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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

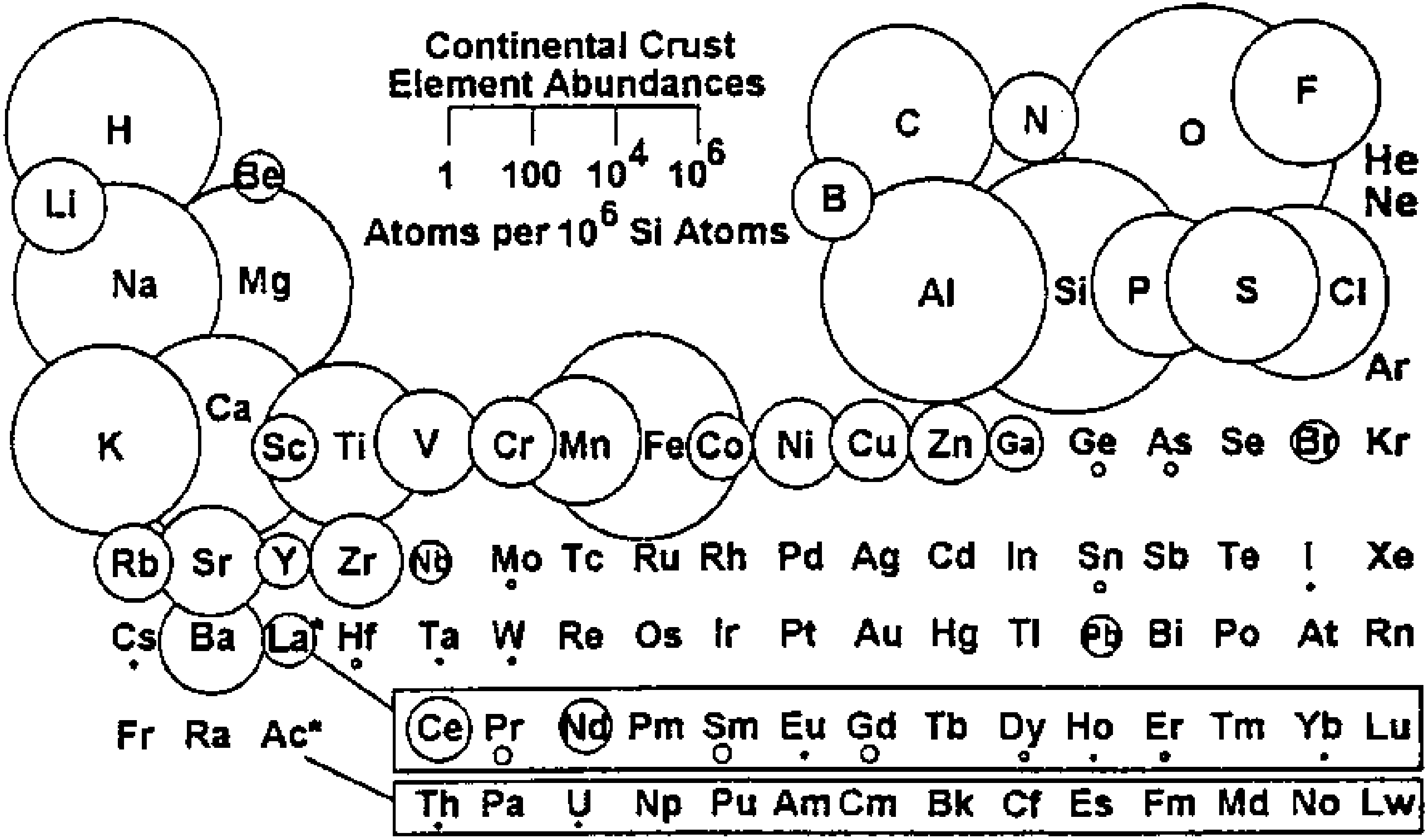
