

Equilibrium solubility

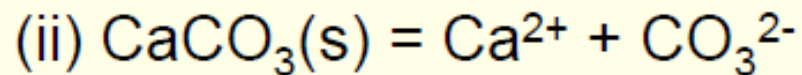
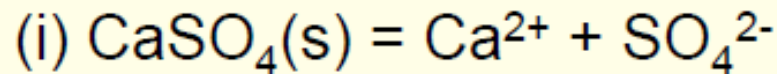
Lecture 2

Geochemical Motivation

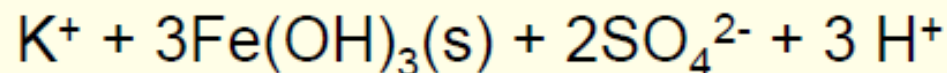
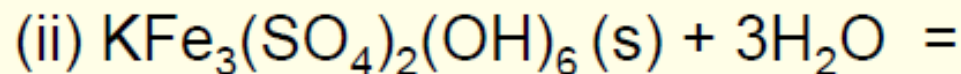
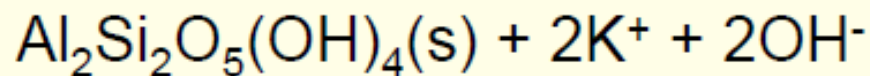
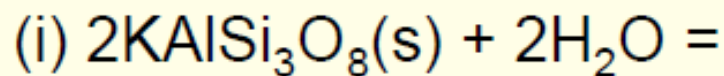
- Solubility equilibria control the major element compositions of natural waters.
- Several important kinds of sedimentary rock are precipitates from aqueous solutions (e.g., carbonates, evaporites).
- Many important kinds of ore-deposits result from precipitation from hydrothermal and diagenetic solutions.

Congruent vs. Incongruent Dissolution

Congruent dissolution (all products are soluble):



Incongruent dissolution (new solids form):

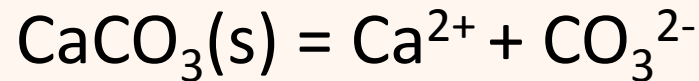


Mineral saturation

- Mineral saturation indicates if a mineral has the tendency to dissolve or form.
- Mineral saturation may be assessed using chemical thermodynamics and the composition of the water.

Equilibrium constant (K) and reaction quotient (Q)

- For the reaction,



- For the reaction an equilibrium constant K can be defined that depends on temperature, pressure and composition
- For the reaction the reaction quotient (Q) can be defined based on aqueous species activities

$$Q = \frac{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{a_{\text{calcite}}}$$

Saturation index

- The saturation index (SI) for the reaction is the ratio of Q over K

$$SI = \log(Q/K)$$

- $SI > 0$ the mineral is supersaturated
- $SI = 0$ the mineral is saturated
- $SI < 0$ the mineral is undersaturated

SI in PHREEQC

INPUT FILE

```
SOLUTION 1 Seawater
  temp      25
  pH        8.22
  pe        4
  redox     pe
  units     mol/l
  density   1.023
  Cl        0.546
  Na        0.546
  Mg        0.0528
  S(6)     0.0282
  Ca        0.0103
  K         0.0102
  C(4)     0.00206
  -water   1 # kg
```

run



SI in PHREEQC

OUTPUT FILE

logQ

logK

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

Phase	SI	log IAP	log KT	
Anhydrite	-0.87	-5.23	-4.36	CaSO4
Aragonite	0.58	-7.75	-8.34	CaCO3
Calcite	0.73	-7.75	-8.48	CaCO3
Dolomite	2.34	-14.75	-17.09	CaMg(CO3)2
Gypsum	-0.66	-5.25	-4.58	CaSO4:2H2O
Halite	-2.46	-0.88	1.58	NaCl

SI in PHREEQC

OUTPUT FILE

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

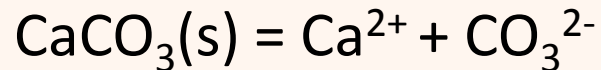
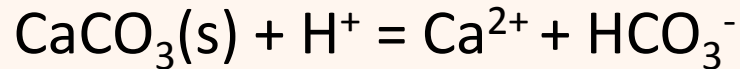
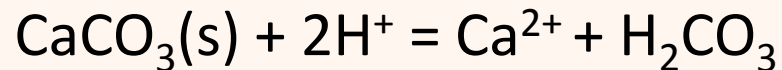
Phase	SI	log IAP	log KT	
Anhydrite	-0.87	-5.23	-4.36	CaSO ₄
Aragonite	0.58	-7.75	-8.34	CaCO ₃
Calcite	0.73	-7.75	-8.48	CaCO ₃
Dolomite	2.34	-14.75	-17.09	CaMg(CO ₃) ₂
Gypsum	-0.66	-5.25	-4.58	CaSO ₄ ·2H ₂ O
Halite	-2.46	-0.88	1.58	NaCl

