Anorthite Hydrolysis

A GENERAL DISCUSSION ON AN>50% PLAGIOCLASE WEATHERING WITH SOME SPECIFIC EXAMPLES THROWN IN FOR GOOD MEASURE

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Fall 2012

Introduction

- Water from weathered material will tend to reflect the composition of the material.
- This presentation is an investigation of what mechanisms might be involved when this generalized concept does not occur.
- PHREEQCI modeling of anorthites will be used and the results related to water samples from a region composed of anorthite lithology.
- Experience with the PHREEQCI model was also a goal of this project.

Plagioclase

- Mixture of Ca/Na aluminosilicates
- Anorthite vs. Albite (and points between)
  - Anorthitic > 50% ++, e.g., $CaAl_2Si_2O_8$
  - Albitic > 50% +, e.g., $NaAlSi_3O_8$
- Degree of Ca vs. Na (and therefore Al/Si ratio) dictates dissolution characteristics

Relative Weathering Rates

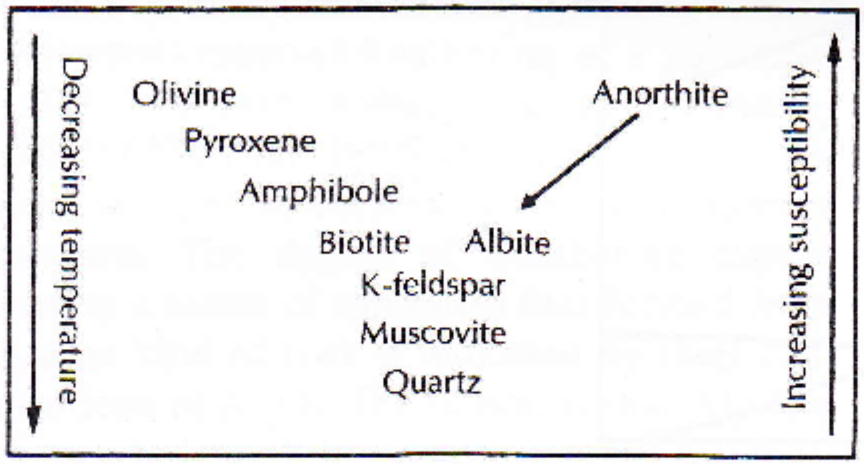


Figure 19.2 Schematic representation of Bowen's reaction series, which is used here to show that minerals that crystallize early and at high temperature from magma (olivine, Ca-plagioclase) are more susceptible to weathering than those that form later at somewhat lower temperatures (muscovite, quartz).

Faure, 1998

Hydrolysis Mechanisms

Albite

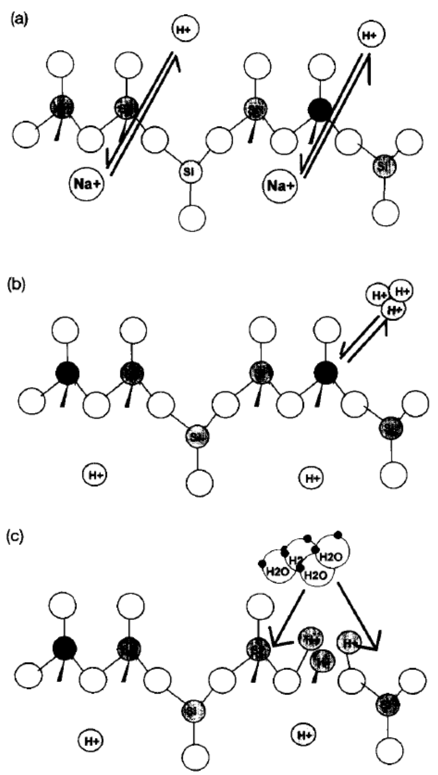


FIG. 9. Schematic illustration depicting the three major steps in the dissolution of an alkali feldspar: (a) The exchange of hydrogen with alkali ions in the feldspar structure. (b) An exchange reaction among aqueous hydrogen ions and Al in the feldspar framework leading to the formation of Al-deficient surface precursor complexes. (c) The irreversible detachment of the precursor complex.

Anorthite

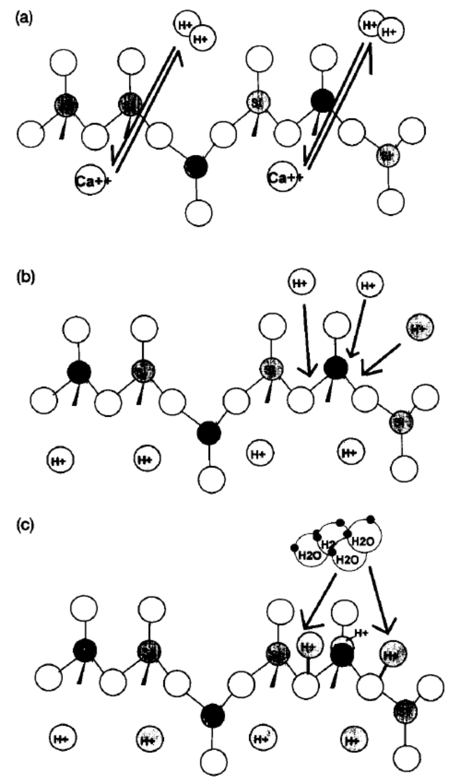
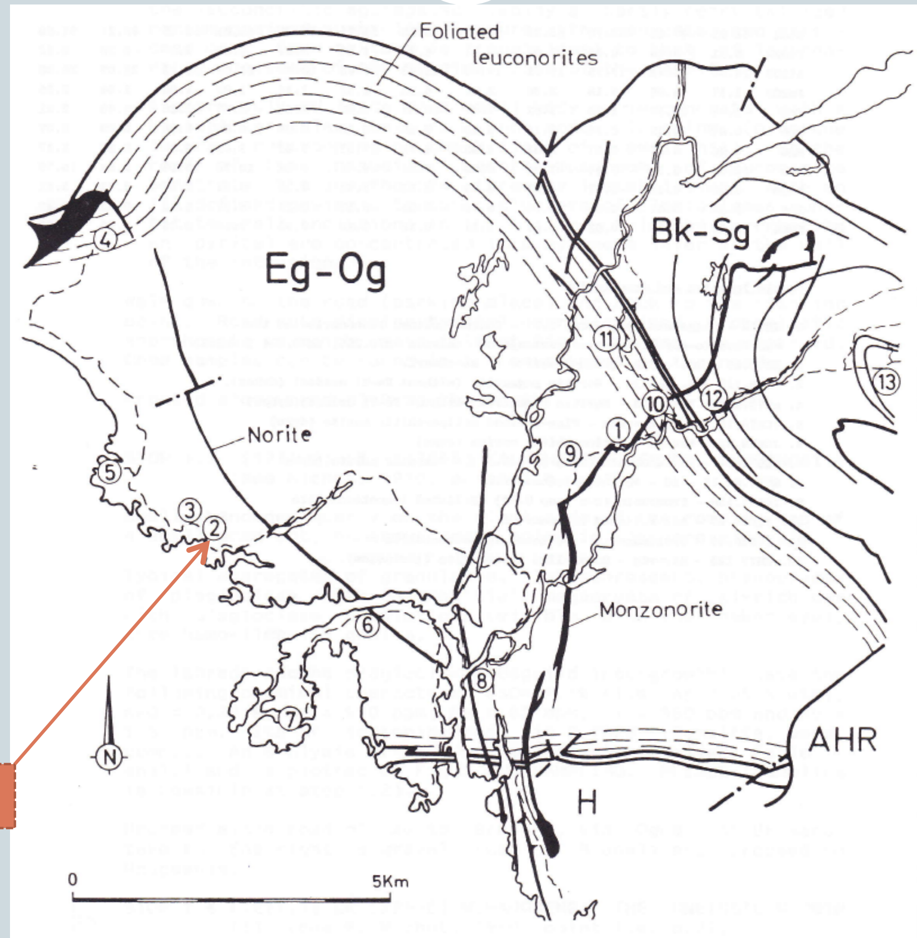


FIG. 10. Schematic illustration depicting the three major steps in the dissolution of anorthite: (a) An exchange of hydrogen with calcium in the feldspar structure. (b) The adsorption of hydrogen ions leading to the formation surface precursor complexes. (c) The irreversible detachment of the precursor complex.