Topics

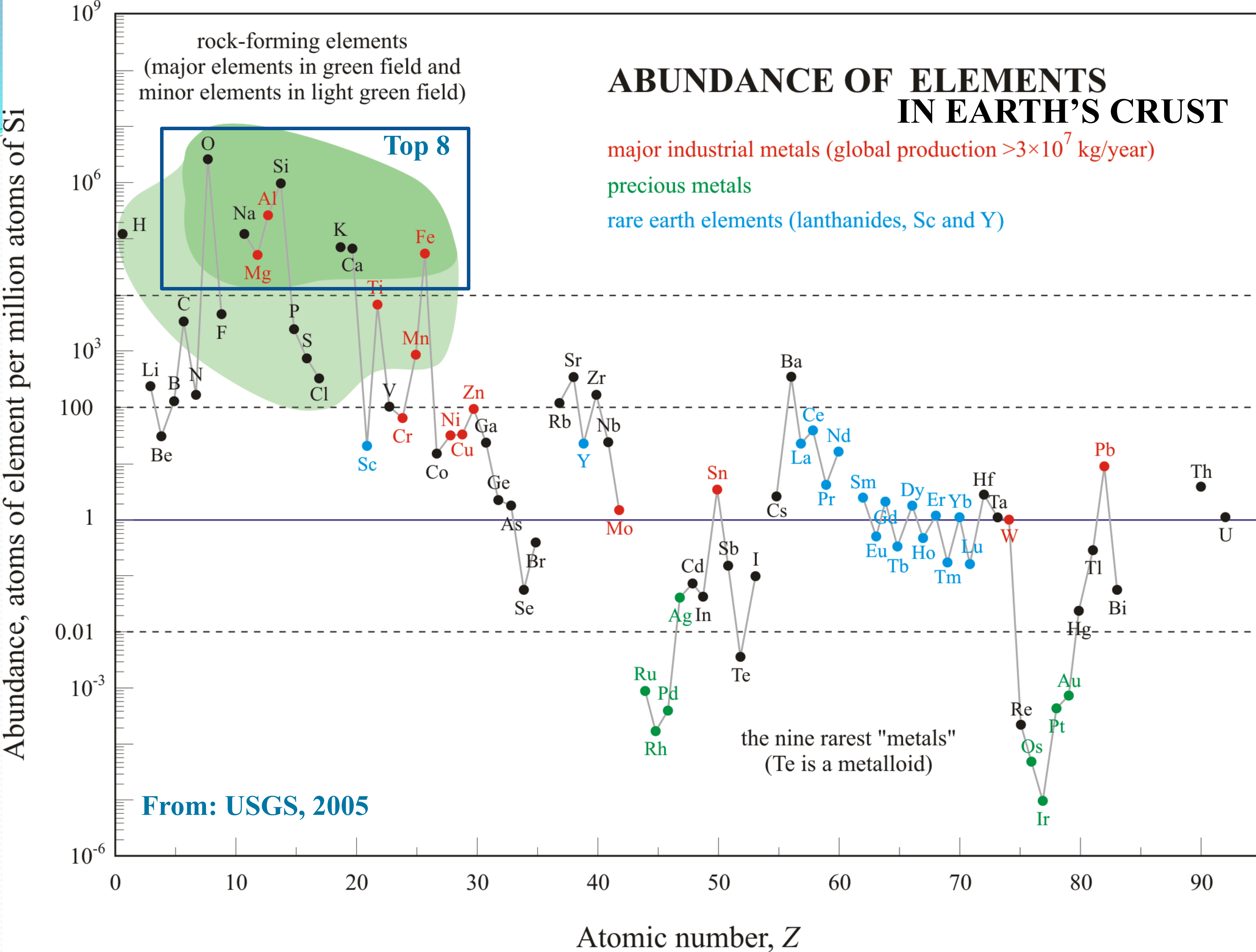
- Hydrolysis
  - Aquo metal ion gives rise to hydroxo complexes
- Magnesium and Iron Hydroxide solubility