Undersaturated

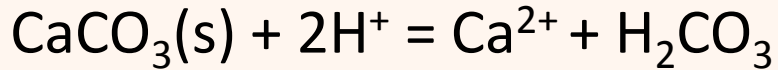
Supersaturated

Calcite solubility - example

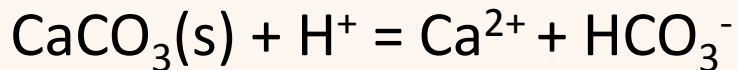
- Mineral solubility depends on aqueous speciation.
- C_{TOT} we have the aqueous species H_2CO_3 , HCO_3^- and CO_3^{2-}
- Calcite solubility can therefore be written according to



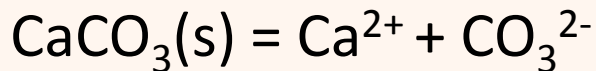
Calcite solubility - example



$$K = a\text{Ca}^{2+}a\text{H}_2\text{CO}_3/(a\text{H}^+)^2$$



$$K = a\text{Ca}^{2+}a\text{HCO}_3^-/a\text{H}^+$$



$$K = a\text{Ca}^{2+}a\text{CO}_3^{2-}$$

Mineral solubility depends on aqueous speciation, for example calcite depends on dissolved CO_2 speciation but also on Ca speciation

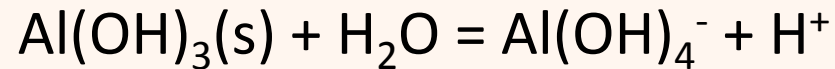
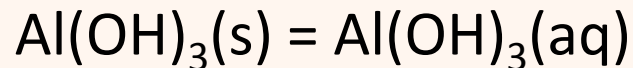
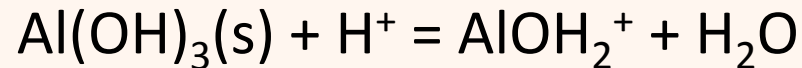
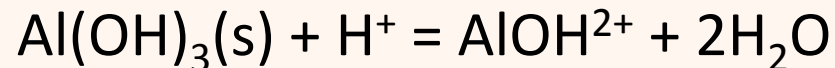
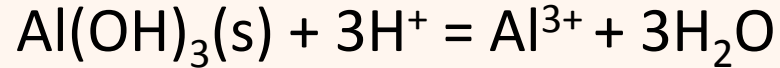
Gibbsite - example

- Lets consider gibbsite solubility ($\text{Al}(\text{OH})_3(\text{s})$) and aluminium speciation
- The hydroxide species we have are: Al^{3+} , AlOH^{2+} , AlOH_2^+ , $\text{Al}(\text{OH})_3(\text{aq})$, $\text{Al}(\text{OH})_4^-$
- The Al_{TOT} becomes

$$A_{\text{TOT}} = m\text{Al}^{3+} + m\text{AlOH}^{2+} + m\text{AlOH}_2^+ + m\text{Al}(\text{OH})_3(\text{aq}) + m\text{Al}(\text{OH})_4^-$$

Gibbsite - example

- The solubility reactions are



Gibbsite - example

- The equilibrium constants become (taken activity of water and pure minerals to be 1)

$$K_1 = a\text{Al}^{3+} / (a\text{H}^+)^3$$

$$K_2 = a\text{AlOH}^{2+} / (a\text{H}^+)^2$$

$$K_3 = a\text{AlOH}_2^+ / a\text{H}^+$$

$$K_4 = a\text{Al}(\text{OH})_3(\text{aq})$$

$$K_5 = a\text{Al}(\text{OH})_4^- \cdot a\text{H}^+$$

Gibbsite - example

- And taken log of all the equilibrium solubility constants , taken $\text{pH} = -\log a\text{H}^+$ and rearranging we have

$$\log K_1 = \log a\text{Al}^{3+} - 3\log a\text{H}^+ \quad \Rightarrow \quad \log a\text{Al}^{3+} = \log K_1 - 3\text{pH}$$

