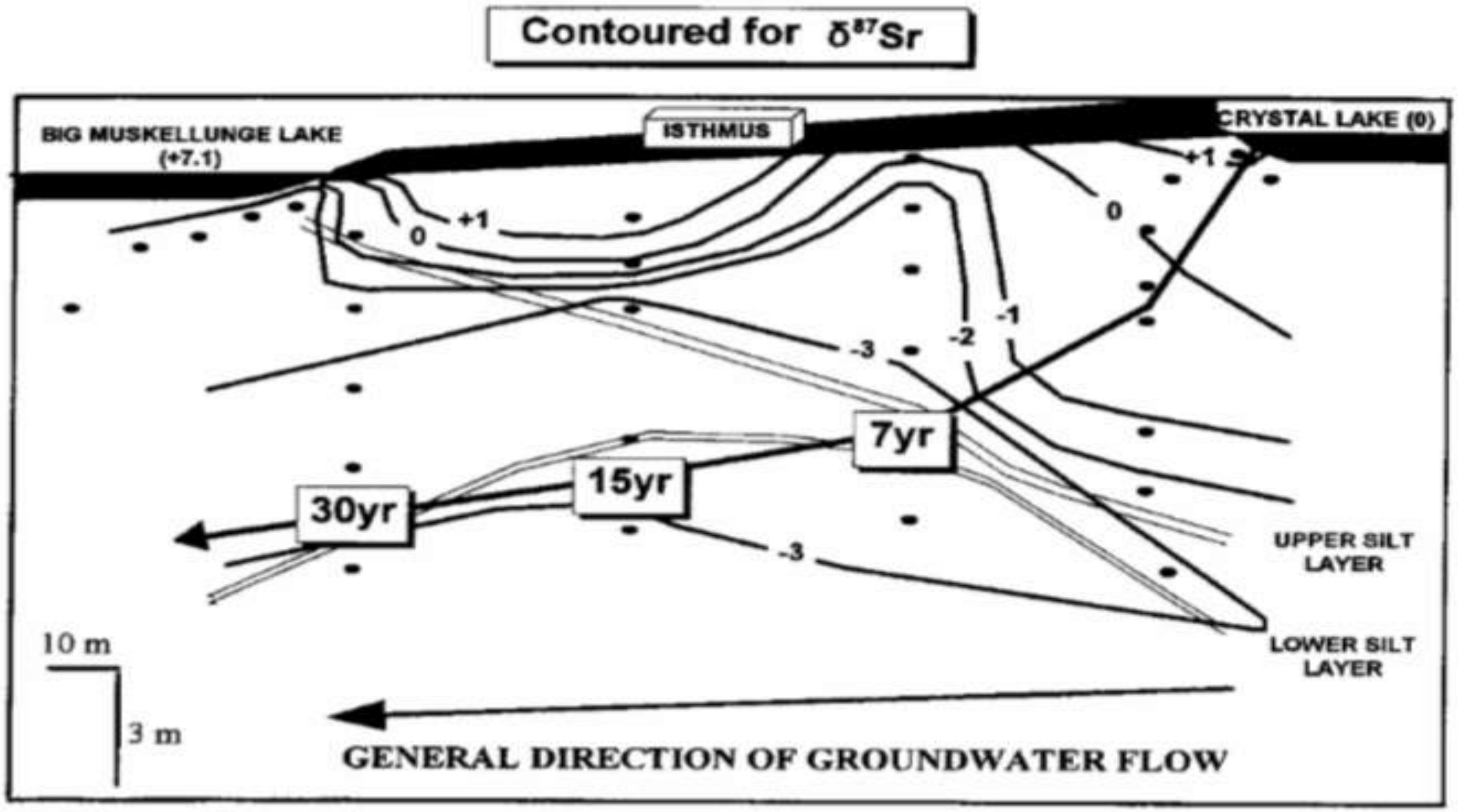
- Phreeqe
- Major increase in calcium, sodium, magnesium, silicon, and alkalinity
  - Explained by dissolution of plagioclase, biotite, and diopside
- Major chemical trends are explained by a model with those dissolutions and precipitation of kaolinite.
- Acidity of initial solution play a major role