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

Elemental Abundance in Crust

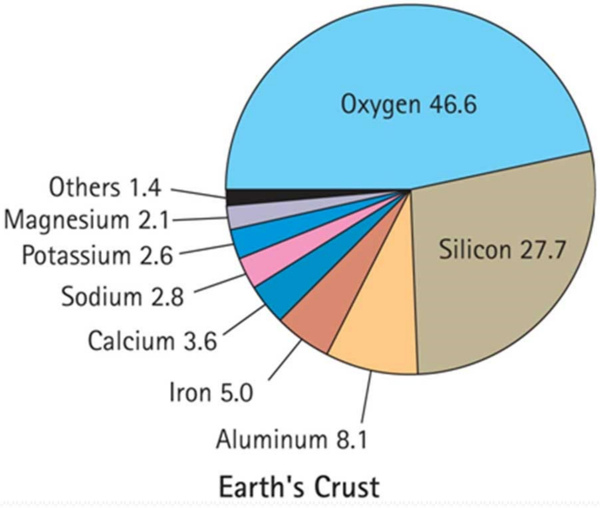




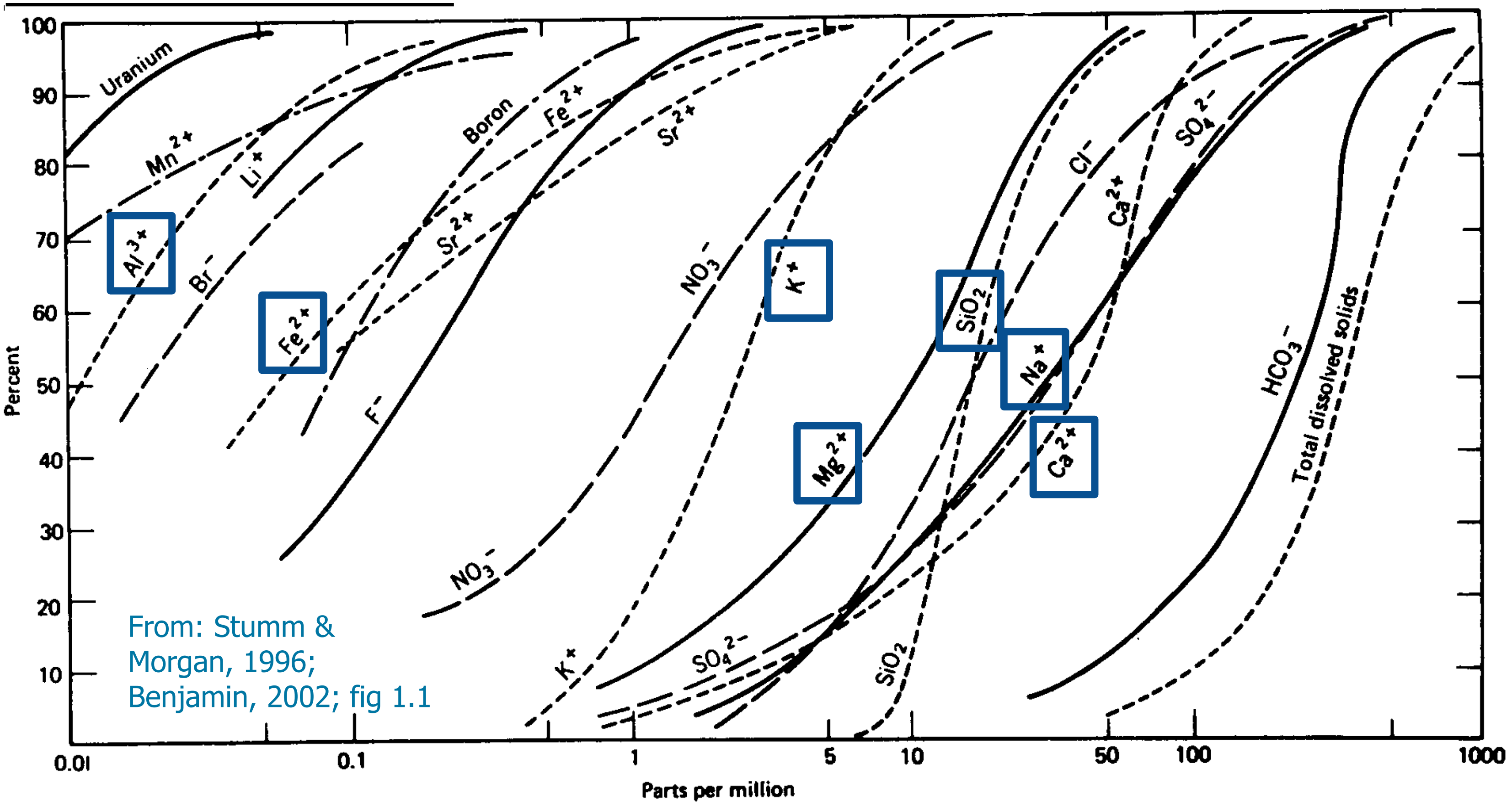
ABUNDANCE OF ELEMENTS IN EARTH'S CRUST

From: USGS, 2005

Abundance of inorganics in fresh water and in earth's crust



Terrestrial water



From: Stumm & Morgan, 1996; Benjamin, 2002; fig 1.1

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)

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?