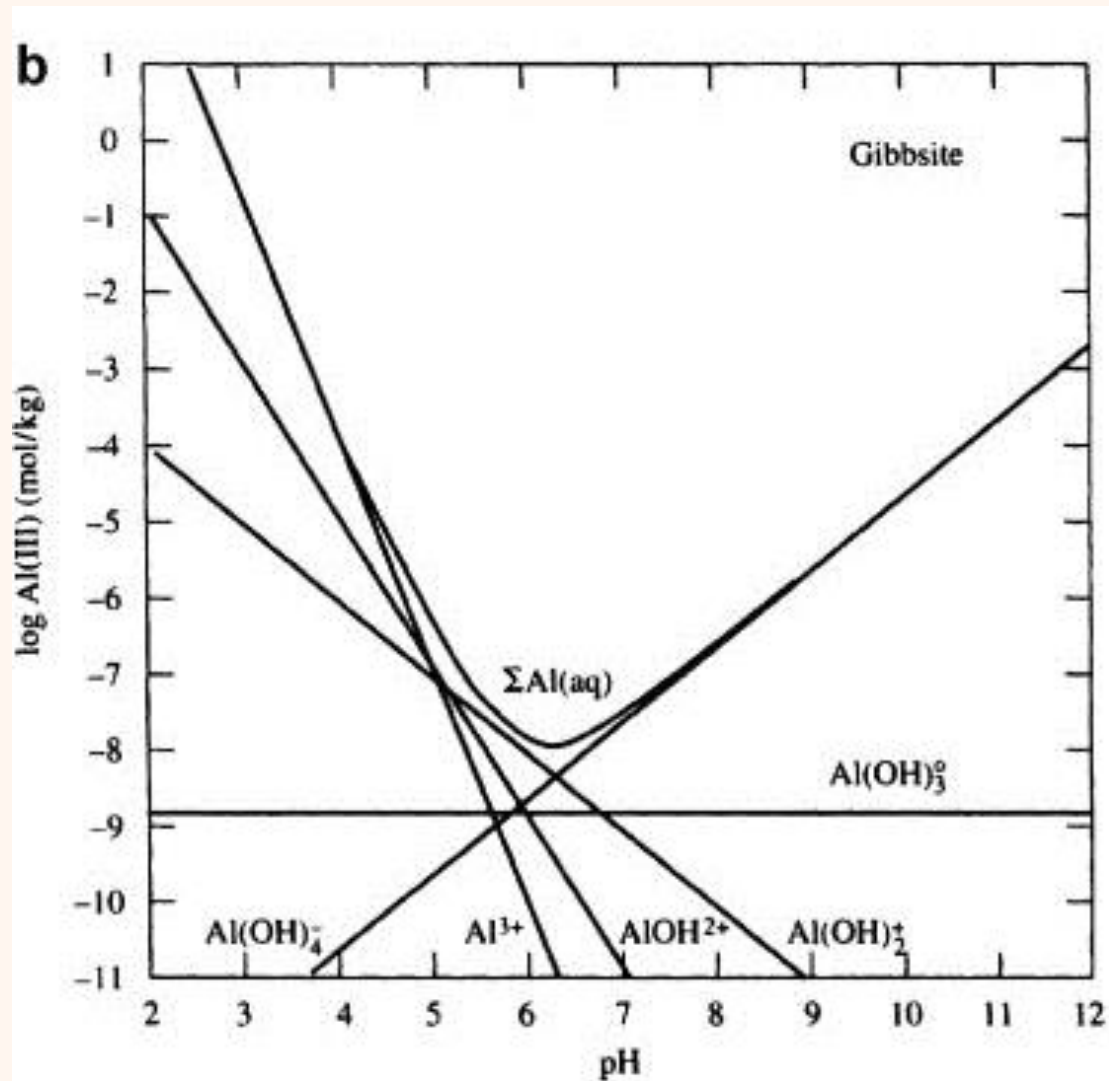
$$\log K_2 = \log a\text{AlOH}^{2+} - 2\log a\text{H}^+ \quad \Rightarrow \quad \log a\text{AlOH}^{2+} = \log K_2 - 2\text{pH}$$

$$\log K_3 = \log a\text{AlOH}_2^+ - \log a\text{H}^+ \quad \Rightarrow \quad \log a\text{AlOH}_2^+ = \log K_3 - \text{pH}$$