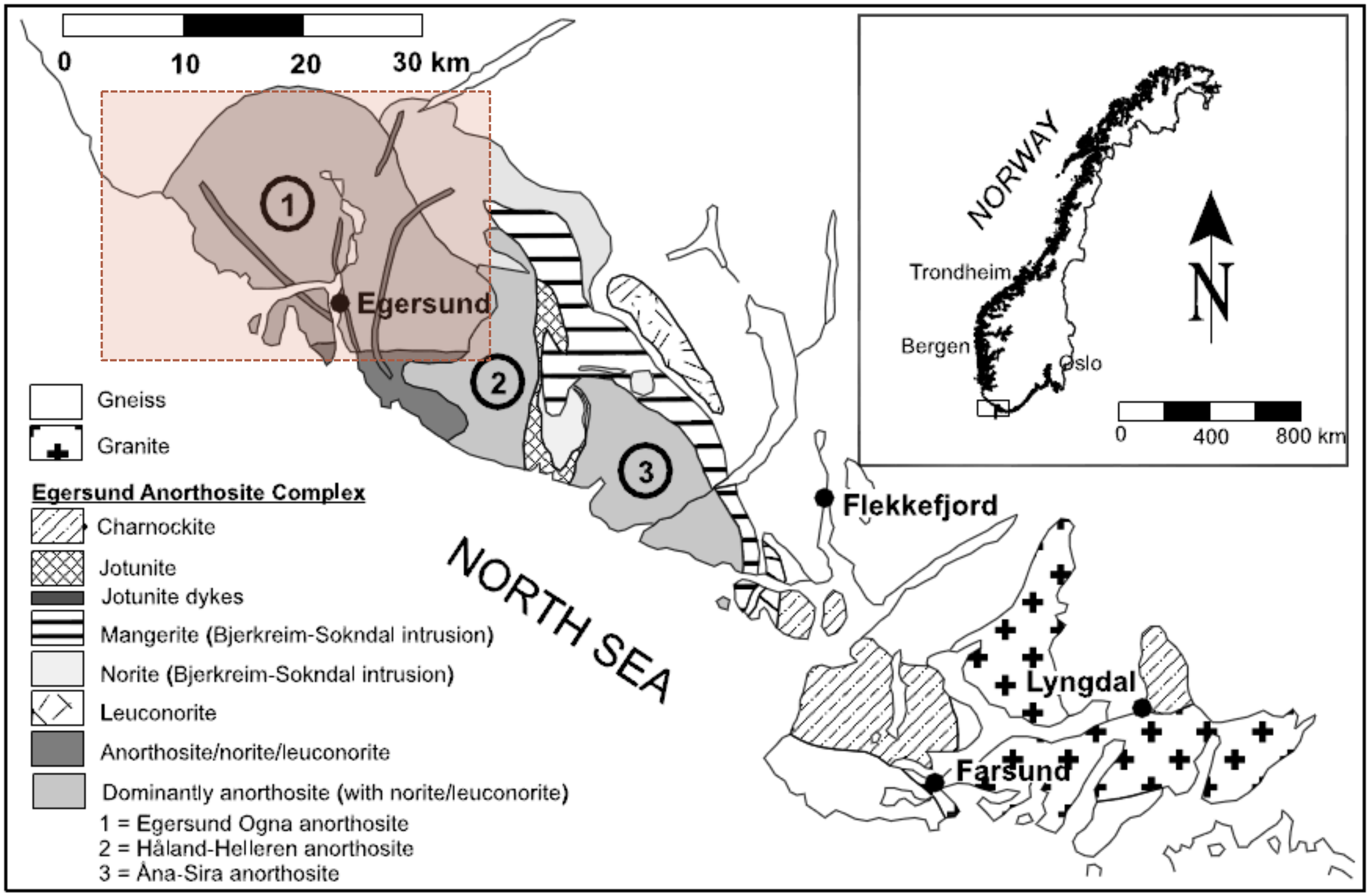
Study Area: Egersund Norway



Sample Location

Display Sample Location, courtesy of B. Saini-Eidukat, The Rogaland Intrusive Massifs, an excursion guide, Duchesne, J. C., 1992

Study Area: Egersund Norway



Map of the Egersund anorthosite complex with inset-map of Norway showing the location of Egersund. Banks, et. al.

Groundwater Quality: Egersund NO

Sample	1	2	3	4	5	6	7	8	9
Eh	+267	+260			+171	+186	+203	+70	+103
pH	5.40	5.59	6.43	7.16	7.90	8.00	8.20	9.72	9.93
Alkalinity	0.5	0.2	0.3	3.2	2.2	3.0	1.0	3.0	3.4
Na	12.3	20.5	27.9	52.9	40.7	28.0	13.1	83.2	103
Ca	12.3	7.86	6.64	37.7	40.9	21.2	18.1	2.49	1.50
Mg	3.16	4.02	2.49	7.18	16.3	19.1	3.52	0.97	0.33
K	0.97	2.16	<0.5	7.53	3.11	3.55	0.57	0.63	<0.5
Cl	24.5	34.2	41.5	53.5	18.1	16.9	22.2	30.9	30.5
SO4	9.55	13.9	11.8	15.8	33.9	27.1	7.02	12.1	18.4
NO3	8.96	12.5	<0.05	7.05	127	9.32	1.64	<0.05	11.7
F	<0.05	<0.05	<0.05	0.06	0.06	0.05	0.05	0.07	0.13
Si	4.19	2.06	4.26	5.01	3.41	14.4	3.68	4.16	5.61
Sra	63.2	57.1	42.6	84.7	287	179	78	23.5	12.9
Ala	49.4	64.8	18.6	9.1	24.8	5.49	5.83	12.1	23.3
Ba	13.8	12.3	11.0	25.5	25.7	17.0	8.48	68.3	449
Lia	0.06	0.06	0.24	0.74	5.58	3.40	1.03	1.02	0.45
IBE%	3.16	+0.69	+1.06	1.86	2.16	3.16	0.62	3.64	2.72
Saturation index (SI)									
Kaolinite	+2.60	+3.10	+5.36	+4.64	+3.79	+3.54	+2.03	- 0.57	- 0.31
Gibbsite	+0.82	+1.38	+2.20	+1.76	+1.51	+0.76	+0.60	- 0.61	- 0.54
Ca-Mont.	- 0.46	- 0.26	+3.06	+2.67	+1.70	+2.24	- 0.26	- 3.07	- 2.67
Chalcedony	- 0.38	- 0.69	- 0.38	- 0.30	- 0.47	+0.15	- 0.44	- 0.53	- 0.48
Calcite	- 3.65	- 4.06	- 3.12	- 0.68	- 0.09	- 0.12	- 0.40	+0.43	+0.34
Log (PCO2)	- 1.00	- 1.59	- 2.26	- 1.98	- 2.89	- 2.85	- 3.51	- 4.71	- 4.95

Typ. Mineralogy Rank—Various Waters

	Groundwater	River Water	Fresh Lake	Ocean
Potassium	8	8	8	6
Sodium	4	6	6	2
Calcium	2	2	2	5
Magnesium	6	7	5	4
Bicarbonate	1	1	1	7
Sulfate	5	4	3	3
Chloride	7	5	7	1
Silica (aq)	3	3	4	11