Solubility of some simple salts

- 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 ?

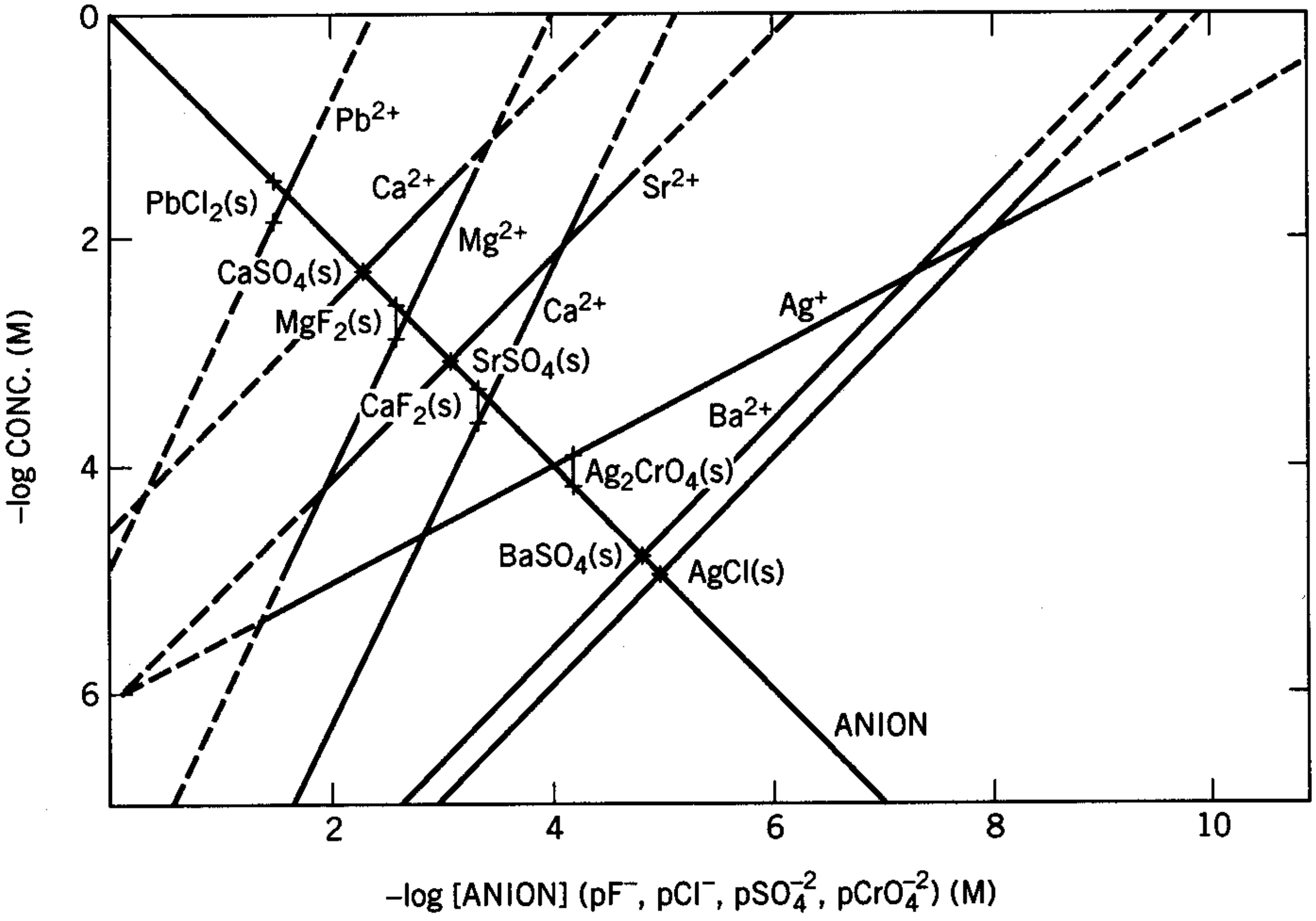
$$\begin{aligned} 10^{-9.96} &= x\left(10^{-3} + x\right) \\ &= x^2 + 10^{-3}x \end{aligned}$$