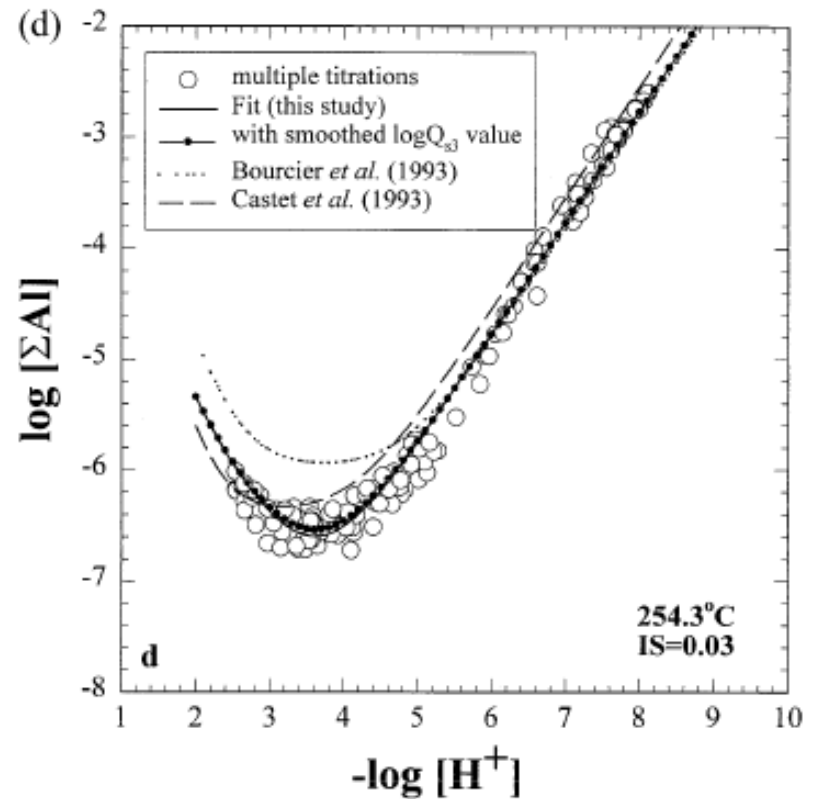
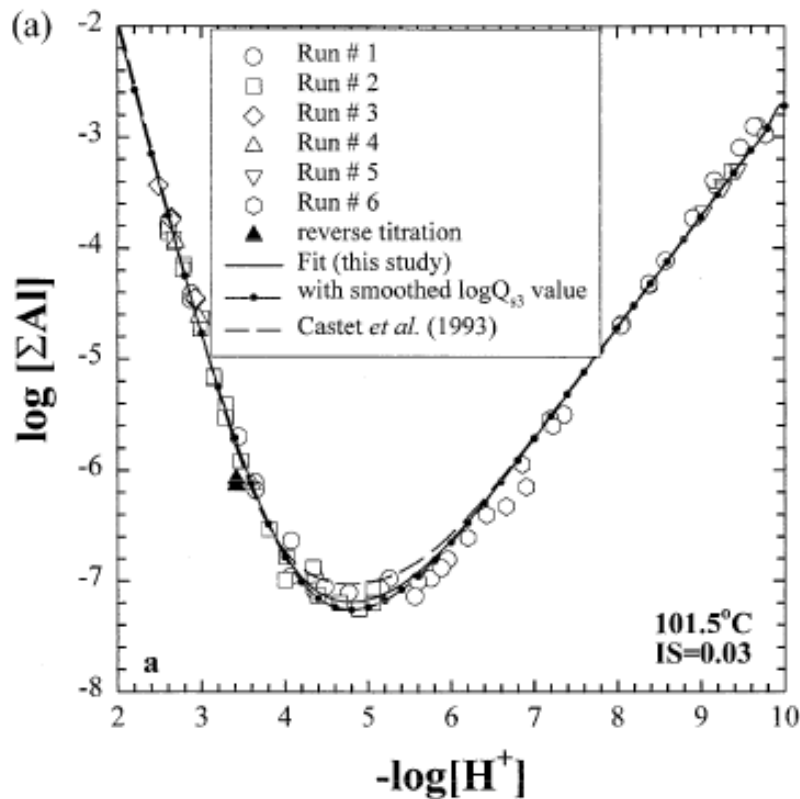
$$\log K_4 = \log a\text{Al}(\text{OH})_3(\text{aq}) \quad \Rightarrow \quad \log a\text{Al}(\text{OH})_3(\text{aq}) = \log K_4$$

$$\log K_5 = \log a\text{Al}(\text{OH})_4^- + \log a\text{H}^+ \quad \Rightarrow \quad \log a\text{Al}(\text{OH})_4^- = \log K_5 + \text{pH}$$