# Bullen’s study

- Expanded on same idea
- Used Strontium isotopes to identify solute sources
  - Isotopes stable in solution and are persistent through chemical processes
  - Different minerals and age of sources vary isotope ratio
- Saturated lake pathway has high Sr concentration, compared to surface water on isthmus




(Bullen et al, 1996)




(Bullen et al, 1996)

# Source of Sr

- Decrease in radiogenic Sr
  - Suggests Crystal lake path obtains Sr from Plagioclase and hornblende
- Upland pathways
  - Sr composition controlled by K-feldspar and biotite
  - Contain much more radiogenic Sr
- Different materials impact Sr differently, this allows for identification water source

TABLE 1. Chemical and strontium isotope data for isthmus groundwaters. Concentrations are in mg/L. Data are for the September, 1992 sampling except where labeled (6/93) which denotes samples collected during June, 1993. Samples are arranged from shallow to deep within individual nests.

| sample | Ca | Mg | Sr | Na | K | Fe | Al | Si | $^{87}Sr/^{86}Sr$ | $\delta^{87}Sr$ |
|---|---|---|---|---|---|---|---|---|---|---|
| nest 1: | | | | | | | | | | |
| k1 (shallow) | 4.12 | 0.92 | 0.017 | 1.98 | 0.51 | 3.00 | 0.01 | 0.87 | 0.71078 | +0.76 |
| k85 | 2.15 | 0.52 | 0.012 | 0.86 | 0.59 | 0.00 | 0.03 | 0.79 | 0.71024 | 0.00 |
| k86 | 1.73 | 0.30 | 0.009 | 0.64 | 0.62 | 0.41 | 0.00 | 1.00 | 0.71018 | -0.08 |
| k86 (6/93) | 1.96 | 0.33 | 0.009 | 0.57 | 0.53 | 0.47 | 0.04 | 0.92 | 0.71018 | -0.08 |
| k87 | 1.70 | 0.26 | 0.011 | 0.61 | 0.55 | 0.51 | 0.00 | 0.92 | 0.71008 | -0.23 |
| k87 (6/93) | 1.89 | 0.37 | 0.011 | 0.59 | 0.52 | 0.69 | 0.23 | 1.25 | 0.71018 | -0.08 |
| k88 | 1.79 | 0.38 | 0.006 | 0.90 | 0.52 | 0.68 | 0.00 | 1.78 | 0.70949 | -1.06 |
| k89 | 2.81 | 0.48 | 0.018 | 0.95 | 0.67 | 0.12 | 0.00 | 2.90 | 0.70832 | -2.70 |
| k2 (deep) | 5.37 | 1.97 | 0.017 | 1.66 | 0.59 | 0.03 | 0.01 | 5.08 | 0.70798 | -3.18 |
| nest 2: | | | | | | | | | | |
| k66 (shallow) | 9.42 | 1.61 | 0.068 | 1.53 | 2.61 | 26.94 | 0.02 | 3.68 | 0.70953 | -1.00 |
| k67 | 2.28 | 0.69 | 0.019 | 1.25 | 0.58 | 2.56 | 0.00 | 4.68 | 0.70812 | -2.98 |
| k68 | 4.26 | 0.99 | 0.027 | 1.35 | 0.74 | 0.00 | 0.00 | 4.26 | 0.70814 | -2.96 |
| k69 | 3.55 | 0.85 | 0.023 | 1.39 | 0.77 | 0.00 | 0.00 | 4.22 | 0.70815 | -2.94 |
| k70 | 2.62 | 0.70 | 0.017 | 1.20 | 0.54 | 0.21 | 0.00 | 4.08 | 0.70778 | -3.46 |
| k70 (6/93) | 2.70 | 0.70 | 0.015 | 1.13 | 0.50 | 0.19 | 0.02 | 3.85 | 0.70786 | -3.35 |
