Chemical weathering and secondary mineral formation

Construction of stability diagrams.

Procedure for constructing activity diagrams

This example is simplified for the purpose of demonstration. The Athens Gneiss can be represented by mineral assemblage: Quartz, Muscovite, Albite, Microcline, Kaolinite and Gibbsite.

Simplifying assumptions:

- Aqueous solution is always present
- Al is always in a solid phase
- Si concentrations is fixed by quartz saturation
- P and T are constant

I. Write reactions for mineral pairs using ions you wish to plot.

Kaolinite + 5 H_2O = 2 Gibbsite + 2 $H_4SiO_4^o$

Qtz + 2 H_2O = $H_4SiO_4^o$

2 Microcline + 9 H_2O + $2H^+$ = $2K^+$ + $H_4SiO_4^o$ + Kaolinite

2 Albite + 9 H_2O + $2H^+$ = $2Na^+$ + $H_4SiO_4^o$ + Kaolinite

Muscovite + 9 H_2O + H^+ = 3 Gibbsite + 3 $H_4SiO_4^o$ + K^+

2 Muscovite + 3 H_2O + 2 H^+ = 3 Kaolinite + 2 K^+

Microcline + 7 H_2O + H^+ = Gibbsite + 3 $H_4SiO_4^o$ + K^+

3 Microcline + 12 H_2O + 2 H^+ = Muscovite + 2 K^+ + 6 $H_4SiO_4^o$

Albite + 7 H_2O + H^+ = Gibbsite + 3 $H_4SiO_4^o$ + Na

3Albite + K^+ + $3H^+$ + 12 H_2O = Muscovite + 3Na +H + $6H_4SiO_4^o$

Albite + K^+ + H^+ = Microcline + Na + H^+

II. determine the ΔG of reaction and solve for K (at equilibrium).

Recall: If ΔG = 0 , then the reaction will not proceed in either direction (at equilibrium state). In this case,

$\Delta G^o = - RT \ln K$

To calculate the $\Delta G_{reaction}$ the $\Delta G^o_{formation}$ must be obtain from a data table such as:

Robie R. A., Hemingway B. S., and Fisher J. R. (1984) *Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10+e5 pascals) pressure and higher temperature:* Bulletin 1452, U.S. Geological Survey, Washington DC.

For the reaction: Kaolinite + 5 H_2O = 2 Gibbsite + 2$H_4SiO_4^o$

- ΔG^o_f Gibbsite = -1155 kJ/mol
- ΔG^o_f Kaolinite = -3799 kJ/mol
- ΔG^o_f H_2O = -237 kJ/mol
- ΔG^o_f $H_4SiO_4^o$ = -1308 kJ/mol

$\Delta G_{reaction}$ = the products - reactants

$\Delta G_{reaction} = (2 \times -1155) + (2 \times -1308) - (-3799) - (5 \times -237) = -59$ kJ/mol

therefore solve for K,

$K = 4.2 \times 10^{-11}$

$K = (a H_4SiO_4^o)^2$

or

$\log K = -10.4$

$\log K = 2 \log a H_4SiO_4^o = -10.4$

III. Determine the coordinate system. Because the silica activity is fixed by quartz saturation, we wish to display the stability relations for all of the above reactions in terms of K^+ , Na^+ and H^+ activities.

The coordinate system is therefore define by the ratios:

a_{K^+} / a_{H^+}

a_{Na^+} / a_{H^+}

IV. Determine the relative stability of the none alkali-bearing phases.

Because kaolinite and gibbsite and quartz do not contain sodium or potassium, their stability's are govern by the silica activity and temperature.

If quartz saturation is always maintained at an activity of $a H_4SiO_4^o = 10^{-3.95}$ the direction of reactions can be assessed.

For example in step II above, it was shown that for the reaction of kaolinite ---> gibbsite

$2 \log a H_4SiO_4^o = -10.4$

Therefore, under these conditions, the equilibrium activity of silica is $10^{-5.4}$.

