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CEE 680: Water Chemistry

Lecture #34

Precipitation and Dissolution: Basics and metal solubility

(Stumm & Morgan, Chapt.7)

Benjamin; Chapter 8.7-8.15

Topics

- Hydrolysis
  - Aquo metal ion gives rise to hydroxo complexes
- Magnesium and Iron Hydroxide solubility

Precipitation and Dissolution

- Environmental Significance
  - Engineered systems
    - coagulation, softening, removal of heavy metals
  - Natural systems
    - composition of natural waters
    - formation and composition of aquatic sediments
    - global cycling of elements
- Composition of natural waters
    - S&M, 3rd ed., figure 15.1 (pg. 873)
    - Benjamin, 2nd ed., figure 1.1

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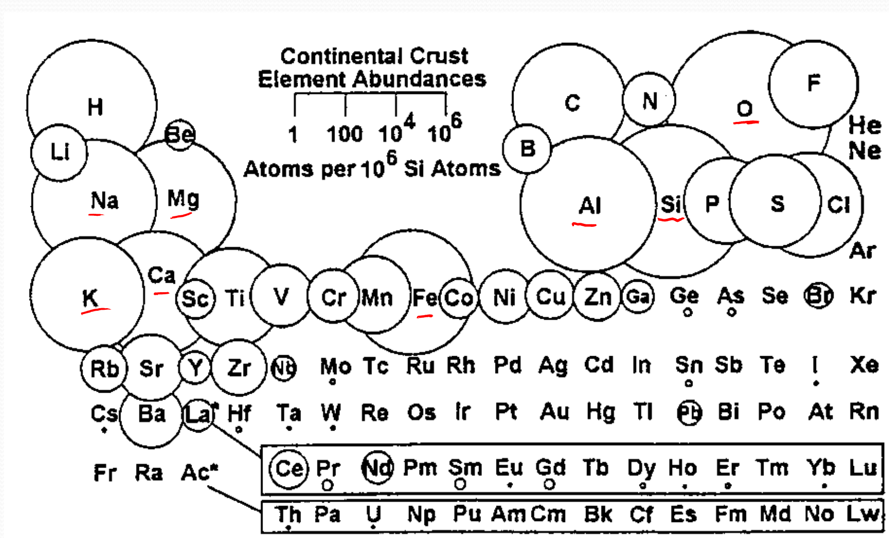
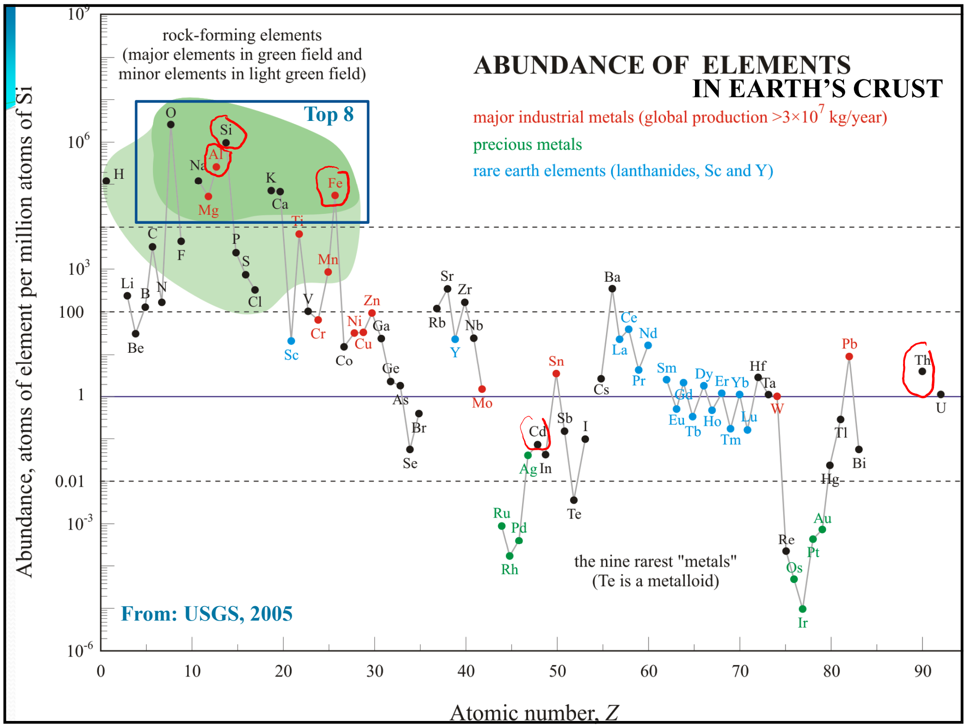
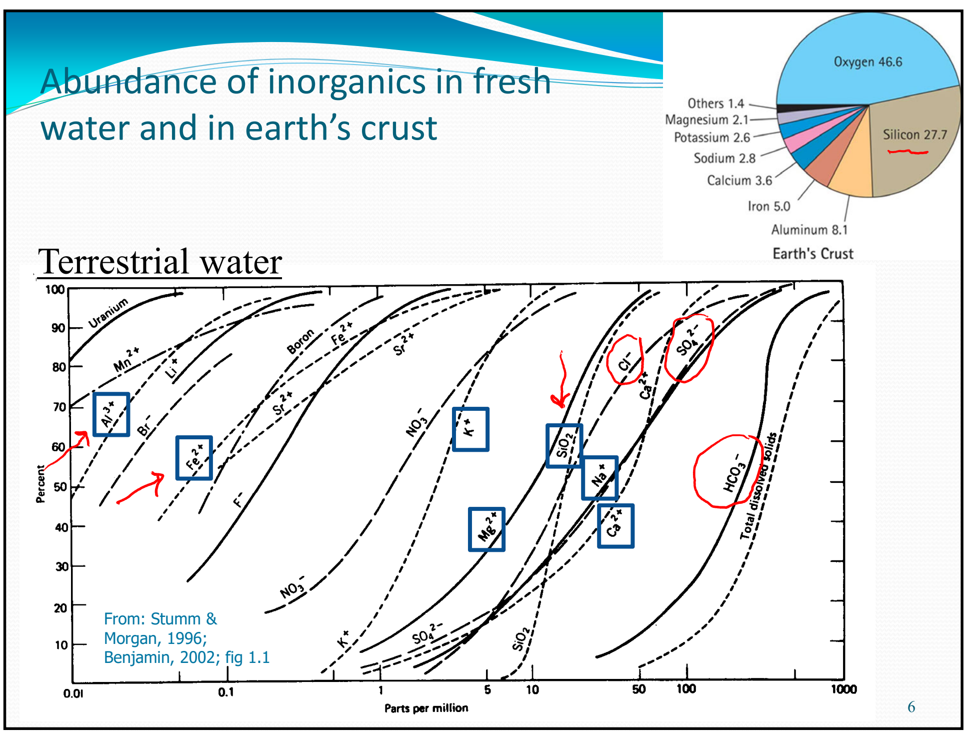
Elemental Abundance in Crust