Gibbsite - example

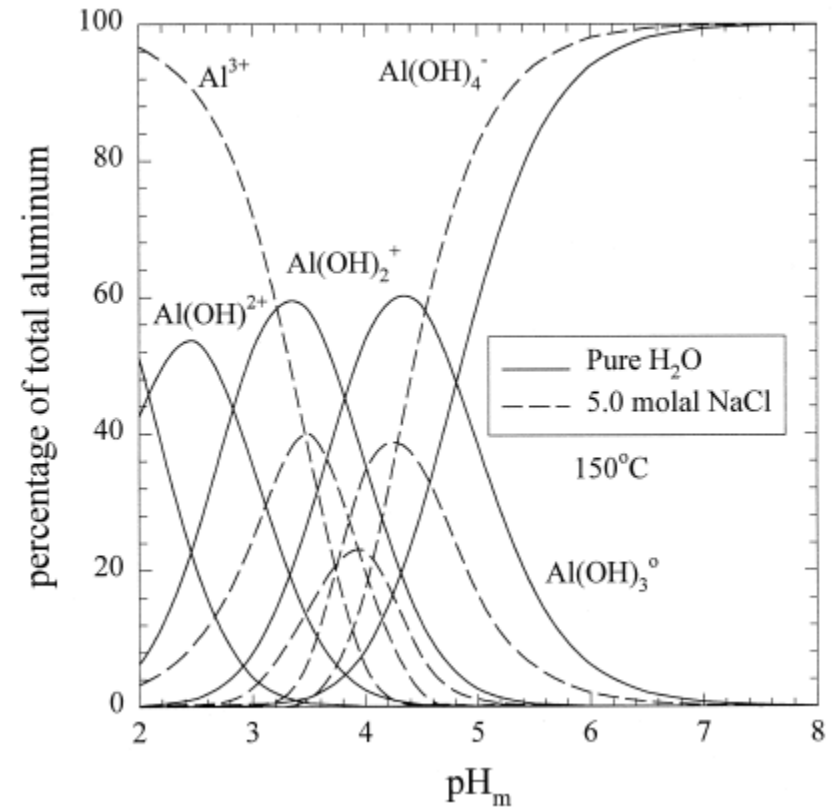
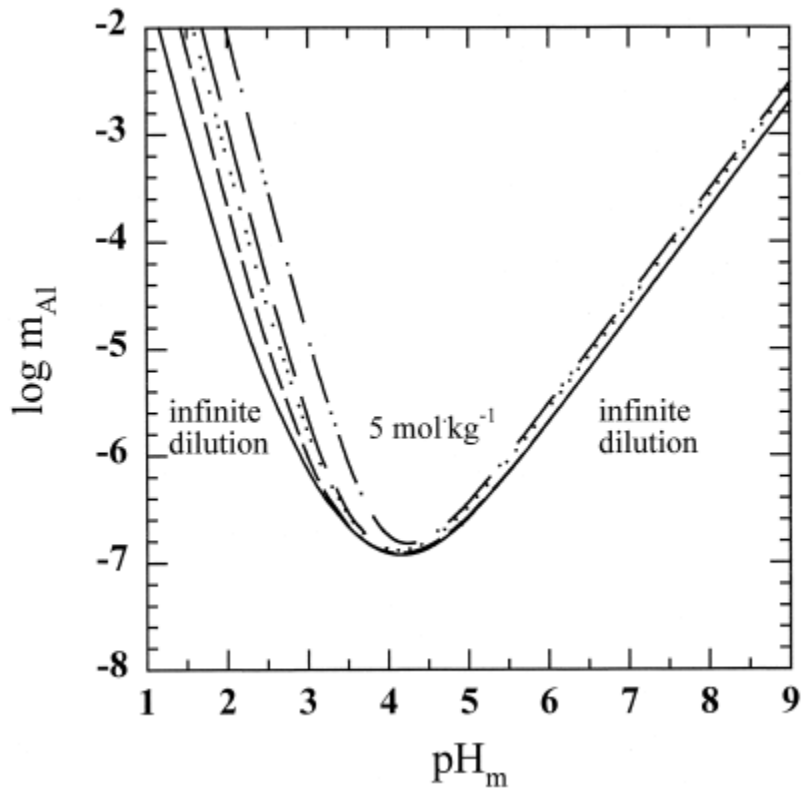