The reaction will be driven to the left and kaolinite is more stable than gibbsite under these conditions.

V. Assess all the reaction pairs.

b = zero intercept

Mineral pairs to be considered

	Halloysite	Kaolinite	Muscovite	Microcline	Albite
Gibbsite	X	X	x	x	x
Halloysite		X	x	x	x
Kaolinite			x	x	x
Muscovite				x	x
Microcline					x

Recall, $\Delta G = -RT \ln K_{eq}$

Simplifying assumptions: 1. solution always present; 2. Al always in solid phase; 3. Silica is fixed by quartz saturation; 4) P and T are constant at 1 bar and 25°C; and 5) Activities of solids and water are unity.

Kaolinite - Gibbsite

$Al_2Si_2O_5(OH)_4 + 5H_2O$ <-----> $2Al(OH)_3 + 2H_4SiO_4^o$

$K_{eq} = a^2_{H4SiO4}{}^o$

$\log(K_{eq}) = 2 \log a_{H4SiO4}{}^o = -10.4$

$$\log a_{H4SiO4}{}^o = -5.20$$

(Note: The activity of dissolved silica at quartz saturation (see below) is greater than the activity of silica with kaolinite and gibbsite in equilibrium (*i.e.* -3.95 > -5.20). Therefore the above reaction proceeds from right to left).

Quartz - Silica

$SiO_2 + 2H_2O$ <-----> $H_4SiO_4^o$

$K_{eq} = a_{H4SiO4}^o$

$\log(K_{eq}) = \log a_{H4SiO4}^o$

$\log a_{H4SiO4}^o = -3.95$

Halloysite - Gibbsite

$Al_2Si_2O_5(OH)_4 + 5H_2O$ <-----> $2Al(OH)_3 + 2H_4SiO_4^o$

$K_{eq} = a^2_{H4SiO4}{}^o$

$\log(K_{eq}) = 2 \log a_{H4SiO4}^o = -7.11$

$\log a_{H4SiO4}^o = -3.56$

(Note: The activity of dissolved silica at quartz saturation is less than the activity of silica with halloysite and gibbsite in equilibrium (*i.e.* $-3.95 < -3.56$). Therefore the above reaction proceeds from left to right. Further note that all gibbsite goes to kaolinite from the kaolinite-gibbsite reaction above).

Microcline - Kaolinite

$2KAlSi_3O_8 + 9H_2O + 2H^+$ <-----> $2K^+ + 4H_4SiO_4^o + Al_2Si_2O_5(OH)_4$

$K_{eq} = (a^2_{K+}\, a^4_{H4SiO4}{}^o) / (a^2_{H+})$

$\log(K_{eq}) = 2 \log (a_{K+} / a_{H+}) + 4 \log a_{H4SiO4}^o = -3.96$

$\log (a_{K+} / a_{H+}) + 2 \log a_{H4SiO4}^o = -1.98$

Recall, that at quartz saturation, $\log a_{H4SiO4}^o = -3.95$, therefore by substitution,

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$\log (a_{K+} / a_{H+}) = 5.92$

Microcline - Halloysite

$2KAlSi_3O_8 + 9H_2O + 2H^+$ <-----> $2K^+ + 4H_4SiO_4^o + Al_2Si_2O_5(OH)_4$

$K_{eq} = (a^2_{K+}\, a^4_{H4SiO4}{}^o) / (a^2_{H+})$

$\log(K_{eq}) = 2 \log (a_{K+} / a_{H+}) + 4 \log a_{H4SiO4}^{o} = -7.22$

$\log (a_{K+} / a_{H+}) + 2 \log a_{H4SiO4}^{o} = -3.61$

Recall, that at quartz saturation, $\log a_{H4SiO4}^{o} = -3.95$, therefore by substitution,

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$$\log (a_{K+} / a_{H+}) = 4.29$$

