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CEE 680: Water Chemistry

Lecture #35

Precipitation and Dissolution: Iron Hydroxides

(Stumm & Morgan, Chapt.7)

Benjamin; Chapter 8.7-8.15

Topics

- Hydrolysis
  - Aquo metal ion gives rise to hydroxo complexes
- Iron Hydroxide solubility
- Other metals

Secondary Drinking Water standards

- From EPA website

Contaminant	Secondary MCL	Noticeable Effects above the Secondary MCL
Aluminum	0.05 to 0.2 mg/L*	colored water
Chloride	250 mg/L	salty taste
Color	15 color units	visible tint
Copper	1.0 mg/L	metallic taste; blue-green staining
Corrosivity	Non-corrosive	metallic taste; corroded pipes/ fixtures staining
Fluoride	2.0 mg/L	tooth discoloration
Foaming agents	0.5 mg/L	frothy, cloudy; bitter taste; odor
Iron	0.3 mg/L	rusty color; sediment; metallic taste; reddish or orange staining
Manganese	0.05 mg/L	black to brown color; black staining; bitter metallic taste

Concentration of inorganics in fresh water

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

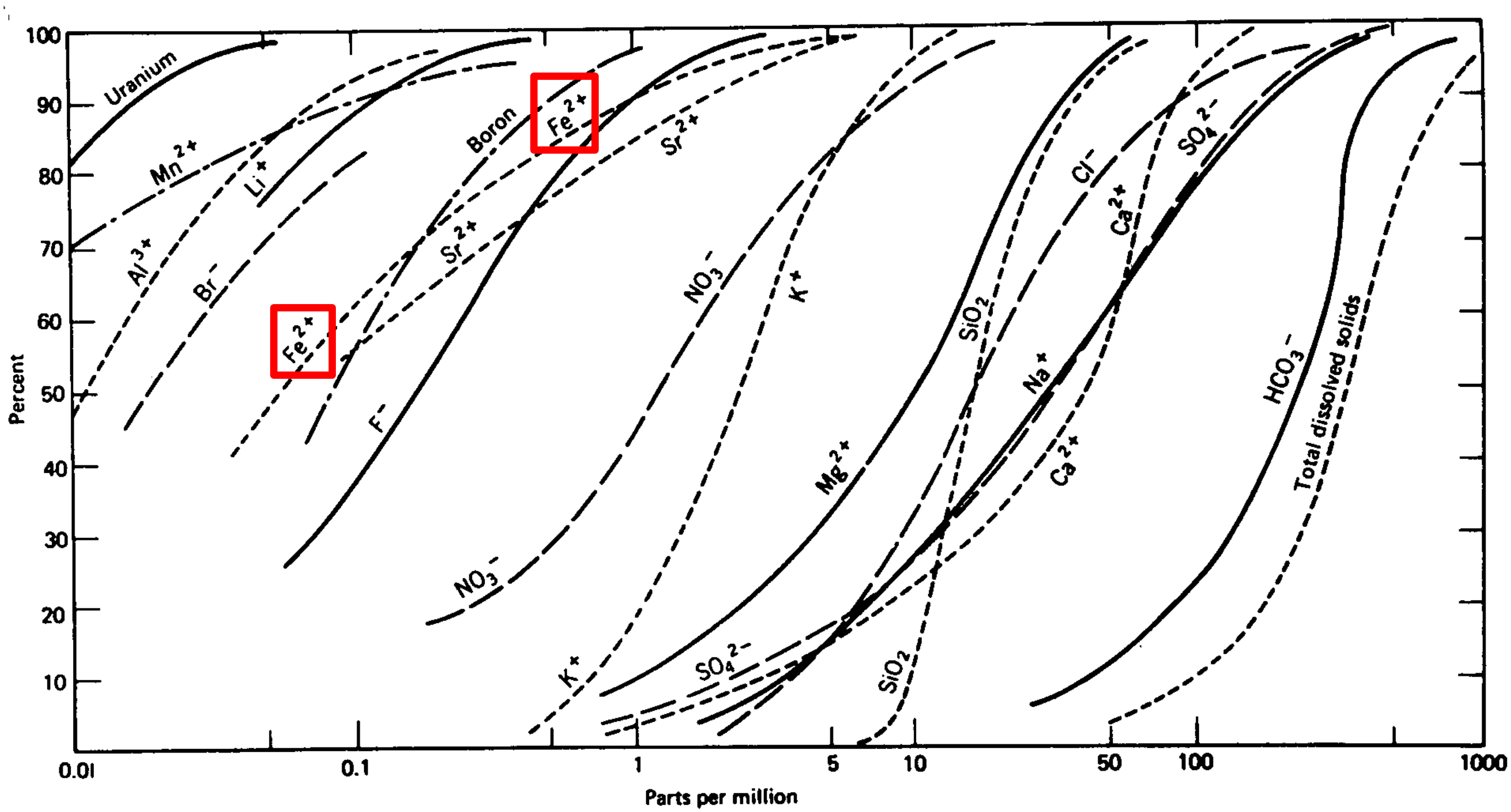


Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)

Ferrous Hydroxide I

- Thermodynamics