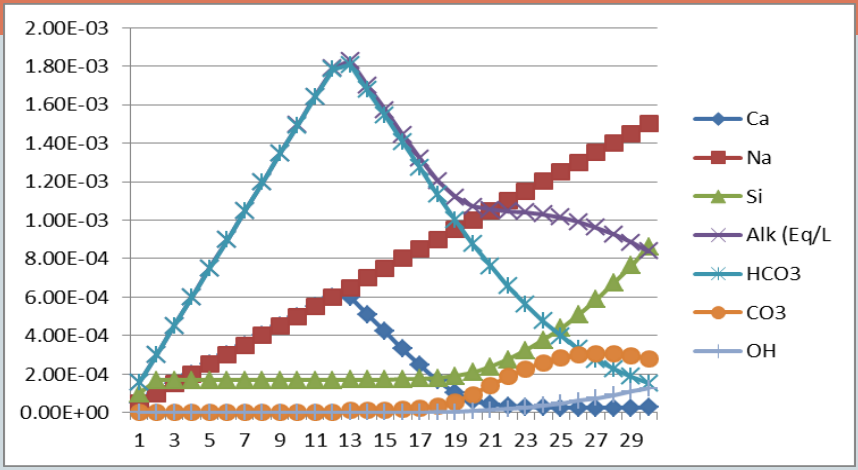
Railsback, *Some Fundamentals of Mineralogy and Geochemistry*

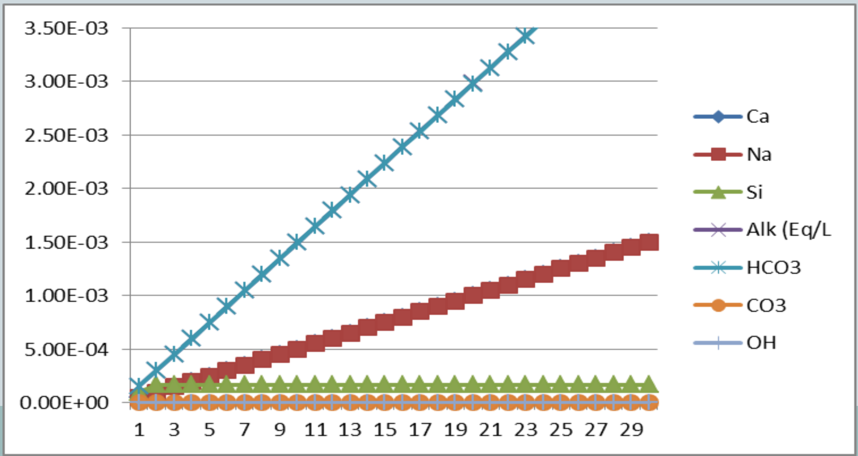
Low Ca^{2+}/High Na^{+} $HCO3^{-}$ Water

- Given predominantly anorthite ($CaAl_2Si_2O_8$) vs albite ($NaAlSi_3O_8$) geology, what are possible explanations?
  - Cation Exchange
  - Calcium species removal via precipitation
  - Open system (free CO2 availability)
  - Closed system (limited CO2 availability)
  - Combination of these last two???