$$x = \frac{-10^{-3} \pm \sqrt{10^{-6} - 4x10^{-9.96}}}{2}$$

$$= 1.097x10^{-7} = 10^{-6.96}$$

common ion effect

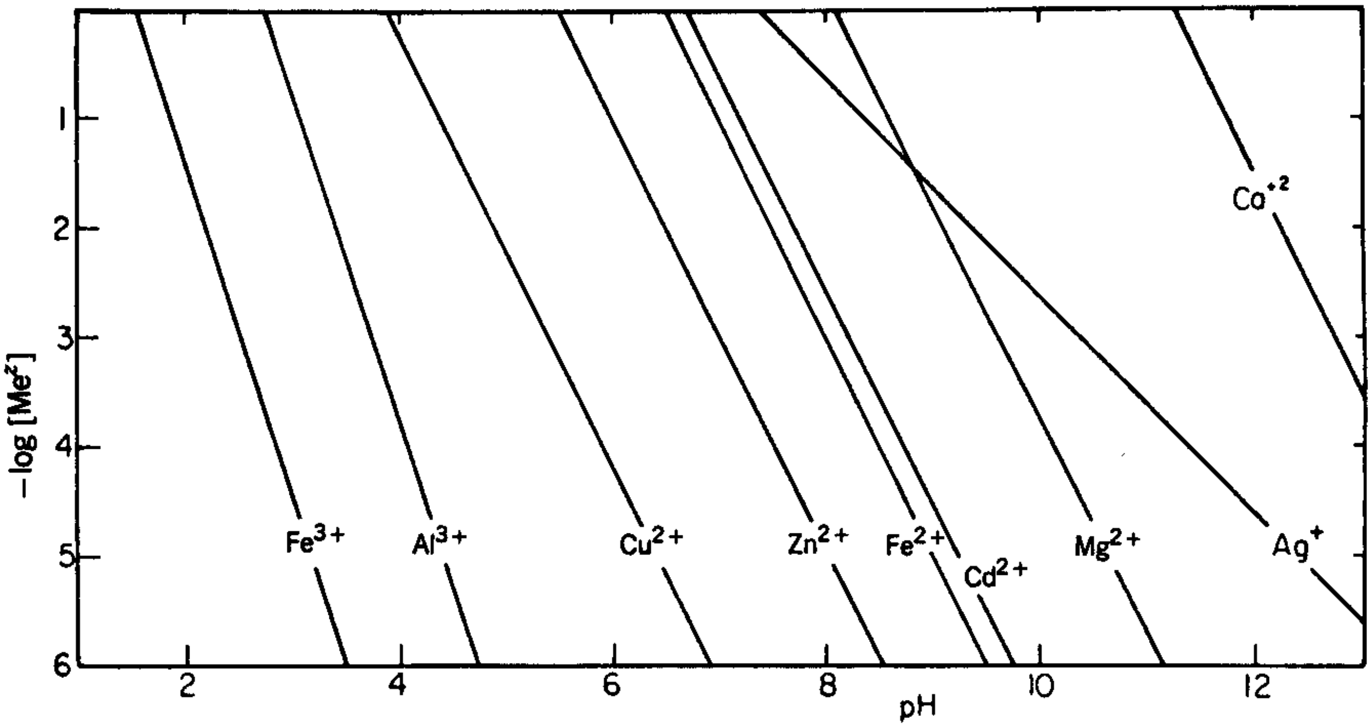
Solubility of “simple” salts



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

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

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