  - $Fe(OH)_2\,(s) = Fe^{+2} + 2OH^-$ $K_{so} = 10^{-15.1}$
  - $Fe^{+2} + OH^- = FeOH^+$ $K_1 = 10^{4.5}$
  - $Fe^{+2} + 3OH^- = Fe(OH)_3^-$ $K_2 = 10^{11.0}$
- Mass Balance
  - $Fe_T = [Fe^{+2}] + [FeOH^+] + [Fe(OH)_3^-]$

Benjamin

-15.9

Constants from Stumm & Morgan, 1996; identical to those from Morel & Hering, 1993

Ferrous Hydroxide II

- Log C vs pH relationships
  - Log $[Fe^{+2}] = 12.9 - 2pH$
  - Log $[FeOH^{+}] = 3.4 - pH$
  - Log $[Fe(OH)_3^{-}] = -18 + pH$

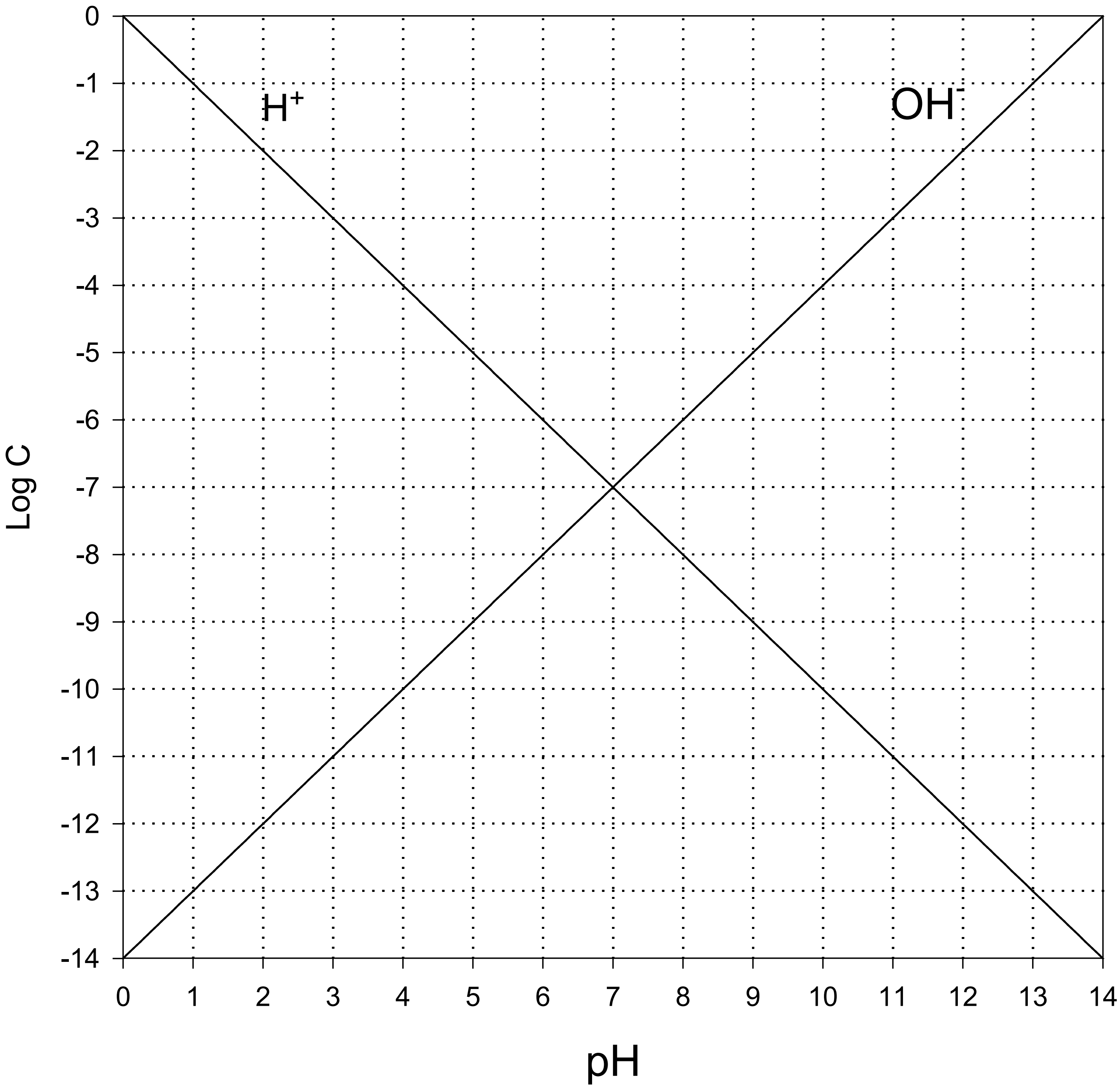
Based on: Constants from Stumm & Morgan, 1996; identical to those from Morel & Hering, 1993