| k71 (deep) | 6.41 | 2.69 | 0.018 | 1.58 | 0.61 | 0.02 | 0.00 | 6.20 | 0.70741 | -3.98 |
| nest 3: | | | | | | | | | | |
| k73 (shallow) | 4.30 | 1.36 | 0.029 | 1.42 | 1.64 | 3.78 | 0.03 | 4.71 | 0.71213 | +2.66 |
| k74 | 3.56 | 1.36 | nd | nd | nd | nd | nd | 6.71 | 0.71026 | +0.03 |
| k75 | 2.39 | 0.65 | 0.018 | 1.49 | 0.58 | 4.75 | 0.00 | 5.17 | 0.70805 | -3.08 |
| k76 | 3.58 | 1.56 | 0.019 | 1.79 | 0.79 | 4.15 | 0.05 | 6.82 | 0.70771 | -3.56 |
| k76 (6/93) | 3.51 | 1.50 | 0.018 | 1.89 | 0.64 | 5.91 | 0.01 | 7.23 | 0.70794 | -3.24 |
| k77 (deep) | 3.09 | 1.03 | 0.006 | 0.40 | 1.60 | 0.58 | 0.11 | 0.34 | 0.71130 | +1.49 |
| k77 (6/93) | 8.92 | 3.88 | 0.057 | 1.87 | 1.32 | 2.72 | 2.79 | 12.53 | 0.70827 | -2.77 |
| nest 4: | | | | | | | | | | |
| k6 (shallow) | 3.82 | 1.50 | 0.024 | 1.62 | 1.04 | 10.41 | 0.03 | 6.53 | 0.70969 | -0.77 |
| k80 | 3.72 | 1.93 | 0.012 | 2.56 | 0.56 | 6.15 | 0.02 | 7.55 | 0.70871 | -2.15 |
| k81 | 5.13 | 2.32 | 0.016 | 2.04 | 0.58 | 4.76 | 0.00 | 7.35 | 0.70782 | -3.41 |
| k82 | 7.05 | 3.25 | 0.018 | 1.77 | 0.58 | 1.94 | 0.01 | 11.03 | 0.70756 | -3.77 |
| k82 (6/93) | 7.01 | 3.16 | 0.018 | 1.68 | 0.56 | 2.22 | 0.00 | 9.09 | 0.70756 | -3.77 |
| k5 (deep) | 7.43 | 3.15 | 0.017 | 1.59 | 0.59 | 0.49 | 0.01 | 8.85 | 0.70825 | -2.80 |
| k5 (6/93) | 7.94 | 3.23 | 0.017 | 1.43 | 0.63 | 0.42 | 0.00 | 8.41 | 0.70821 | -2.86 |

(Bullen et al, 1996)

# Bullen's conclusions

- Mineral dissolution reactions may change along flow paths, and differ along contrasting flow paths
- A broad range of radiogenic Sr was produced by weathering
- Compositions of Sr rely heavily on initial environmental conditions
- Contributions from different minerals change along a pathway, nature isn't a simple system

# MFCRWSD

http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx

**Map Unit Legend**

**Kandiyohi County, Minnesota (MN067)**

| Map Unit Symbol | Map Unit Name | Acres in AOI | Percent of AOI |
|---|---|---|---|
| L318A | Lundlake silty clay loam, 0 to 1 percent slopes | 0.9 | 14.4% |
| L324A | Forestcity, overwash-Forestcity complex, 1 to 4 percent slopes | 1.3 | 20.7% |
| L336A | Arctander, overwash-Arctander complex, 1 to 4 percent slopes | 0.6 | 9.2% |
| L357C2 | Koronis-Sunburg complex, 6 to 12 percent slopes, moderately eroded | 3.4 | 55.2% |
| W | Water | 0.0 | 0.5% |
| **Totals for Area of Interest** | | **6.2** | **100.0%** |