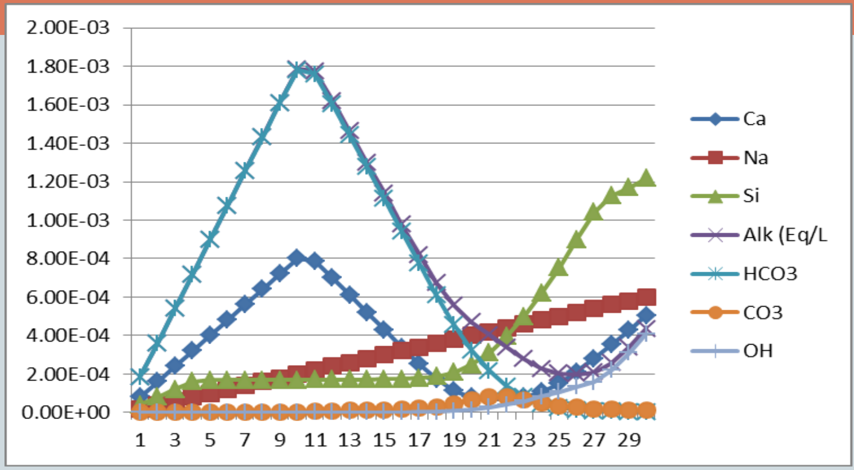
Labradorite / Bytownite Weathering

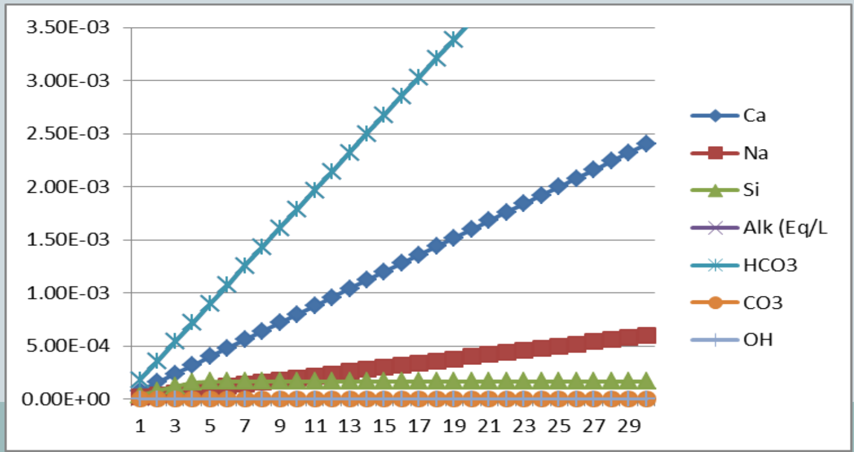
Labradorite Closed/Open



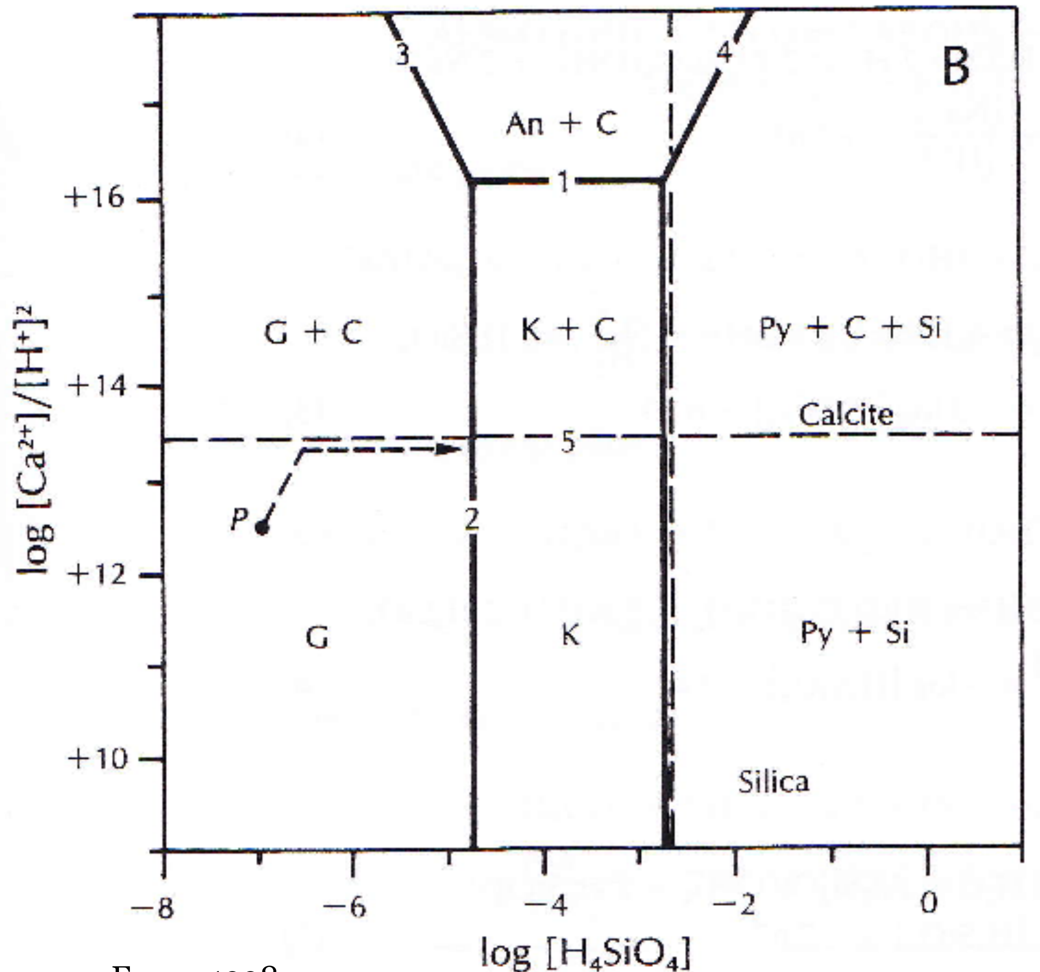


Bytownite Closed/Open





Anorthite Rich Stability Diagram



Faure, 1998

Weathering Stages

Reactions which characterize the various stages of hydrochemical evolution of groundwater in plagioclase-dominated rocks, coupled with calcite saturation and precipitation as a mechanism for limiting calcium concentrations.

1: $2NaCaAl_3Si_5O_{16} + 8CO_2 + 9H_2O = 2Ca^{2+} + 2Na^+ + 6HCO_3^- + 4SiO_2 + 3Al_2Si_2O_5(OH)_4 + 2CO_2$

2: $4NaCaAl_3Si_5O_{16} + 8CO_2 + 14H_2O = 4CaCO_3 + 4Na^+ + 4HCO_3^- + 8SiO_2 + 6Al_2Si_2O_5(OH)_4$

3: $6NaCaAl_3Si_5O_{16} + 8CO_2 + 19H_2O = 6CaCO_3 + 6Na^+ + 2CO_3^{2-} + 2OH^- + 12SiO_2 + 9Al_2Si_2O_5(OH)_4$

4: $8NaCaAl_3Si_5O_{16} + 8CO_2 + 28H_2O = 8CaCO_3 + 8Na^+ + 8OH^- + 16SiO_2 + 12Al_2Si_2O_5(OH)_4$

5: $12NaCaAl_3Si_5O_{16} + 8CO_2 + 46H_2O = 8CaCO_3 + 4Ca^{2+} + 12Na^+ + 20OH^- + 24SiO_2 + 18Al_2Si_2O_5(OH)_4$

6: $20NaCaAl_3Si_5O_{16} + 8CO_2 + 82H_2O = 8CaCO_3 + 12Ca^{2+} + 20Na^+ + 44OH^- + 40SiO_2 + 30Al_2Si_2O_5(OH)_4$

PHREEQCI Weathering Model

```
TITLE Open -1.5 PCO2
SOLUTION 1
   temp      7
   pH        4.6 charge
   pe        8
   redox     pe
   units     mol/l
   density   1
   -water    1 # kg
REACTION 1
   Na         0.4
   Ca         1.6
   Al         3.6
   SiO2       4.4
   0.0015 moles in 30 steps
EQUILIBRIUM_PHASES 1
   Calcite   0 0
   Chalcedony 0 0
   Gibbsite  0 0
   Kaolinite 0 0
   O2(g)     -0.7 10
   CO2(g)    -1.5 10
SELECTED_OUTPUT
   -file                BytOpen1.5
   -totals              Ca  Na  Si  Alkalinity
   -molalities          HCO3-  CO3-2  OH-  CO2(g)
   -equilibrium_phases  Calcite  Chalcedony  Gibbsite
   -saturation_indices  Calcite  Chalcedony  Ca-Montmorillonite
                        Gibbsite  CO2(g)
   -gases               O2(g)  CO2(g)
END
```

```
TITLE Closed-1.5 PCO2
SOLUTION 1
   temp      7
   pH        4.6 charge
   pe        8
   units     mol/l
   C(4)      0.001914
REACTION 1
   Na         0.4
   Ca         1.6
   Al         3.6
   SiO2       4.4
   0.0015 moles in 30 steps
EQUILIBRIUM_PHASES 1
   Calcite   0 0
   Chalcedony 0 0
   Gibbsite  0 0
   Kaolinite 0 0
   O2(g)     -0.7 10
SELECTED_OUTPUT
   -file                BytClose1.5
   -totals              Ca  Na  Si  Alkalinity
   -molalities          HCO3-  CO3-2  OH-  CO2(g)
   -equilibrium_phases  Calcite  Chalcedony  Gibbsite
   -saturation_indices  Calcite  Chalcedony  Ca-
Montmorillonite                 Gibbsite CO2(g)
   -gases               O2(g)  CO2(g)
END
```