Ferrous Hydroxide III

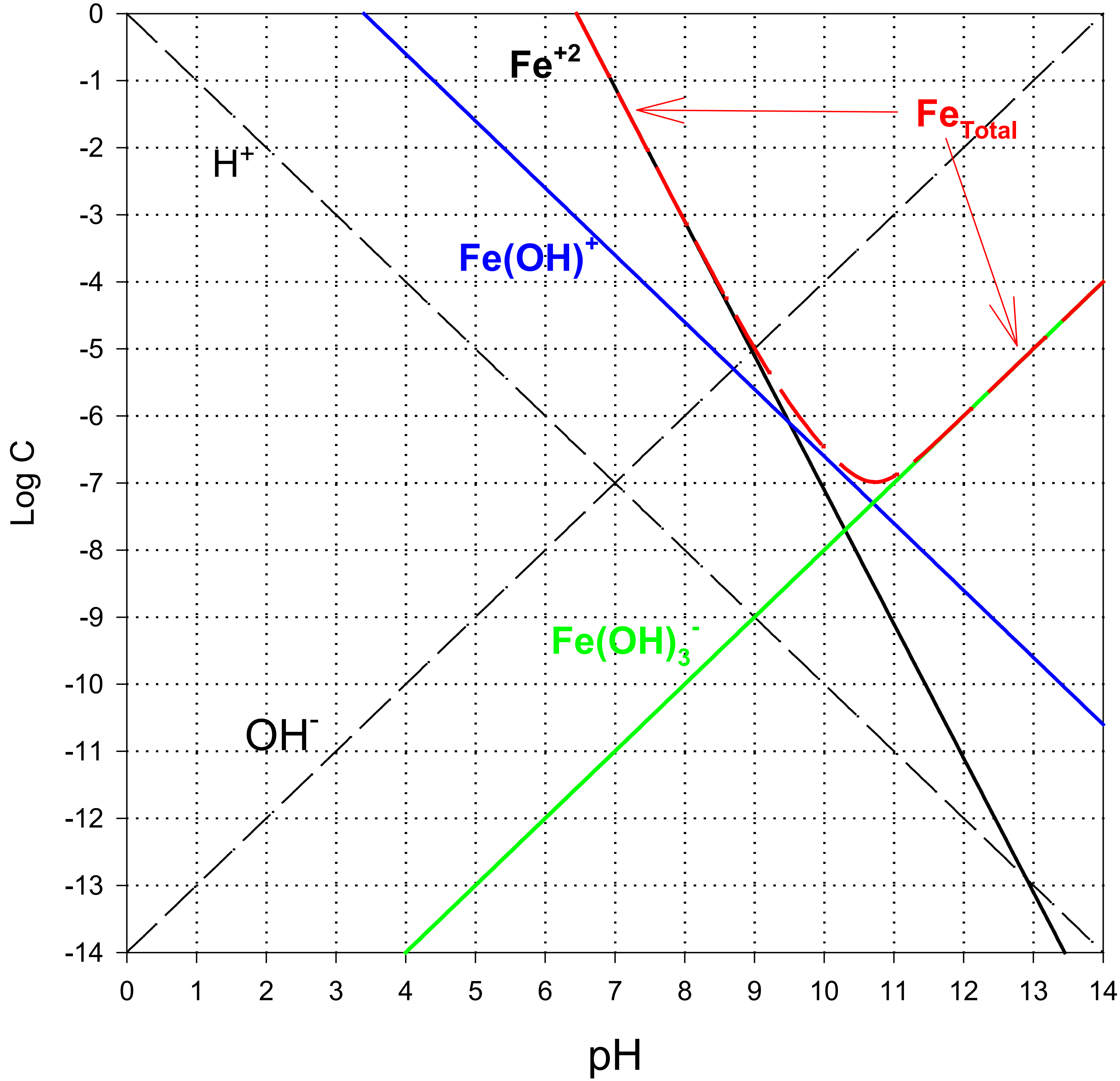
- Tableaux

	Components		
Species	Fe(OH)2 (s	H+	Log K
Fe+2	1	2	13.3
FeOH+	1	1	4.6
Fe(OH)3-	1	-1	-19.08