- Majority of area of interest is Korinis-Sunburg complex
  - Korinis soil accounts for 60%
  - Mollic Hapludalf
  - Glacial till

http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx

# Assumptions

- Majority of infiltrating water is going to flow through Suburg-Koronis Complex
- Sundburg and Koronis soil units are similar in composition (Mollic Hapludalfs)
- Only taking into account infiltration of water from surface of isthmus
- New housing development doesn't impact infiltration or soil chemistry

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| sample | Ca | Mg | Sr | Na | K | Fe | Al | Si | $^{87}Sr/^{86}Sr$ | $\delta^{87}Sr$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **nest 1:** | | | | | | | | | | |
| k1 (shallow) | 4.12 | 0.92 | 0.017 | 1.98 | 0.51 | 3.00 | 0.01 | 0.87 | 0.71078 | +0.76 |
| k85 | 2.15 | 0.52 | 0.012 | 0.86 | 0.59 | 0.00 | 0.03 | 0.79 | 0.71024 | 0.00 |
| k86 | 1.73 | 0.30 | 0.009 | 0.64 | 0.62 | 0.41 | 0.00 | 1.00 | 0.71018 | -0.08 |
| k86 (6/93) | 1.96 | 0.33 | 0.009 | 0.57 | 0.53 | 0.47 | 0.04 | 0.92 | 0.71018 | -0.08 |
| k87 | 1.70 | 0.26 | 0.011 | 0.61 | 0.55 | 0.51 | 0.00 | 0.92 | 0.71008 | -0.23 |
| k87 (6/93) | 1.89 | 0.37 | 0.011 | 0.59 | 0.52 | 0.69 | 0.23 | 1.25 | 0.71018 | -0.08 |
| k88 | 1.79 | 0.38 | 0.006 | 0.90 | 0.52 | 0.68 | 0.00 | 1.78 | 0.70949 | -1.06 |
| k89 | 2.81 | 0.48 | 0.018 | 0.95 | 0.67 | 0.12 | 0.00 | 2.90 | 0.70832 | -2.70 |
| k2 (deep) | 5.37 | 1.97 | 0.017 | 1.66 | 0.59 | 0.03 | 0.01 | 5.08 | 0.70798 | -3.18 |
| **nest 2:** | | | | | | | | | | |
| k66 (shallow) | 9.42 | 1.61 | 0.068 | 1.53 | 2.61 | 26.94 | 0.02 | 3.68 | 0.70953 | -1.00 |
| k67 | 2.28 | 0.69 | 0.019 | 1.25 | 0.58 | 2.56 | 0.00 | 4.68 | 0.70812 | -2.98 |
| k68 | 4.26 | 0.99 | 0.027 | 1.35 | 0.74 | 0.00 | 0.00 | 4.26 | 0.70814 | -2.96 |
| k69 | 3.55 | 0.85 | 0.023 | 1.39 | 0.77 | 0.00 | 0.00 | 4.22 | 0.70815 | -2.94 |
| k70 | 2.62 | 0.70 | 0.017 | 1.20 | 0.54 | 0.21 | 0.00 | 4.08 | 0.70778 | -3.46 |
| k70 (6/93) | 2.70 | 0.70 | 0.015 | 1.13 | 0.50 | 0.19 | 0.02 | 3.85 | 0.70786 | -3.35 |
| k71 (deep) | 6.41 | 2.69 | 0.018 | 1.58 | 0.61 | 0.02 | 0.00 | 6.20 | 0.70741 | -3.98 |
| **nest 3:** | | | | | | | | | | |
| k73 (shallow) | 4.30 | 1.36 | 0.029 | 1.42 | 1.64 | 3.78 | 0.03 | 4.71 | 0.71213 | +2.66 |
| k74 | 3.56 | 1.36 | nd | nd | nd | nd | nd | 6.71 | 0.71026 | +0.03 |
| k75 | 2.39 | 0.65 | 0.018 | 1.49 | 0.58 | 4.75 | 0.00 | 5.17 | 0.70805 | -3.08 |
| k76 | 3.58 | 1.56 | 0.019 | 1.79 | 0.79 | 4.15 | 0.05 | 6.82 | 0.70771 | -3.56 |
| k76 (6/93) | 3.51 | 1.50 | 0.018 | 1.89 | 0.64 | 5.91 | 0.01 | 7.23 | 0.70794 | -3.24 |
| k77 (deep) | 3.09 | 1.03 | 0.006 | 0.40 | 1.60 | 0.58 | 0.11 | 0.34 | 0.71130 | +1.49 |
| k77 (6/93) | 8.92 | 3.88 | 0.057 | 1.87 | 1.32 | 2.72 | 2.79 | 12.53 | 0.70827 | -2.77 |
| **nest 4:** | | | | | | | | | | |
| k6 (shallow) | 3.82 | 1.50 | 0.024 | 1.62 | 1.04 | 10.41 | 0.03 | 6.53 | 0.70969 | -0.77 |
| k80 | 3.72 | 1.93 | 0.012 | 2.56 | 0.56 | 6.15 | 0.02 | 7.55 | 0.70871 | -2.15 |
| k81 | 5.13 | 2.32 | 0.016 | 2.04 | 0.58 | 4.76 | 0.00 | 7.35 | 0.70782 | -3.41 |
| k82 | 7.05 | 3.25 | 0.018 | 1.77 | 0.58 | 1.94 | 0.01 | 11.03 | 0.70756 | -3.77 |
| k82 (6/93) | 7.01 | 3.16 | 0.018 | 1.68 | 0.56 | 2.22 | 0.00 | 9.09 | 0.70756 | -3.77 |
| k5 (deep) | 7.43 | 3.15 | 0.017 | 1.59 | 0.59 | 0.49 | 0.01 | 8.85 | 0.70825 | -2.80 |
| k5 (6/93) | 7.94 | 3.23 | 0.017 | 1.43 | 0.63 | 0.42 | 0.00 | 8.41 | 0.70821 | -2.86 |