Mineral solubility depends on temperature, pressure and composition



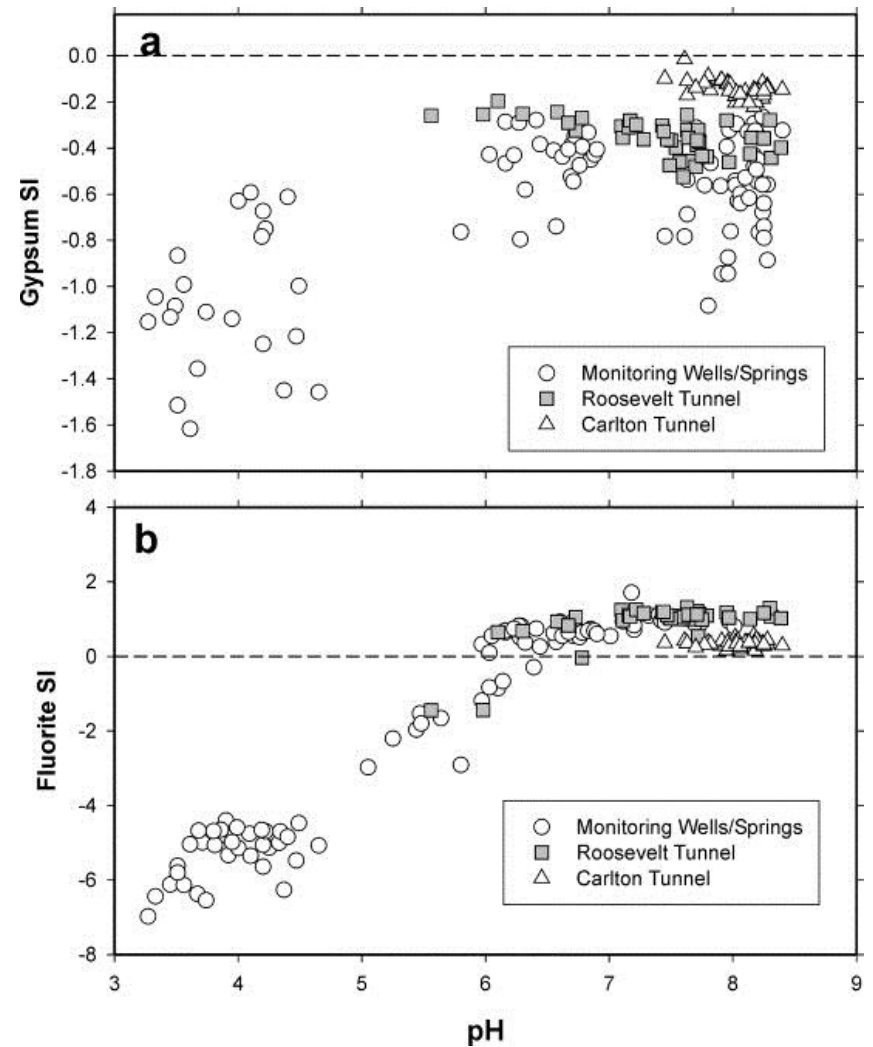
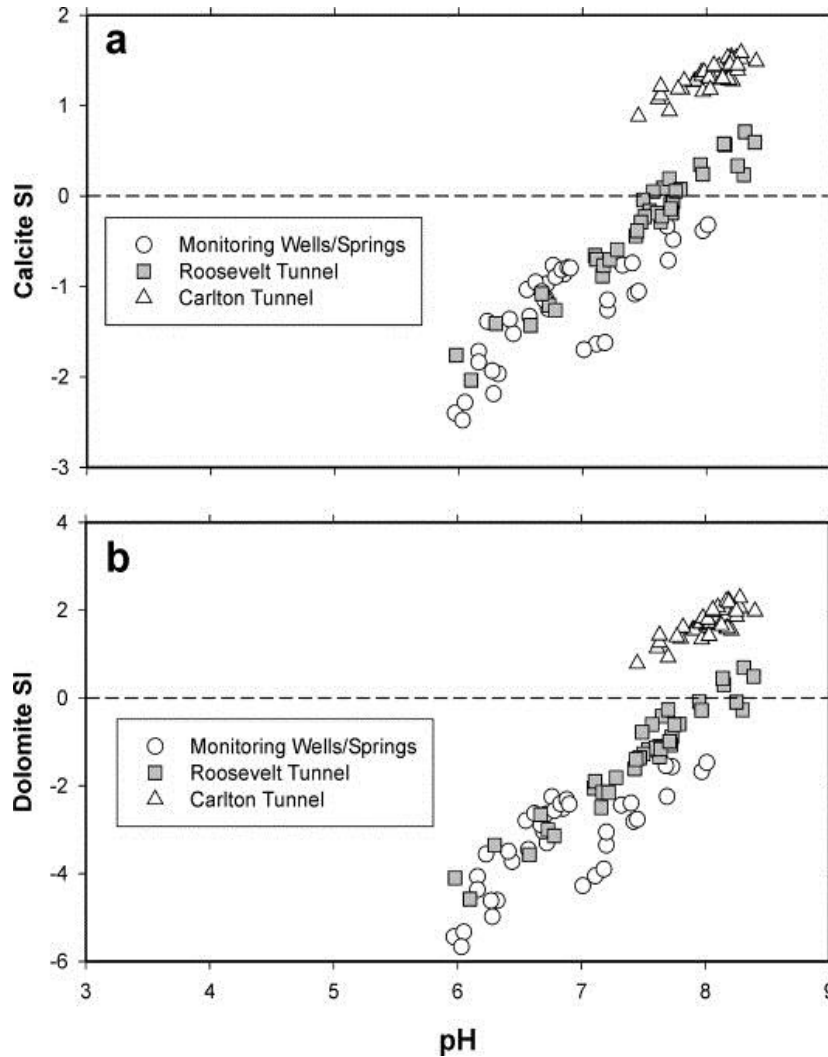
Benezeth et al (2001)