Albite - Kaolinite

$2NaAlSi_3O_8 + 9H_2O + 2H^+$ <-----> $2Na^+ + 4H_4SiO_4^o + Al_2Si_2O_5(OH)_4$

$K_{eq} = (a^2_{Na+}\, a^4_{H4SiO4}{}^{o}) / (a^2_{H+})$

$\log(K_{eq}) = 2 \log (a_{Na+} / a_{H+}) + 4 \log a_{H4SiO4}^{o} = -0.44$

$\log (a_{Na+} / a_{H+}) + 2 \log a_{H4SiO4}^{o} = -0.22$

Recall, that at quartz saturation, $\log a_{H4SiO4}^{o} = -3.95$, therefore by substitution,

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$$\log (a_{Na+} / a_{H+}) = 7.68$$

Albite - Halloysite

$2NaAlSi_3O_8 + 9H_2O + 2H^+$ <-----> $2Na^+ + 4H_4SiO_4^o + Al_2Si_2O_5(OH)_4$

$K_{eq} = (a^2_{Na+}\, a^4_{H4SiO4}{}^{o}) / (a^2_{H+})$

$\log(K_{eq}) = 2 \log (a_{Na+} / a_{H+}) + 4 \log a_{H4SiO4}^{o} = -3.71$

$\log (a_{Na+} / a_{H+}) + 2 \log a_{H4SiO4}^{o} = -1.85$

Recall, that at quartz saturation, $\log a_{H4SiO4}^{o\ o} = -3.95$, therefore by substitution,

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$$\log (a_{Na+} / a_{H+}) = 6.05$$

Muscovite - Gibbsite

$KAl_3Si_3O_{10}(OH)_2 + 9H_2O + H^+$ <-----> $K^+ + 3H_4SiO_4^o + 3Al(OH)_3$

$K_{eq} = (a_{K+}\, a^3_{H4SiO4}{}^{o}) / (a_{H+})$

$\log(K_{eq}) = \log(a_{K+} / a_{H+}) + 3 \log a_{H4SiO4^o} = -11.16$

$\log(a_{K+} / a_{H+}) + 3 \log a_{H4SiO4^o} = -11.16$

Recall, that at quartz saturation, $\log a_{H4SiO4^o} = -3.95$, therefore by substitution,

$$\log(a_{K+} / a_{H+}) = 0.69$$

Muscovite - Kaolinite

$2KAl_3Si_3O_{10}(OH)_2 + 3H_2O + 2H^+ \Longleftrightarrow 2K^+ + 3\ Al_2Si_2O_5(OH)_4$

$K_{eq} = \log(a^2_{K+} / a^2_{H+})$

$\log(K_{eq}) = 2 \log(a_{K+} / a_{H+}) = 8.81$

$$\log(a_{K+} / a_{H+}) = 4.40$$

Muscovite - Halloysite

$2KAl_3Si_3O_{10}(OH)_2 + 3H_2O + 2H^+ \Longleftrightarrow 2K^+ + 3\ Al_2Si_2O_5(OH)_4$

$K_{eq} = \log(a^2_{K+} / a^2_{H+})$

$\log(K_{eq}) = 2 \log(a_{K+} / a_{H+}) = -0.99$

$$\log(a_{K+} / a_{H+}) = -0.49$$

Microcline - Gibbsite

$2KAlSi_3O_8 + 7H_2O + H^+ \Longleftrightarrow K^+ + 3H_4SiO_4^o + Al(OH)_3$

$K_{eq} = (a_{K+}\ a^3_{H4SiO4^o}) / (a_{H+})$

$\log(K_{eq}) = \log(a_{K+} / a_{H+}) + 3 \log a_{H4SiO4^o} = -7.17$

$\log (a_{K+} / a_{H+}) + 3\ a_{H4SiO4^o} = -7.17$

Recall, that at quartz saturation, $\log a_{H4SiO4^o} = -3.95$, therefore by substitution,

$$\log(a_{K+} / a_{H+}) = 4.68$$

Microcline - Muscovite

$3KAlSi_3O_8 + 12H_2O + 2H^+$ <-----> $2K^+ + 6H_4SiO_4^o + KAl_3Si_3O_{10}(OH)_2$