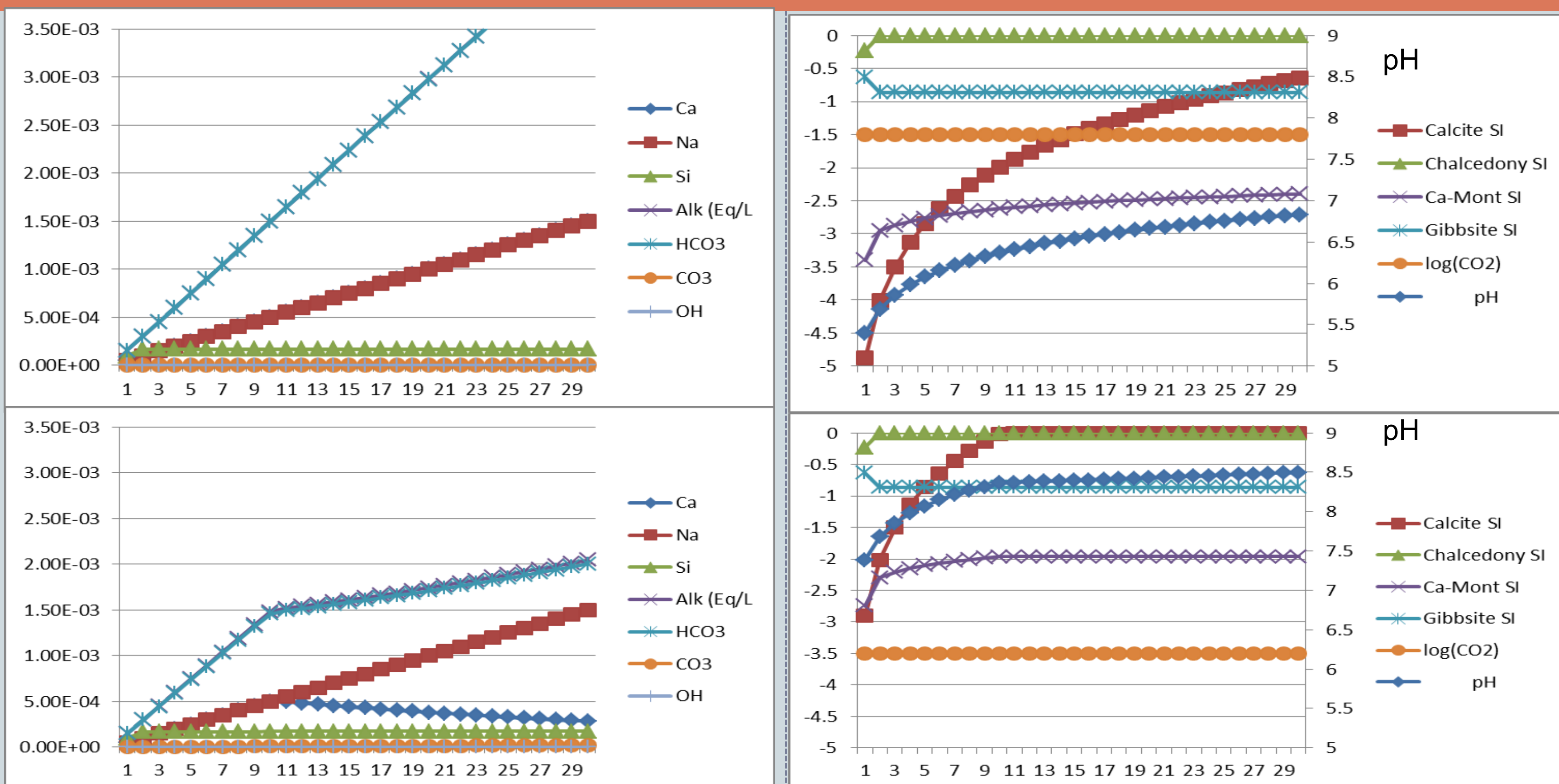
Open System: Labradorite

Molalities

Saturation Indices

Log(CO2)=-1.5 @ Start

Log(CO2)=-3.5 @ Start



Weathering Steps

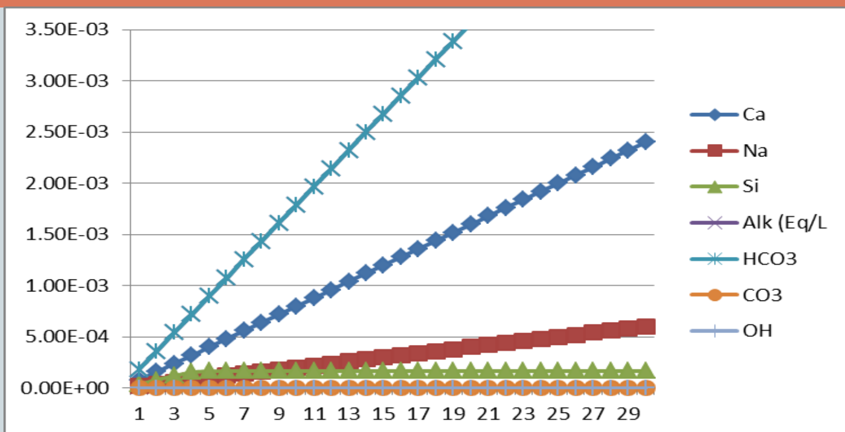
Weathering Steps

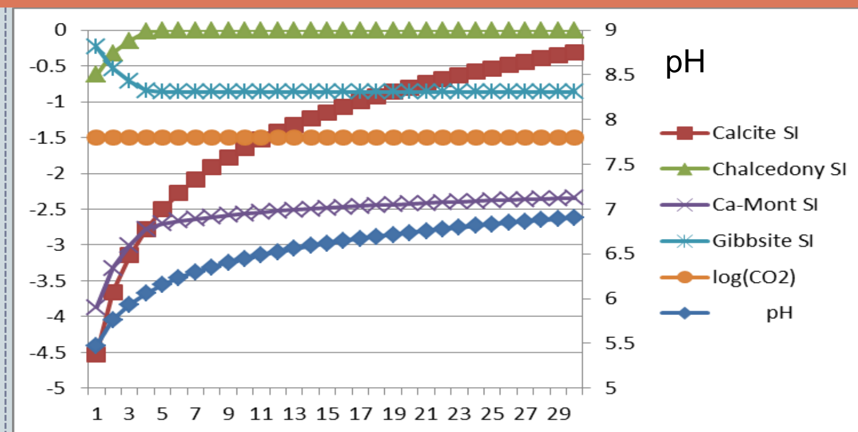
Open System: Bytownite

Molalities

Saturation Indices

Log(CO2)=-1.5 @ Start





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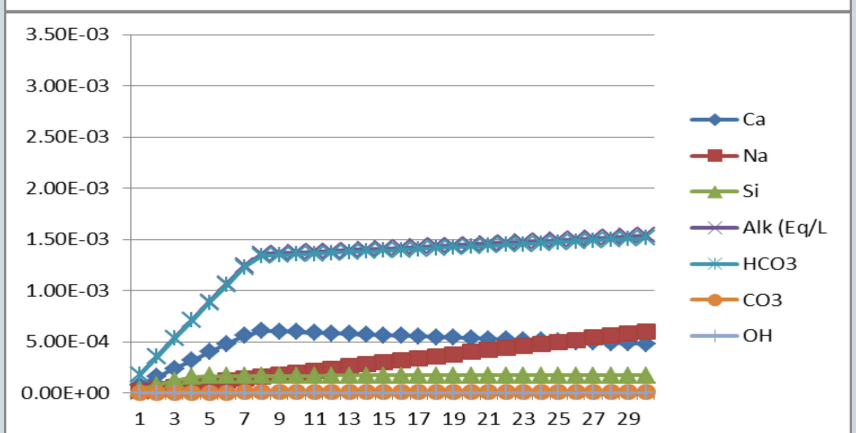