H+	0	1	0
OH-	0	-1	-14
Log(conc.)	0		

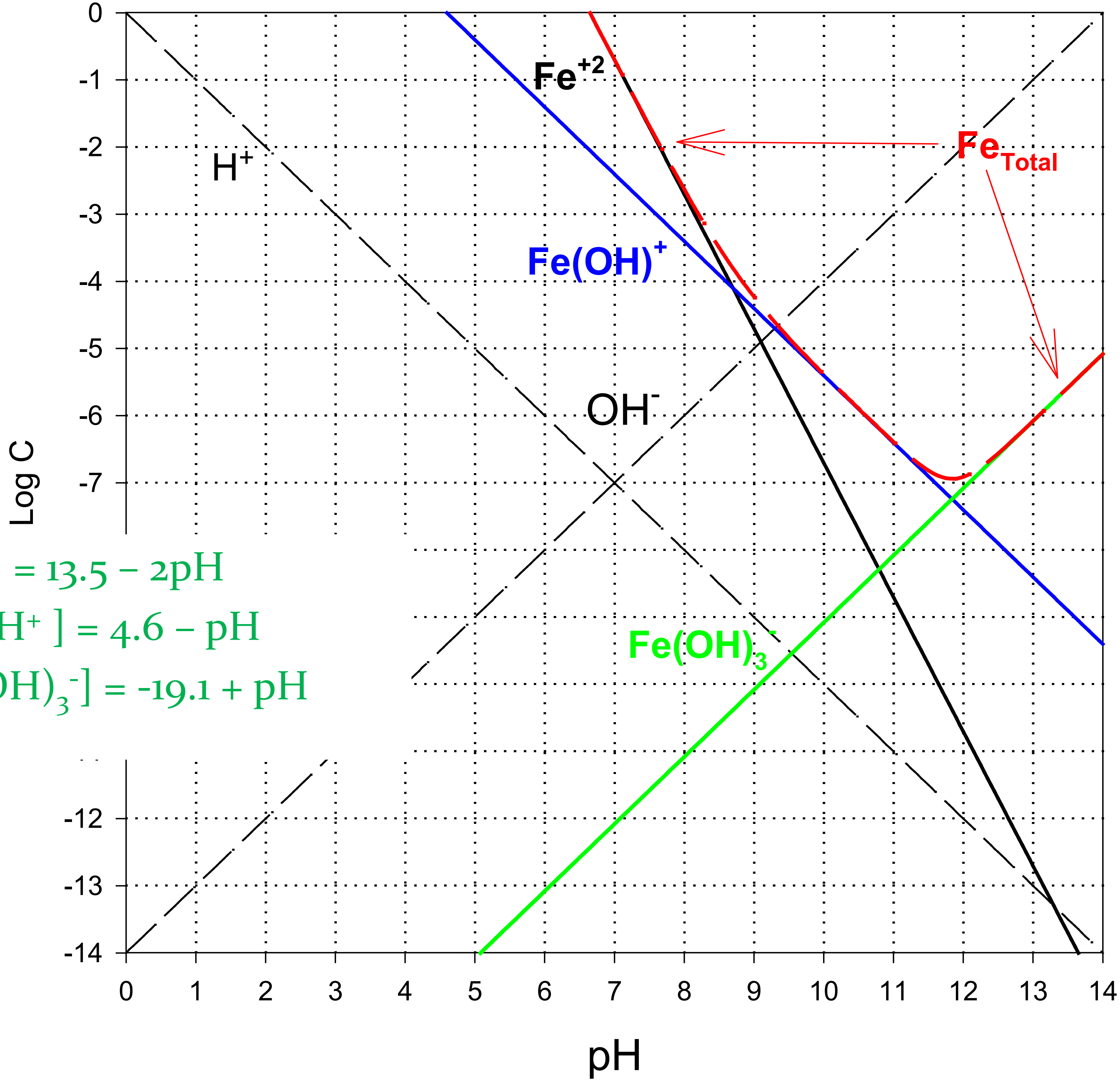
Log[	Fe+2	]	=	13.3	-2	pH
Log[	FeOH+	]	=	4.6	-1	pH
Log[	Fe(OH)3-	]	=	-19.08	1	pH