$K_{eq} = (a^2_{K+}\ a^6_{H4SiO4}{}^o) / (a^2_{H+})$

$\log(K_{eq}) = 2\log(a_{K+} / a_{H+}) + 6\log a_{H4SiO4}{}^o = -10.34$

$\log(a_{K+} / a_{H+}) + 3\log a_{H4SiO4}{}^o = -5.17$

Recall, that at quartz saturation, $\log a_{H4SiO4}{}^o = -3.95$, therefore by substitution,

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$$\log(a_{K+} / a_{H+}) = 6.68$$

Albite - Gibbsite

$2NaAlSi_3O_8 + 7H_2O + H^+$ <-----> $Na^+ + 3H_4SiO_4^o + Al(OH)_3$

$K_{eq} = (a_{Na+}\ a^3_{H4SiO4}{}^o) / (a_{H+})$

$\log(K_{eq}) = \log(a_{Na+} / a_{H+}) + 3\log a_{H4SiO4}{}^o = -5.41$

$\log(a_{Na+} / a_{H+}) + 3\log a_{H4SiO4}{}^o = -5.41$

Recall, that at quartz saturation, $\log a H4SiO4^o = -3.95$, therefore by substitution,

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$$\log(a_{Na+} / a_{H+}) = 6.44$$

Albite - Muscovite

$3NaAlSi_3O_8 + 12H_2O + 2H^+ + K^+$ <-----> $3Na^+ + 6H_4SiO_4^o + KAl_3Si_3O_{10}(OH)_2$

$K_{eq} = (a^3_{Na+}\ a^6_{H4SiO4}{}^o) / (a^2_{H+} + a_{K+})$

$K_{eq} = (a^3_{Na+}\ a^6_{H4SiO4}{}^o\ a_{H+}) / (a^3_{H+} + a_{K+})$

$\log(K_{eq}) = 3\log(a_{Na+} / a_{H+}) + \log(a_{H+} / a_{K+}) + 6\log a_{H4SiO4}{}^o = -5.07$

$3\log(a_{Na+} / a_{H+}) - \log(a_{K+} / a_{H+}) + 6\log a_{H4SiO4}{}^o = -5.07$

Recall, that at quartz saturation, $\log a H4SiO4^o = -3.95$, therefore by substitution,