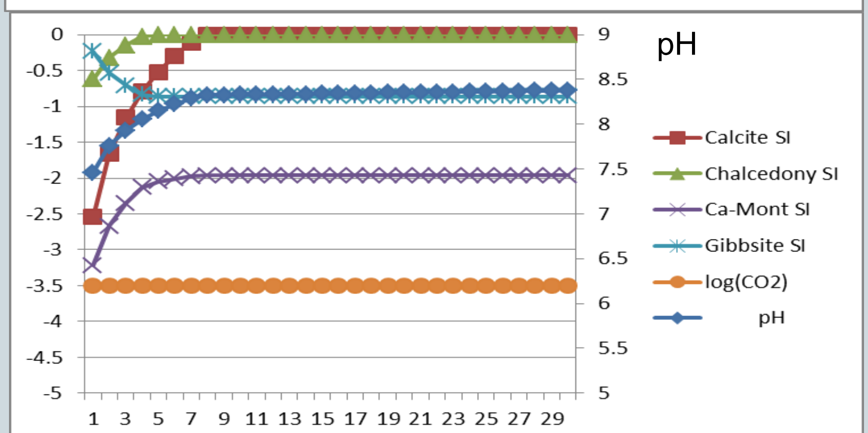

Weathering Steps

Weathering Steps

Closed System: Labradorite

Molalities

Saturation Indices

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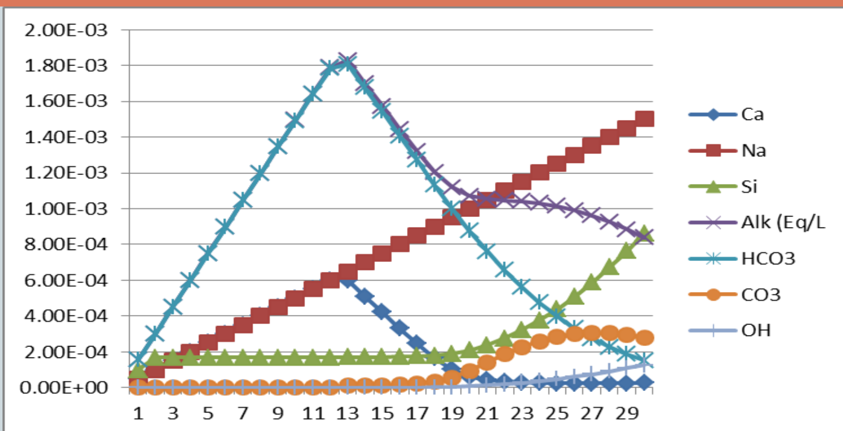
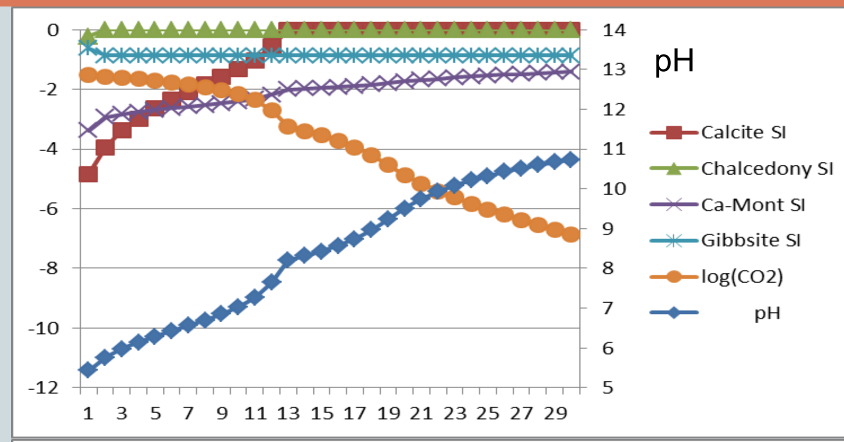
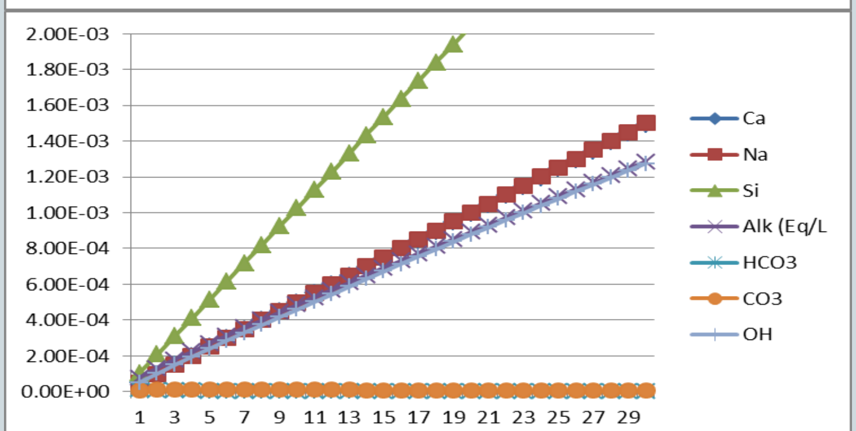
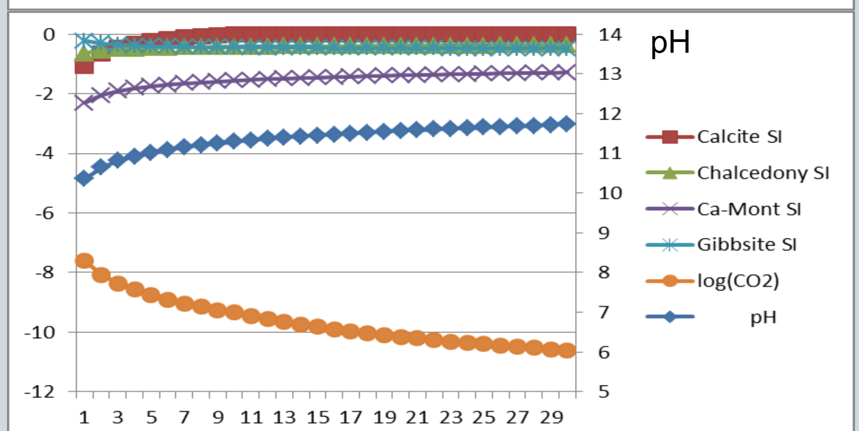