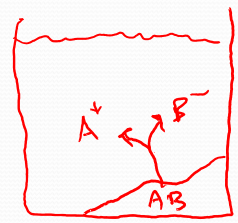

ABUNDANCE OF ELEMENTS IN EARTH'S CRUST
rock-forming elements (major elements in green field and minor elements in light green field)
Top 8
major industrial metals (global production >3×10^7 kg/year)
precious metals
rare earth elements (lanthanides, Sc and Y)
the nine rarest "metals" (Te is a metalloid)
From: USGS, 2005
Abundance, atoms of element per million atoms of Si
Atomic number, Z


Abundance of inorganics in fresh water and in earth's crust
Oxygen 46.6
Silicon 27.7
Aluminum 8.1
Iron 5.0
Calcium 3.6
Sodium 2.8
Potassium 2.6
Magnesium 2.1
Others 1.4
Earth's Crust
Terrestrial water
Percent
Parts per million
From: Stumm & Morgan, 1996; Benjamin, 2002; fig 1.1
6

Solubility Products

- General Equilibrium
  - $A_mB_n(s) \leftrightarrow mA^{+n} + nB^{-m}$

    Solid **Cation** **Anion**
- Solubility Product Equation
  - $K_{so} = [A^{+n}]^m[B^{-m}]^n$
    - also sometimes written: K_{sp}
- Example
  - Calcium Carbonate
    - sources: Smith & Martell; S&M, table 7.1 (pg.362-364)



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K_{so} and Q

- Reaction Quotient (Q)
  - computed value from actual measurements
    - may not be at thermodynamic equilibrium
  - comparison with K_{sp} will tell you about tendency toward dissolution or precipitation
    - $Q>K_{so}$, then water will precipitate solid phase
    - $Q<K_{so}$, then water will dissolve solid phase
- Example: Calcium Carbonate solubility
  - Ca^{+2} = 40 mg/L and CO_3^{-2} = 100 mg/L as $CaCO_3$
    - what is Q?
    - if K_{so} is $10^{-8.34}$, what does this tell us?

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Solubility of some simple salts

$[Ba^{+2}] = [SO_4^{-2}] = x$

- Barium sulfate
  - $BaSO_4 = Ba^{+2} + SO_4^{-2}$
  - $K_{so} = 10^{-9.96} = [Ba^{+2}][SO_4^{-2}]$
- How much will dissolve, and what will the barium and sulfate concentrations be?

$$10^{-9.96} = x^2$$
$$x = 10^{-4.98}$$

- How much will dissolve in a 1mM solution of Na_2SO_4 ?

$$10^{-9.96} = x\left(10^{-3} + x\right)$$
$$= x^2 + 10^{-3}x$$
$$x = \frac{-10^{-3} \pm \sqrt{10^{-6} - 4x10^{-9.96}}}{2}$$
$$= 1.097x10^{-7} = 10^{-6.96}$$

common ion effect

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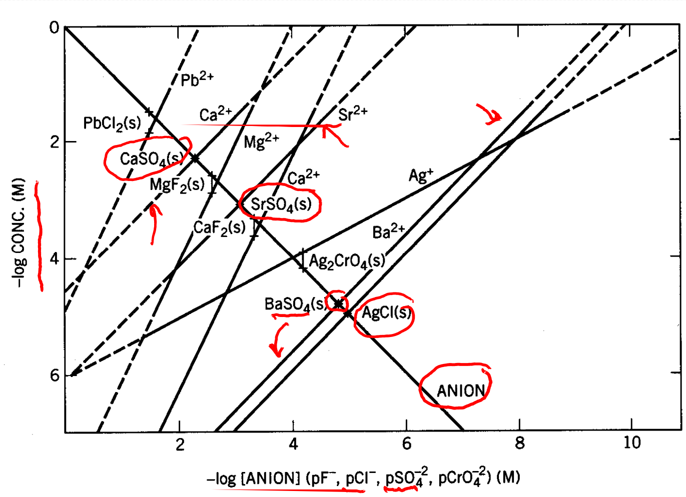
Solubility of "simple" salts



Stumm & Morgan, 1996, Figure 7.1, pg. 354

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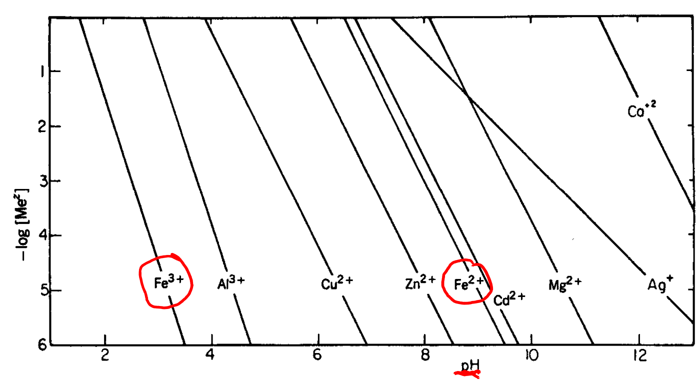
Solubility of oxides & hydroxides