## Shallow sample

------------------------Saturation indices------------------------

| Phase | SI | log IAP | log KT | |
|---|---|---|---|---|
| Al(OH)3(a) | -8.25 | 2.55 | 10.80 | Al(OH)3 |
| Albite | -15.60 | -10.94 | 4.66 | NaAlSi3O8 |
| Anorthite | -26.36 | -0.74 | 25.62 | CaAl2Si2O8 |
| Aragonite | -5.32 | -13.66 | -8.34 | CaCO3 |
| Ca-Montmorillonite | -16.46 | -8.67 | 7.78 | Ca0.165Al2.33Si3.67O10(OH)2 |
| Calcite | -5.18 | -13.66 | -8.48 | CaCO3 |
| CH4(g) | -123.23 | -167.16 | -43.93 | CH4 |
| Chalcedony | -0.57 | -4.12 | -3.55 | SiO2 |
| Chlorite(14A) | -67.20 | 1.18 | 68.38 | Mg5Al2Si3O10(OH)8 |
| Chrysotile | -35.45 | -3.25 | 32.20 | Mg3Si2O5(OH)4 |
| CO2(g) | 2.25 | -15.90 | -18.15 | CO2 |
| Dolomite | -10.77 | -27.86 | -17.09 | CaMg(CO3)2 |
| Fe(OH)3(a) | -0.36 | 17.55 | 17.91 | Fe(OH)3 |
| Gibbsite | -5.56 | 2.55 | 8.11 | Al(OH)3 |
| Goethite | 5.58 | 17.60 | 12.02 | FeOOH |
| H2(g) | -37.84 | -37.84 | 0.00 | H2 |
| H2O(g) | -1.56 | -0.05 | 1.51 | H2O |
| Hematite | 13.21 | 35.24 | 22.03 | Fe2O3 |
| Illite | -20.59 | -8.72 | 11.86 | K0.6Mg0.25Al2.3Si3.5O10(OH)2 |
| K-feldspar | -13.03 | -10.94 | 2.09 | KAlSi3O8 |
| K-mica | -18.44 | -5.73 | 12.70 | KAl3Si3O10(OH)2 |
| Kaolinite | -10.52 | -3.08 | 7.43 | Al2Si2O5(OH)4 |
| N2(g) | -0.66 | -3.92 | -3.26 | N2 |
| NH3(g) | -54.20 | -58.72 | -4.52 | NH3 |
| O2(g) | -7.54 | 75.58 | 83.12 | O2 |
| Quartz | -0.14 | -4.12 | -3.98 | SiO2 |
| Sepiolite | -24.89 | -9.13 | 15.76 | Mg2Si3O7.5OH:3H2O |
| Sepiolite(d) | -27.79 | -9.13 | 18.66 | Mg2Si3O7.5OH:3H2O |
| Siderite | -6.28 | -17.17 | -10.89 | FeCO3 |
| SiO2(a) | -1.41 | -4.12 | -2.71 | SiO2 |
| Strontianite | -6.87 | -16.14 | -9.27 | SrCO3 |
| Talc | -32.83 | -11.43 | 21.40 | Mg3Si4O10(OH)2 |