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

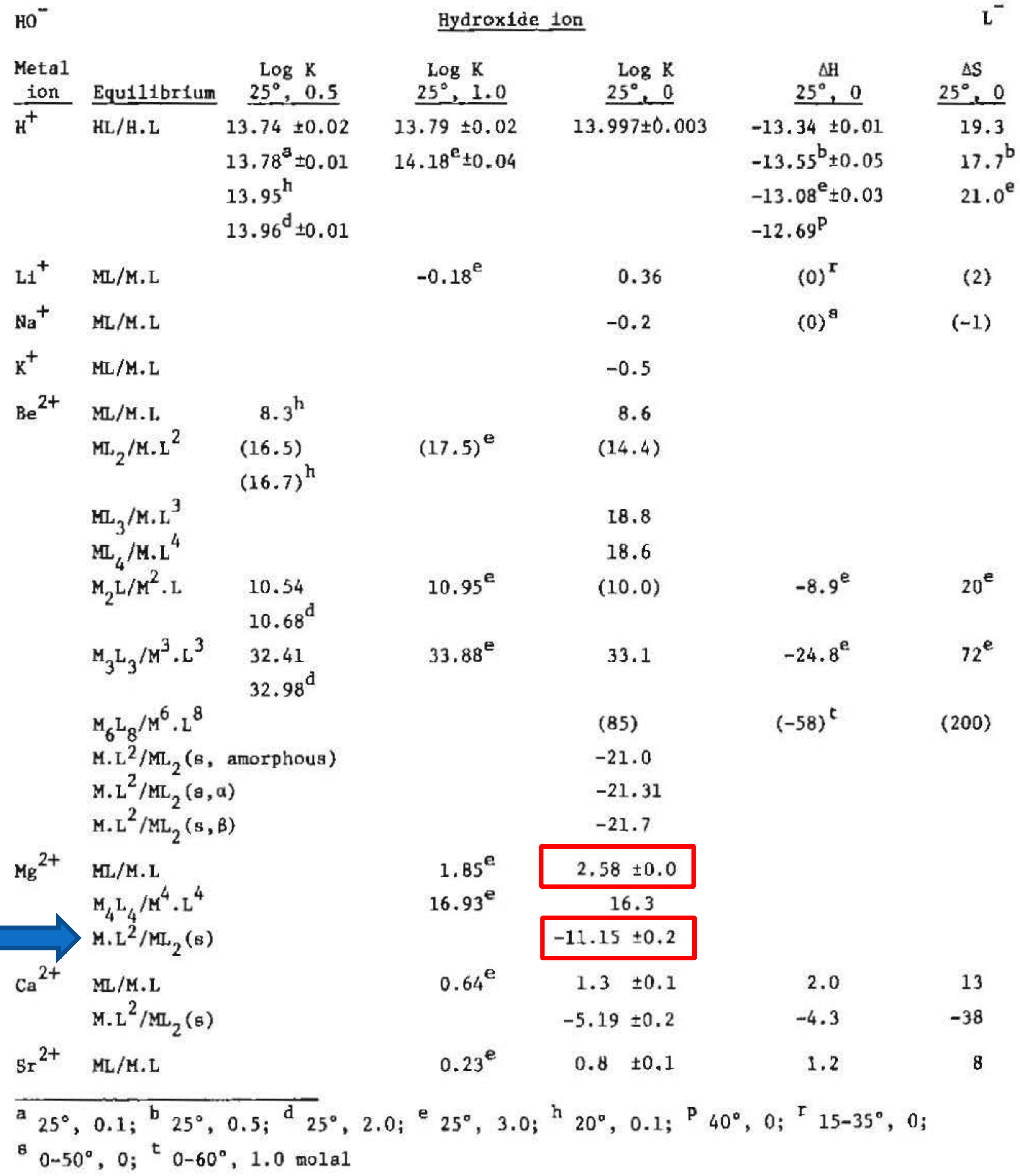
2.56 Stumm
2.12 Benjamin
2.6 Morel
2.58 Smith

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

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[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^+