- Does not consider the hydroxometal complexes



Stumm & Morgan, 1996, Figure 7.3, pg. 365

Solubility of metal hydroxides

- Adds complexity
  - hydroxide concentration is controlled by pH and therefore affected by buffering
  - many "hydrolyzing" metals have soluble hydroxide species too
- Example: Magnesium Hydroxide
  - Weakly hydrolyzes
  - Only one soluble hydroxide species
  - Practical: we remove Mg by precipitative softening

Magnesium Hydroxide

- Thermodynamics
  - $Mg(OH)_2\ (s) = Mg^{+2} + 2OH^-$ $K_{so} = 10^{-11.16}$
  - $Mg^{+2} + OH^- = MgOH^+$ $K_1 = 10^{2.6}$
- Mass Balance
  - $Mg_T = [Mg^{+2}] + [MgOH^+]$

-11.79 Benjamin
-11.1 Morel
-10.74 Butler
-12.9 SM&P
-11.16 Brezonik
-11.15 Smith

2.56 Stumm
2.12 Benjamin
2.6 Morel
2.58 Smith

Total dissolved concentration: does not include precipitated Mg

$Mg(OH)_{2\ (s)}$ is crystalline Brucite

- Smith & Martell

$Mg(OH)_2$ solid

HO^- Hydroxide ion L^-

Metal ion	Equilibrium	Log K 25°, 0.5	Log K 25°, 1.0	Log K 25°, 0	ΔH 25°, 0	ΔS 25°, 0
H^+	HL/H.L	13.74 ±0.02	13.79 ±0.02	13.997±0.003	-13.34 ±0.01	19.3
		13.78[a]±0.01	14.18[e]±0.04		-13.55[b]±0.05	17.7[b]
		13.95[h]			-13.08[e]±0.03	21.0[e]
		13.96[d]±0.01			-12.69[p]	
Li^+	ML/M.L		-0.18[e]	0.36	(0)[r]	(2)
Na^+	ML/M.L			-0.2	(0)[s]	(-1)
K^+	ML/M.L			-0.5		
Be^{2+}	ML/M.L	8.3[h]		8.6		
	$ML_2/M.L^2$	(16.5)	(17.5)[e]	(14.4)		
		(16.7)[h]				
	$ML_3/M.L^3$			18.8		
	$ML_4/M.L^4$			18.6		
	$M_2L/M^2.L$	10.54	10.95[e]	(10.0)	-8.9[e]	20[e]
		10.68[d]				
	$M_3L_3/M^3.L^3$	32.41	33.88[e]	33.1	-24.8[e]	72[e]
		32.98[d]				
	$M_6L_8/M^6.L^8$			(85)	(-58)[t]	(200)
	$M.L^2/ML_2$(s, amorphous)			-21.0		
	$M.L^2/ML_2$(s,α)			-21.31		
	$M.L^2/ML_2$(s,β)			-21.7		
Mg^{2+}	ML/M.L		1.85[e]	2.58 ±0.0		
	$M_4L_4/M^4.L^4$		16.93[e]	16.3		
	$M.L^2/ML_2$(s)			-11.15 ±0.2		
Ca^{2+}	ML/M.L		0.64[e]	1.3 ±0.1	2.0	13
	$M.L^2/ML_2$(s)			-5.19 ±0.2	-4.3	-38
Sr^{2+}	ML/M.L		0.23[e]	0.8 ±0.1	1.2	8