Log(CO2)=-3.5 @ Start





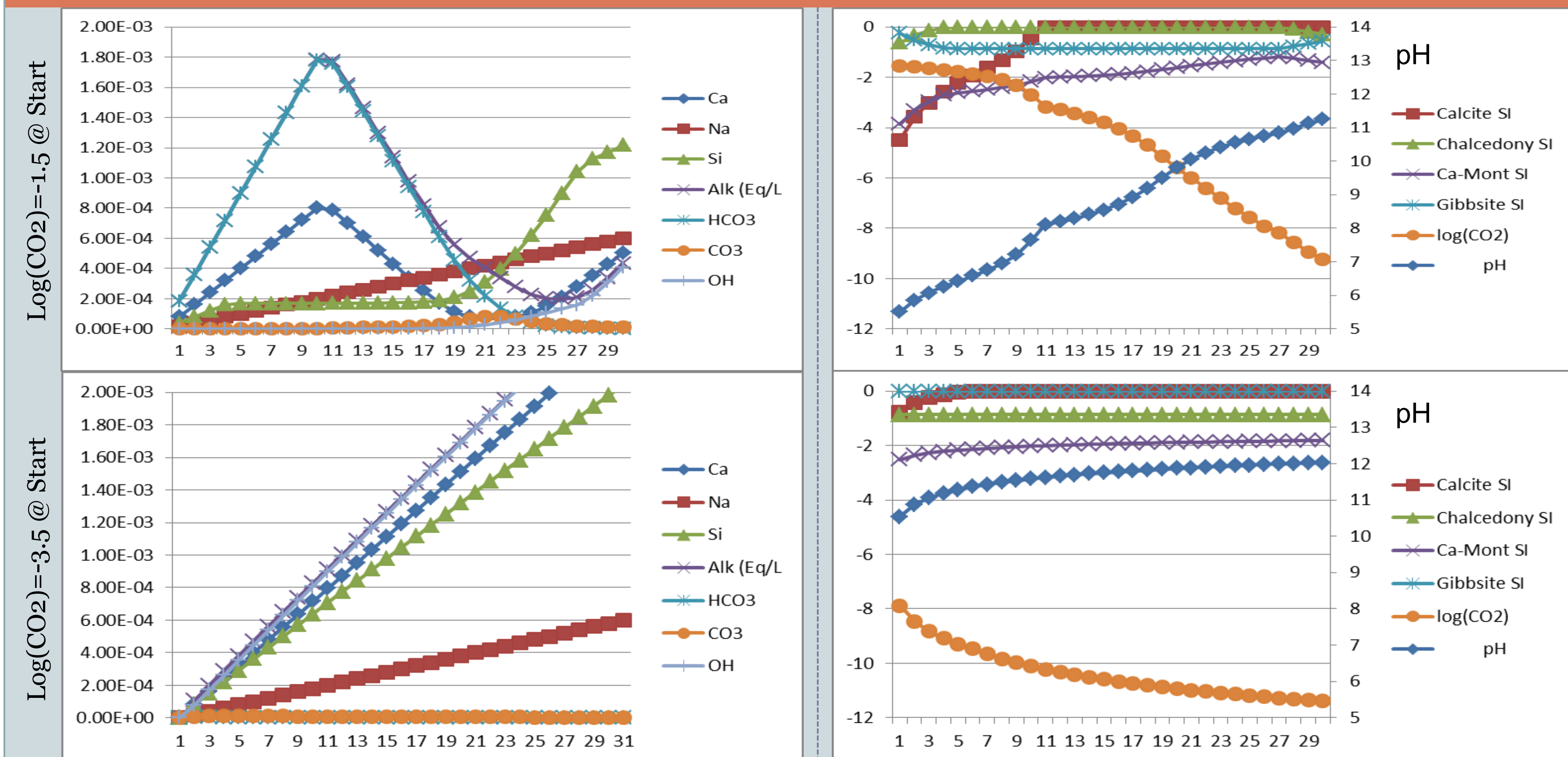
Weathering Steps

Weathering Steps

Closed System: Bytownite

Molalities

Saturation Indices



Weathering Steps

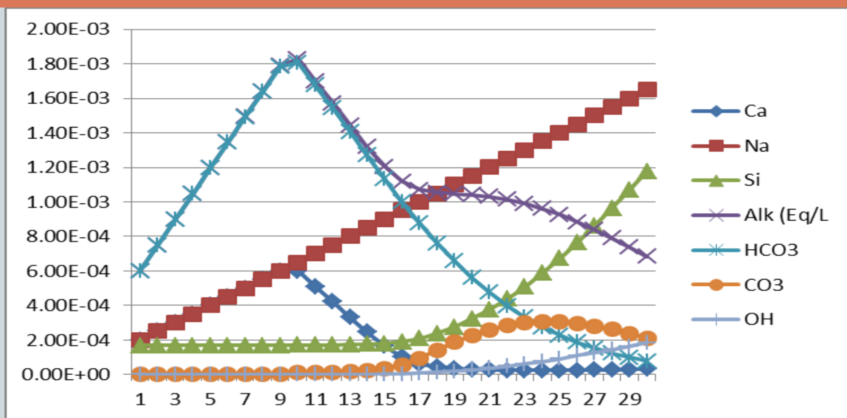
Weathering Steps

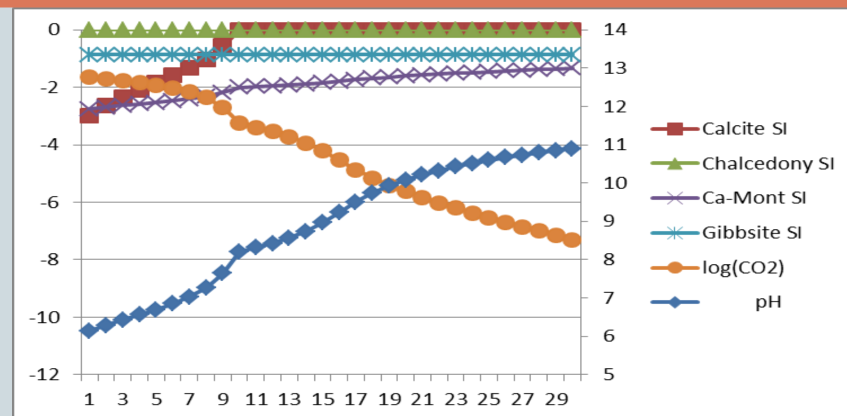
Labradorite Open then Closed Models

Molalities

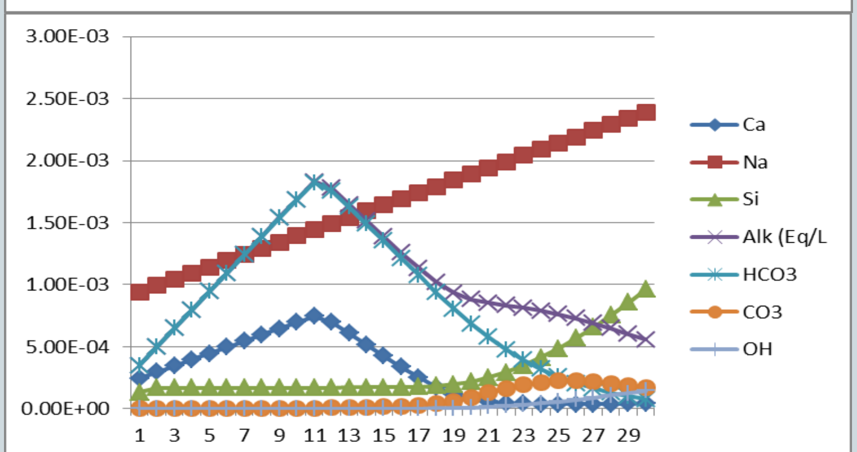
Saturation Indices

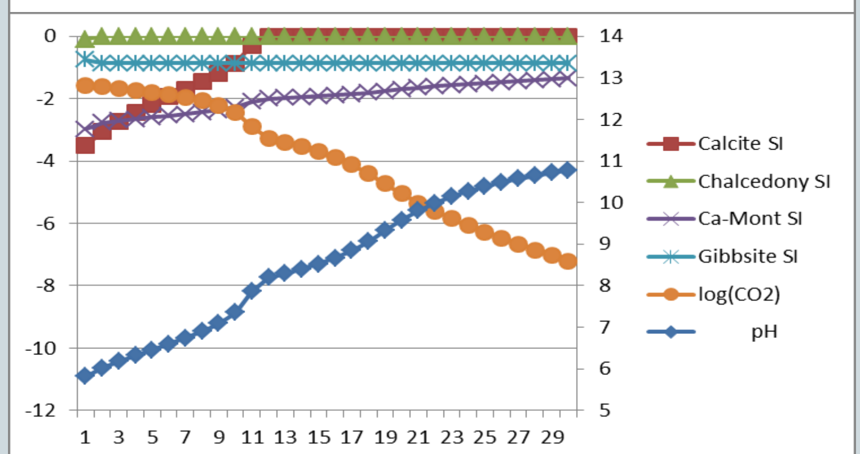
'Theoretical'