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



Based on: Constants from Stumm & Morgan, 1996; identical to those from Morel & Hering, 1993



- Log $[Fe^{+2}] = 13.5 - 2pH$
- Log $[FeOH^{+}] = 4.6 - pH$
- Log $[Fe(OH)_3^{-}] = -19.1 + pH$

Based on:
Constants from
Snoeyink &
Jenkins, 1980

Trivalent Metal Hydrolysis

- Case for iron

$$Fe(H_2O)_6^{+3} \longleftrightarrow FeOH(H_2O)_5^{+2} + H^+ \longleftrightarrow Fe(OH)_2(H_2O)_4^{+} + 2H^+$$

$$Fe(OH)_2(H_2O)_4^{+} \longleftrightarrow Fe(OH)_3(H_2O)_3 + 3H^+ \longleftrightarrow Fe(OH)_4(H_2O)_2^{-} + 4H^+$$

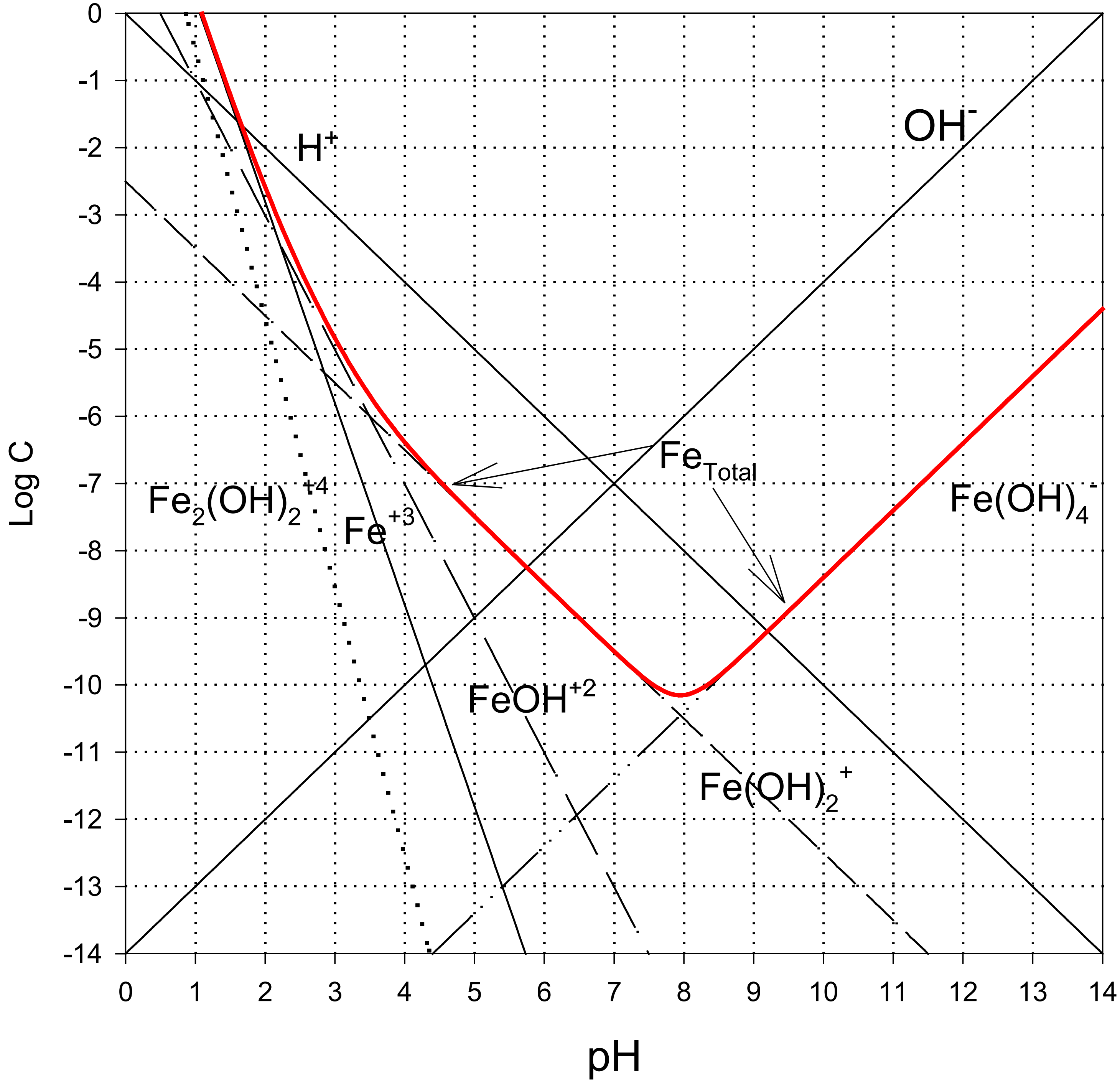
$$Fe(OH)_3(H_2O)_3 \Longrightarrow Fe(OH)_3\ (s)$$