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

$$[Mg^{+2}] = {}^{K_{so}}\!\big/_{[OH^-]^2}$$

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

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

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

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

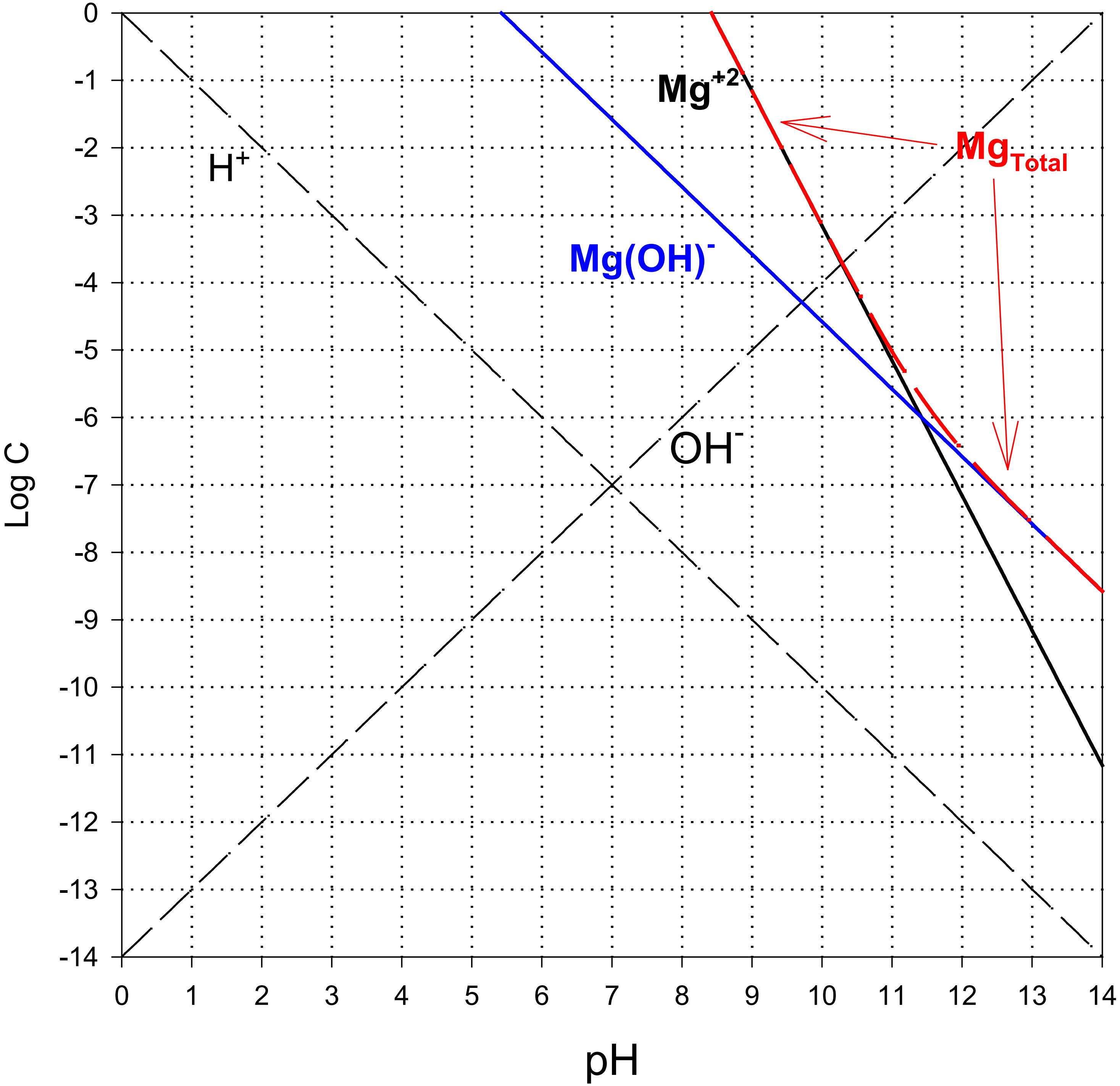
$$K_1 = \frac{[MgOH^+]}{[Mg^{+2}][OH^-]}$$

$$\begin{aligned}[MgOH^+] &= K_1[Mg^{+2}][OH^-] \\ &= K_1[Mg^{+2}]\,{}^{K_W}\!\big/_{[H^+]} \\ &= 10^{2.6}\left\{10^{16.84}[H^+]^2\right\}{}^{10^{-14}}\!\big/_{[H^+]} \\ &= 10^{5.44}[H^+]\end{aligned}$$

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

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


Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
H+
OH-
Mg+2
Mg(OH)-
MgTotal

- To next lecture

Calcium Phosphate

- Providence, RI example
    - See Edwards & Giammar manuscripts