$3\log(a_{Na+} / a_{H+}) - \log(a_{K+} / a_{H+}) = 18.63$

$$\log(a_{Na+} / a_{H+}) = 1/3 \log(a_{K+} / a_{H+}) + 6.21$$

Albite - Microcline

$NaAlSi_3O_8 + K^+ + H^+$ <-----> $Na^+ + H^+ + KaAlSi_3O_8$

$K_{eq} = (a_{Na+}\ a_{H+}) / (a_{K+}\ a_{H+})$

$\log(K_{eq}) = \log(a_{Na+} / a_{H+}) + \log(a_{K+} / a_{H+}) = 1.76$

$\log(a_{Na+} / a_{H+}) - \log(a_{K+} / a_{H+}) = 1.76$

$$\log(a_{Na+} / a_{H+}) = \log(a_{K+} / a_{H+}) + 1.76$$

Kaolinite - Halloysite

$Al_2Si_2O_5(OH)_4$ <-----> $Al_2Si_2O_5(OH)_4$

$\log(K_{eq}) = -3.27$

VI. Plot lines on coordinates and determine stable forms.

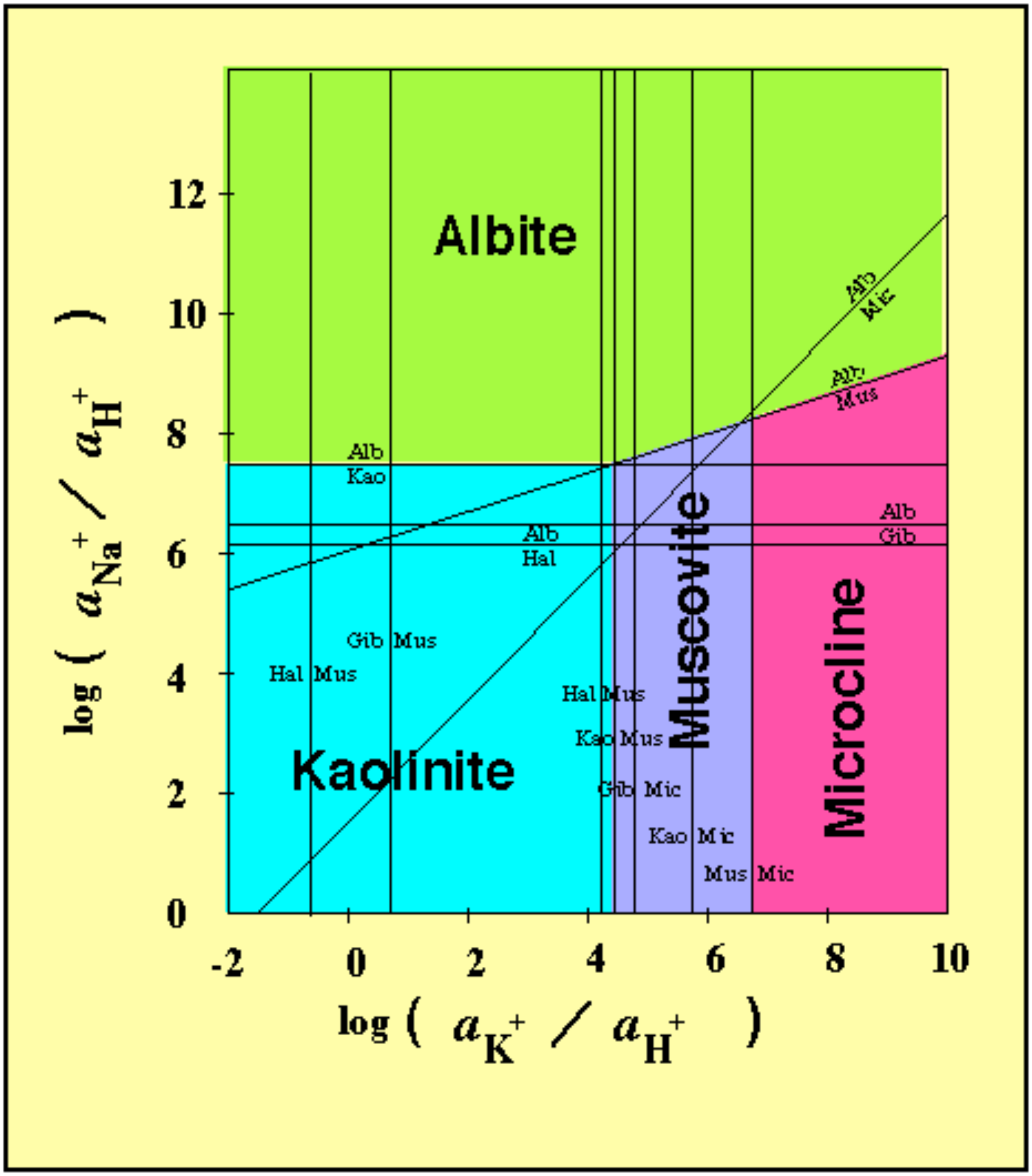
Form of equations is y = mx +b

where

$y = \log(a_{Na+} / a_{H+})$

$x = \log(a_{K+} / a_{H+})$

m is the log coefficient


Albite
Muscovite
Microcline
Kaolinite
Alb
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Mic
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Hal Mus
Hal Mus
Kao Mus
Gib Mic
Kao Mic
Mus Mic
log (a_{Na^+} / a_{H^+})
log (a_{K^+} / a_{H^+})
12
10
8
6
4
2
0
-2
0
2
4
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10