Sample





Weathering Steps

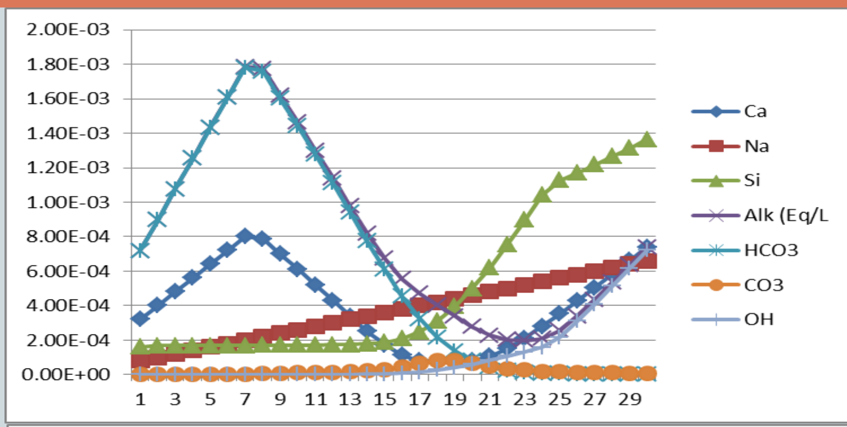
Weathering Steps

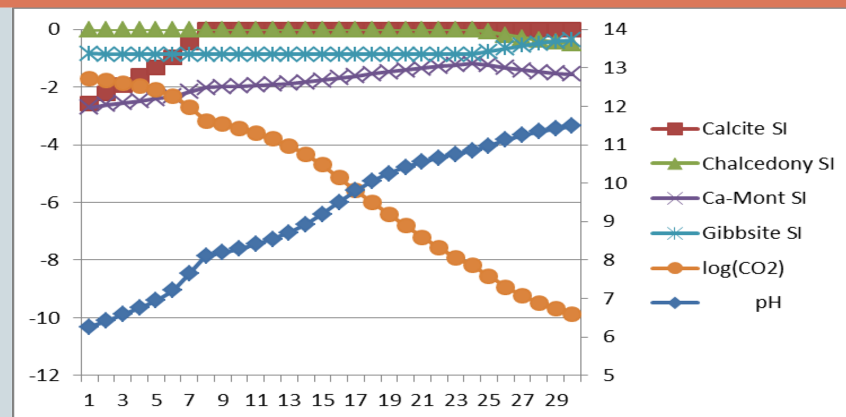
Bytownite Open then Closed Models

Molalities

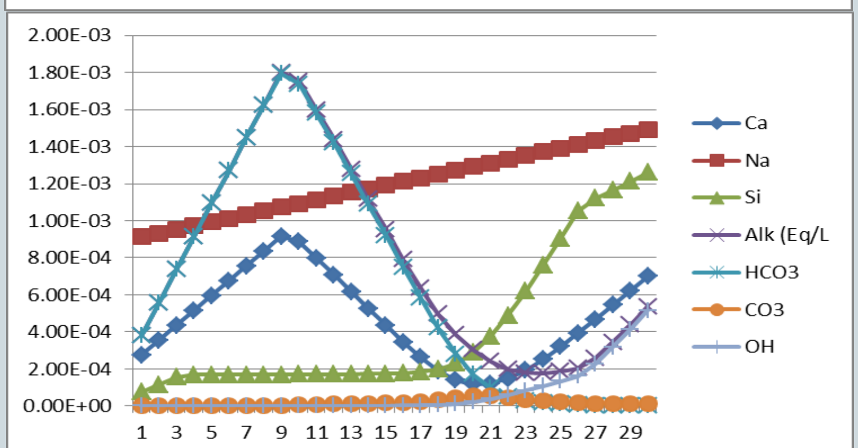
Saturation Indices

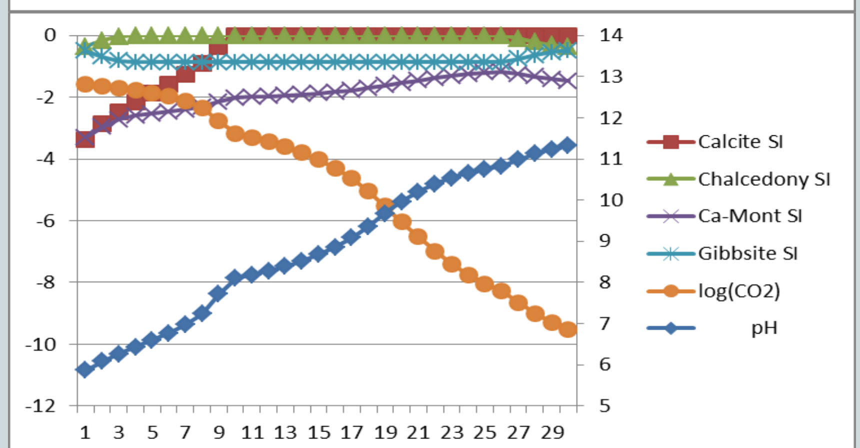
'Theoretical'





Sample



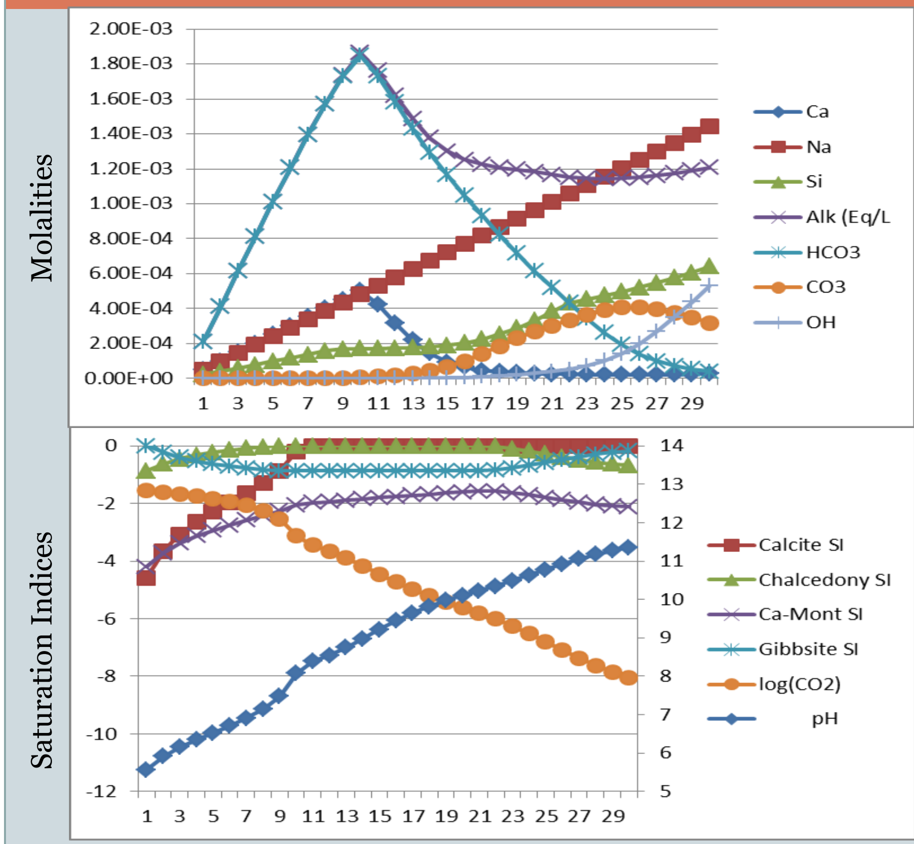


Weathering Steps

Weathering Steps

Display Sample Weathering

Closed System, $\log(CO_2)=-1.5$



Weathering Steps

Compositional Analysis*

Analyte	Percent
SiO_2	53.61
TiO_2**	0.11
Al_2O_3	24.84
FeO	1.48
Fe_2O_3	1.17
MnO	0.07
MgO	3.46
CaO	10.04
Na_2O	4.80
K_2O	0.35
P_2O_5	0.02

*From Duchesne. **TiO_2 not included in modeling run.

Groundwater Quality: Egersund NO

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Na	12.3	20.5	27.9	52.9	40.7	28.0	13.1	83.2	103
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Mg	3.16	4.02	2.49	7.18	16.3	19.1	3.52	0.97	0.33
K	0.97	2.16	<0.5	7.53	3.11	3.55	0.57	0.63	<0.5
Cl	24.5	34.2	41.5	53.5	18.1	16.9	22.2	30.9	30.5
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Si	4.19	2.06	4.26	5.01	3.41	14.4	3.68	4.16	5.61
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Saturation index (SI)									
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Ca-Mont.	0.46	0.26	+3.06	+2.67	+1.70	+2.24	0.26	3.07	2.67
Chalcedony	0.38	0.69	0.38	0.30	0.47	+0.15	0.44	0.53	0.48
Calcite	3.65	4.06	3.12	0.68	0.09	0.12	0.40	+0.43	+0.34
Log (PCO2)	1.00	1.59	2.26	1.98	2.89	2.85	3.51	4.71	4.95

Samples: Varying Stage of Weathering

- Two Specific Examples of Weathering Stage

Sample	Na	Ca	HCO3	pH
$2NaCaAl_3Si_5O_{16} + 8CO_2 + 9H_2O = 2Ca^{2+} + 2Na^+ + 6HCO_3^- + 4SiO_2 + 3Al_2Si_2O_5(OH)_4 + 2CO_2$				
4	52.9	37.7	195	7.16
$6NaCaAl_3Si_5O_{16} + 8CO_2 + 19H_2O = 6CaCO_3 + 6Na^+ + 2CO_3^{2-} + 2OH^- + 12SiO_2 + 9Al_2Si_2O_5(OH)_4$				
9	103	1.5	183	9.93

Conclusions / Future Work

- Water development to a Na rich bicarbonate water is possible without requiring cation exchange.
- Mechanisms for this route suggested in paper appear plausible
- Possible reasons for non-ideality
  - Simplistic model assumptions relative to complex environment
  - Just beginning to understand the PHREEQ model
- For the future:
  - Look at inverse modeling
  - Model weathering to better approximate actual water concentrations

References

- Oelkers,E. and Schott, J., Experimental study of anorthite dissolution and the relative mechanism of feldspar hydrolysis: *Geochimica et Cosmochimica Acta*, v. 59, pp. 5039-5053
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- Thanks to B. Saini-Eidukat for use of in class sample of Anorthite