Mineral solubility depends on temperature and composition

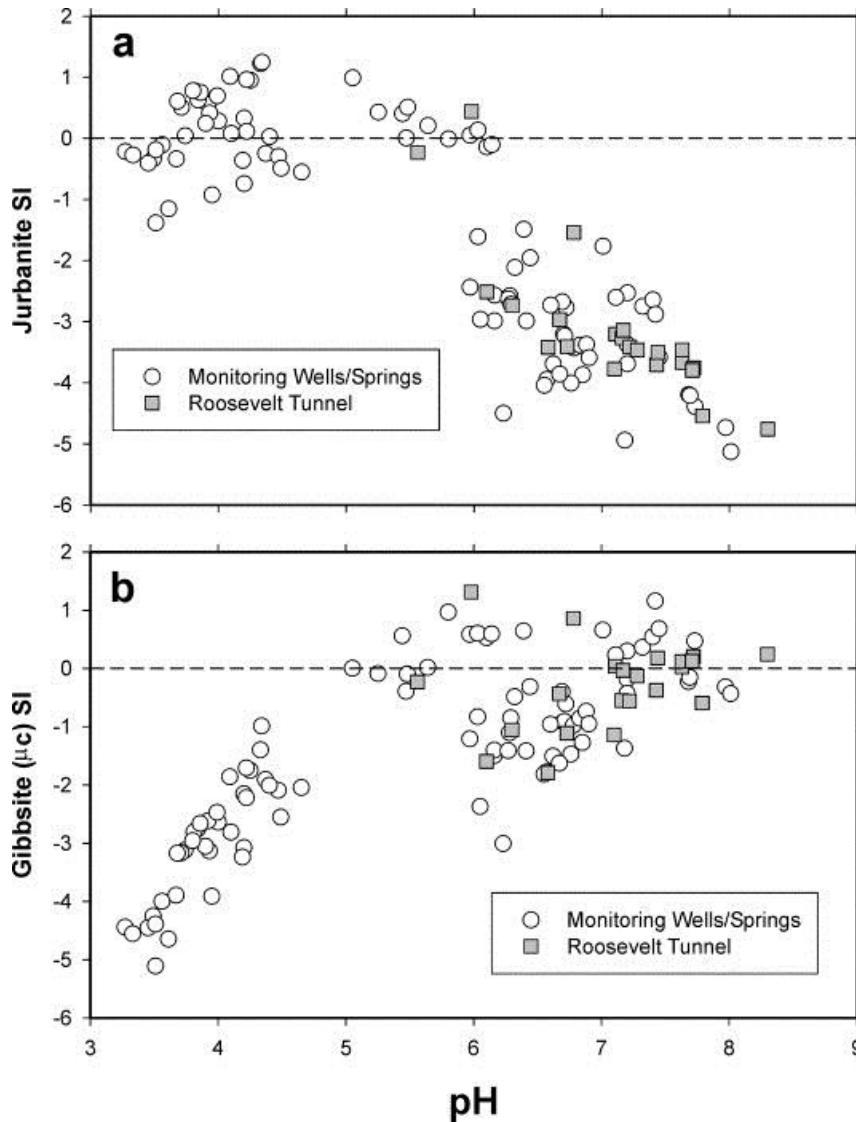


Palmer et al (2001)