## Deep Sample

------------------------Saturation indices------------------------

| Phase | SI | log IAP | log KT | |
|---|---|---|---|---|
| Aragonite | -5.72 | -14.06 | -8.34 | CaCO3 |
| Calcite | -5.58 | -14.06 | -8.48 | CaCO3 |
| CH4(g) | -119.51 | -163.44 | -43.93 | CH4 |
| Chalcedony | -0.34 | -3.89 | -3.55 | SiO2 |
| Chrysotile | -35.04 | -2.84 | 32.20 | Mg3Si2O5(OH)4 |
| CO2(g) | 2.25 | -15.90 | -18.15 | CO2 |
| Dolomite | -11.19 | -28.28 | -17.09 | CaMg(CO3)2 |
| Fe(OH)3(a) | -3.72 | 14.19 | 17.91 | Fe(OH)3 |
| Goethite | 2.22 | 14.24 | 12.02 | FeOOH |
| H2(g) | -36.91 | -36.91 | 0.00 | H2 |
| H2O(g) | -1.56 | -0.05 | 1.51 | H2O |
| Hematite | 6.49 | 28.52 | 22.03 | Fe2O3 |
| N2(g) | -0.66 | -3.92 | -3.26 | N2 |
| NH3(g) | -52.80 | -57.33 | -4.52 | NH3 |
| O2(g) | -9.39 | 73.73 | 83.12 | O2 |
| Quartz | 0.09 | -3.89 | -3.98 | SiO2 |
| Sepiolite | -24.24 | -8.48 | 15.76 | Mg2Si3O7.5OH:3H2O |
| Sepiolite(d) | -27.14 | -8.48 | 18.66 | Mg2Si3O7.5OH:3H2O |
| Siderite | -9.18 | -20.07 | -10.89 | FeCO3 |
| SiO2(a) | -1.18 | -3.89 | -2.71 | SiO2 |
| Strontianite | -7.68 | -16.95 | -9.27 | SrCO3 |
| Talc | -31.97 | -10.57 | 21.40 | Mg3Si4O10(OH)2 |

# Calculations

- Mollisols are high in organic material
  - C, P, N,K
- Same parent material
- Same physical properties
  - Majority sand sized particles
  - Some silt/clay
- Sr containing compound, less saturated in deeper sample

# Conclusion

- Even though local soil is much higher in organic matter, some of the same concepts hold true.
  - Sr is less saturated as you go down in depth

# References


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