[a] 25°, 0.1; [b] 25°, 0.5; [d] 25°, 2.0; [e] 25°, 3.0; [h] 20°, 0.1; [p] 40°, 0; [r] 15-35°, 0; [s] 0-50°, 0; [t] 0-60°, 1.0 molal

Magnesium Hydroxide

- Tableau
  - $[Mg^{+2}] = 10^{16.84}[H^+]^2$
  - same as:
    - $[Mg^{+2}] = 10^{-11.16}/[OH^+]^2$

	Reactants		
Components	MgOH2 (Brucite	H+	Log K
Mg+2	1	2	16.84
MgOH+	1	1	5.42
H+	0	1	0

Magnesium Hydroxide II

- From the K_{so} and K_w develop an equation for the free metal in terms of H^+

$$K_{so} = [Mg^{+2}][OH^-]^2$$

$$[Mg^{+2}] = K_{so} / [OH^-]^2$$

$$[Mg^{+2}] = \frac{K_{so}}{K_W^2}[H^+]^2$$

$$[Mg^{+2}] = 10^{16.84}[H^+]^2$$

$$Log[Mg^{+2}] = 16.84 - 2pH$$

- Then use the K_1 to get an equation for the soluble hydroxide species

$$K_1 = \frac{[MgOH^+]}{[Mg^{+2}][OH^-]}$$

$$[MgOH^+] = K_1[Mg^{+2}][OH^-]$$

$$= K_1[Mg^{+2}]^{K_W}/_{[H^+]}$$

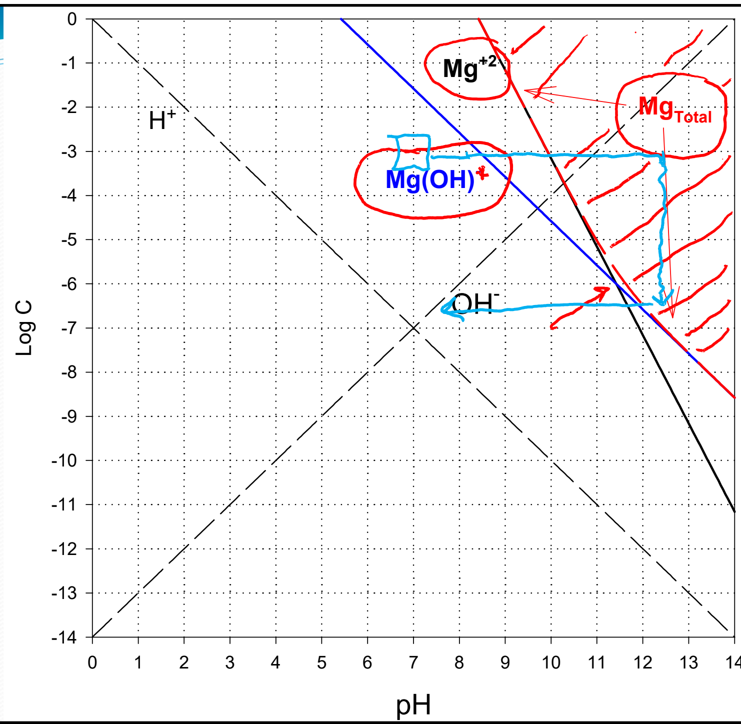
$$= 10^{2.6}\{10^{16.84}[H^+]^2\}^{10^{-14}}/_{[H^+]}$$

$$= 10^{5.44}[H^+]$$

$$Log[MgOH^+] = 5.44 - pH$$

Magnesium Hydroxide III

- Total Magnesium
  - Mg_T $= [Mg^{+2}] + [MgOH^{+}]$
  - Follows upper line where lines are well separated
  - Falls 0.3 log units above intersection of any two major species
- Applications
  - Mg is a hardness cation
  - Solubility is controlled by hydroxide precipitate
  - Easily removed by softening at high pH



- To next lecture

Calcium Phosphate

- Providence, RI example
  - See Edwards & Giammar manuscripts