Mineral saturation in nature

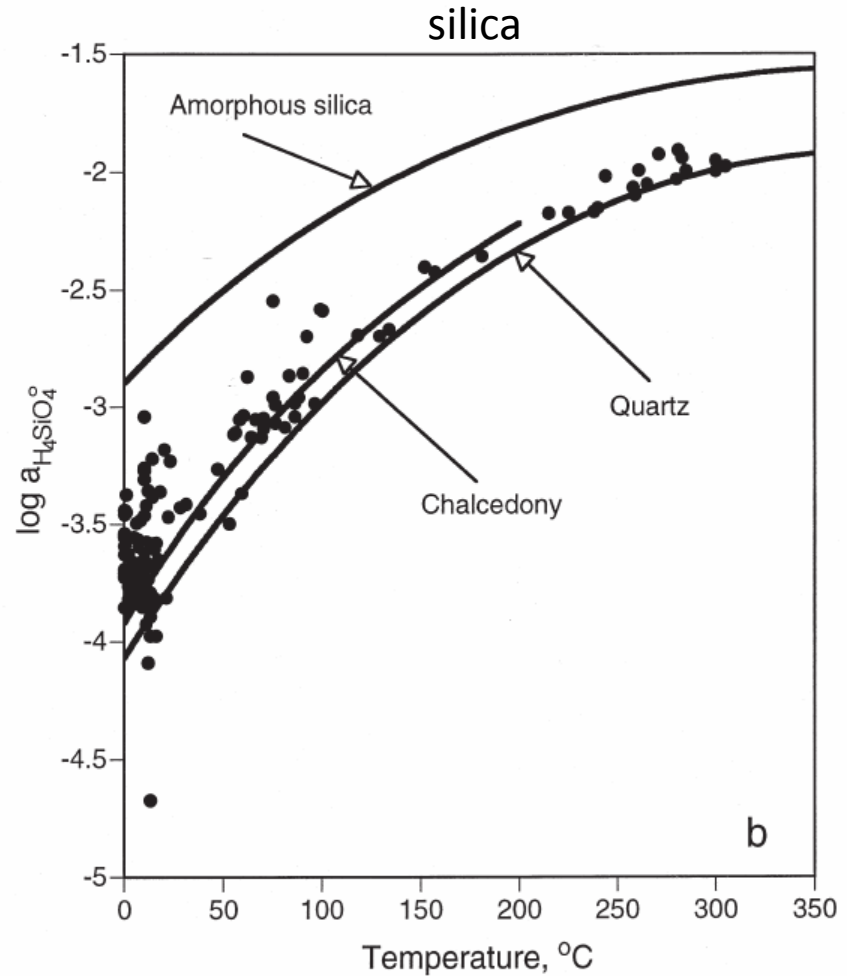
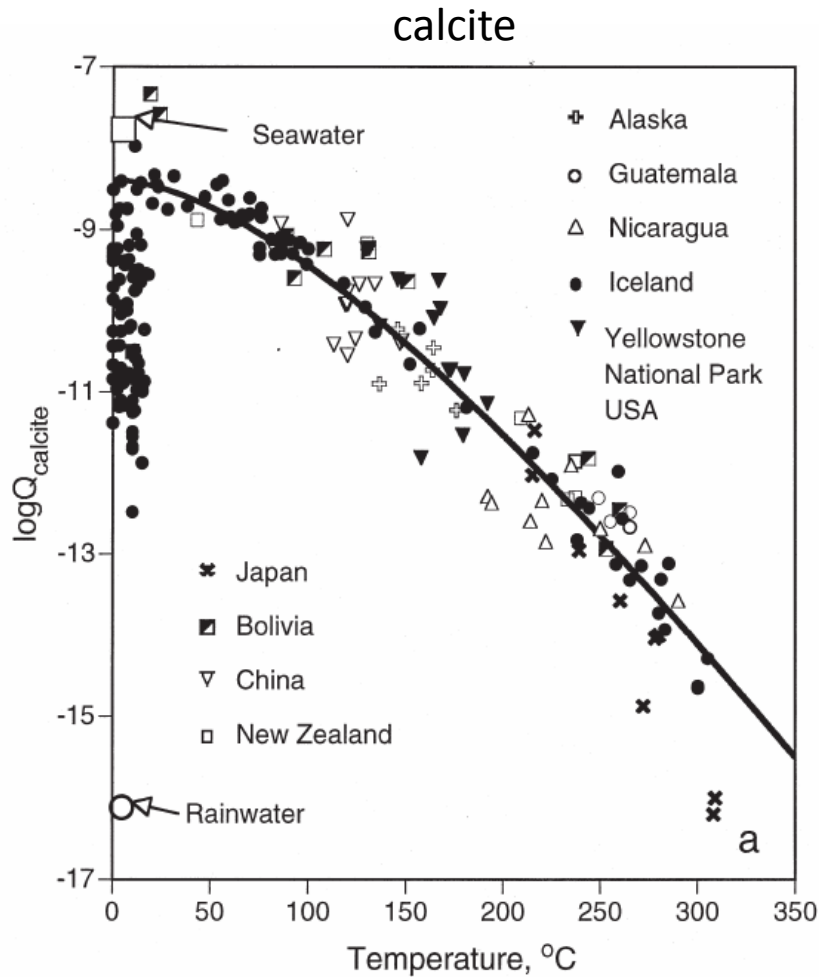


Mineral saturation in nature



Based on mineral saturation states one can predict if a particular water is undersaturated, supersaturated or saturated with a particular mineral. These calculations depend on aqueous species distribution and mineral solubilities that depend on temperature, pressure and composition

Mineral saturation as a function of temperature



Mineral saturation in geothermal water