Ferric Hydroxide I

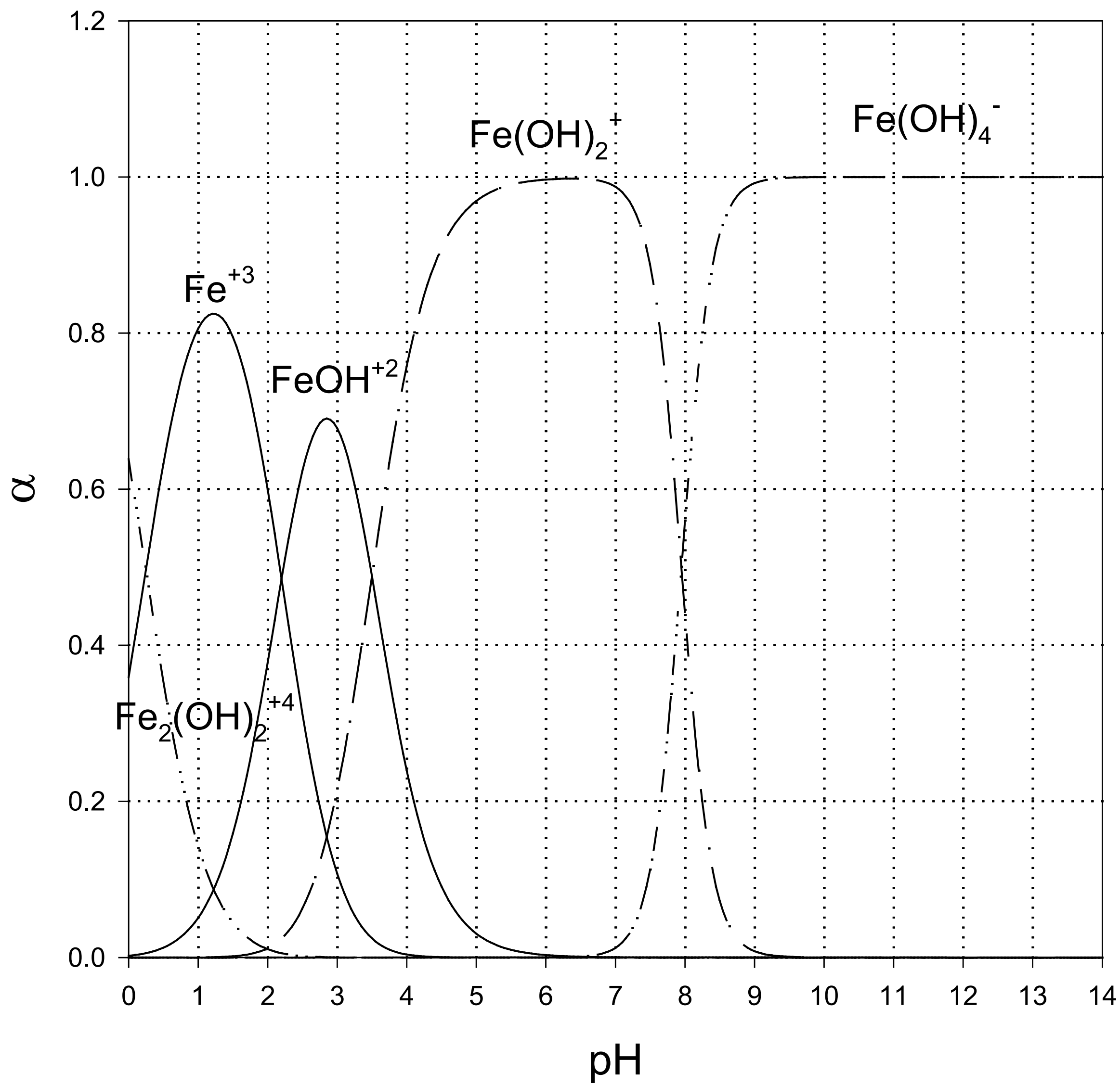
- Thermodynamics
  - $Fe(OH)_3\ (s) = Fe^{+3} + 3OH^-$ $\quad K_{so} = 10^{-38.8}$
  - $FeOH^{+2} = Fe^{+3} + OH^-$ $\quad K_1 = 10^{-11.8}$
  - $Fe(OH)_2^+ = FeOH^{+2} + OH^-$ $\quad K_2 = 10^{-10.5}$
  - $Fe(OH)_4^- = Fe(OH)_2^+ + 2OH^-$ $\quad K_3 = 10^{-12.1}$
  - $Fe_2(OH)_2^{+4} = 2Fe^{+3} + 2OH^-$ $\quad K_{22} = 10^{-25.05}$
- Mass Balance
  - $Fe_T = [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^+] + [Fe(OH)_4^-] + [Fe_2(OH)_2^{+4}]$

Ferric Hydroxide II

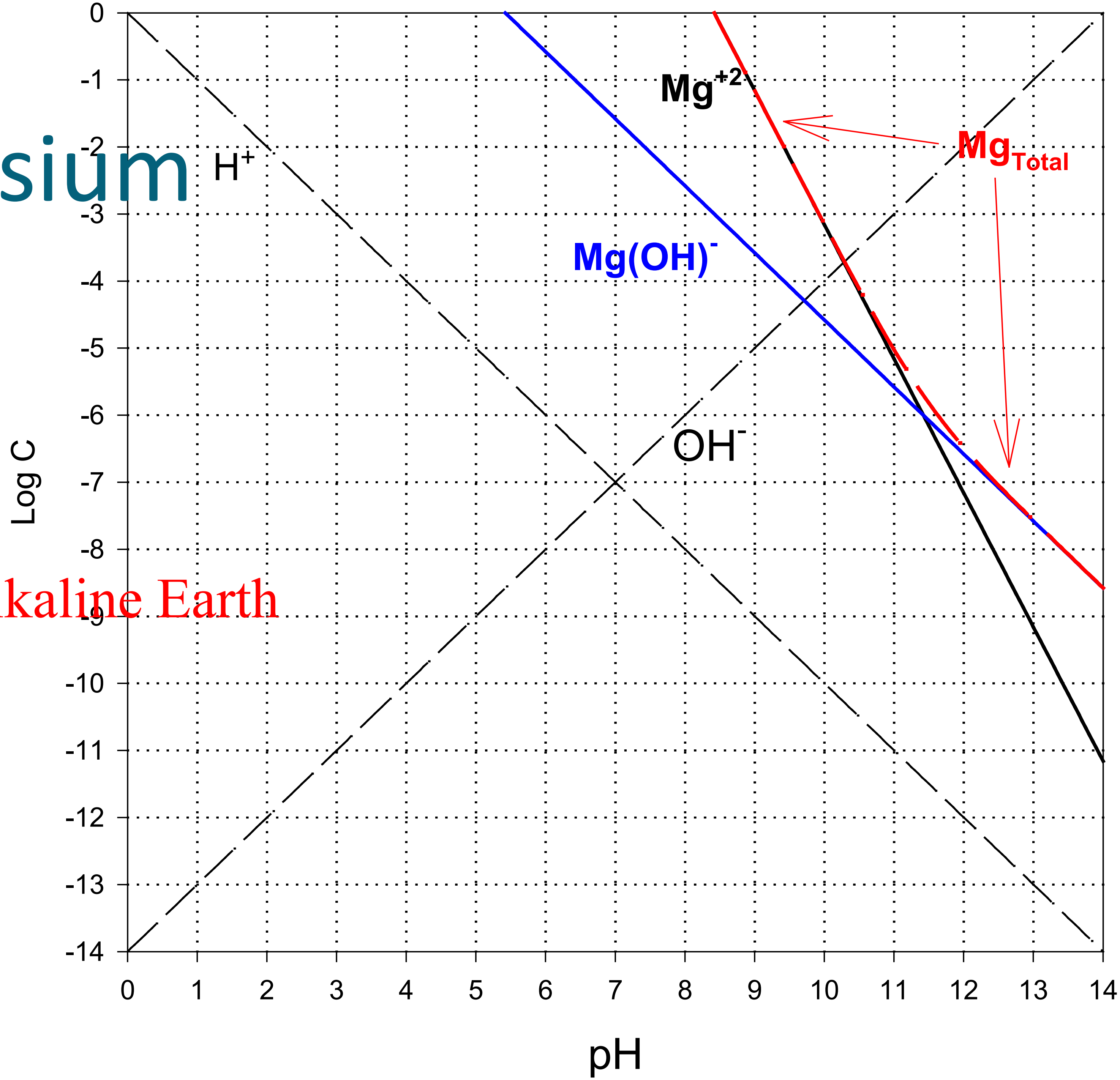
- Log C vs pH relationships
  - Log $[Fe^{+3}] = 3.2 - 3pH$
  - Log $[FeOH^{+2}] = 1.0 - 2pH$
  - Log $[Fe(OH)_2^{+}] = -2.5 - pH$
  - Log $[Fe(OH)_4^{-}] = -18.4 + pH$
  - Log $[Fe_2(OH)_2^{+4}] = 3.45 - 4pH$


0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
Log C
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH
H+
OH-
Fe Total
Fe2(OH)2 +4
Fe+3
FeOH+2
Fe(OH)2 +
Fe(OH)4 -

Ferric Hydroxide IV



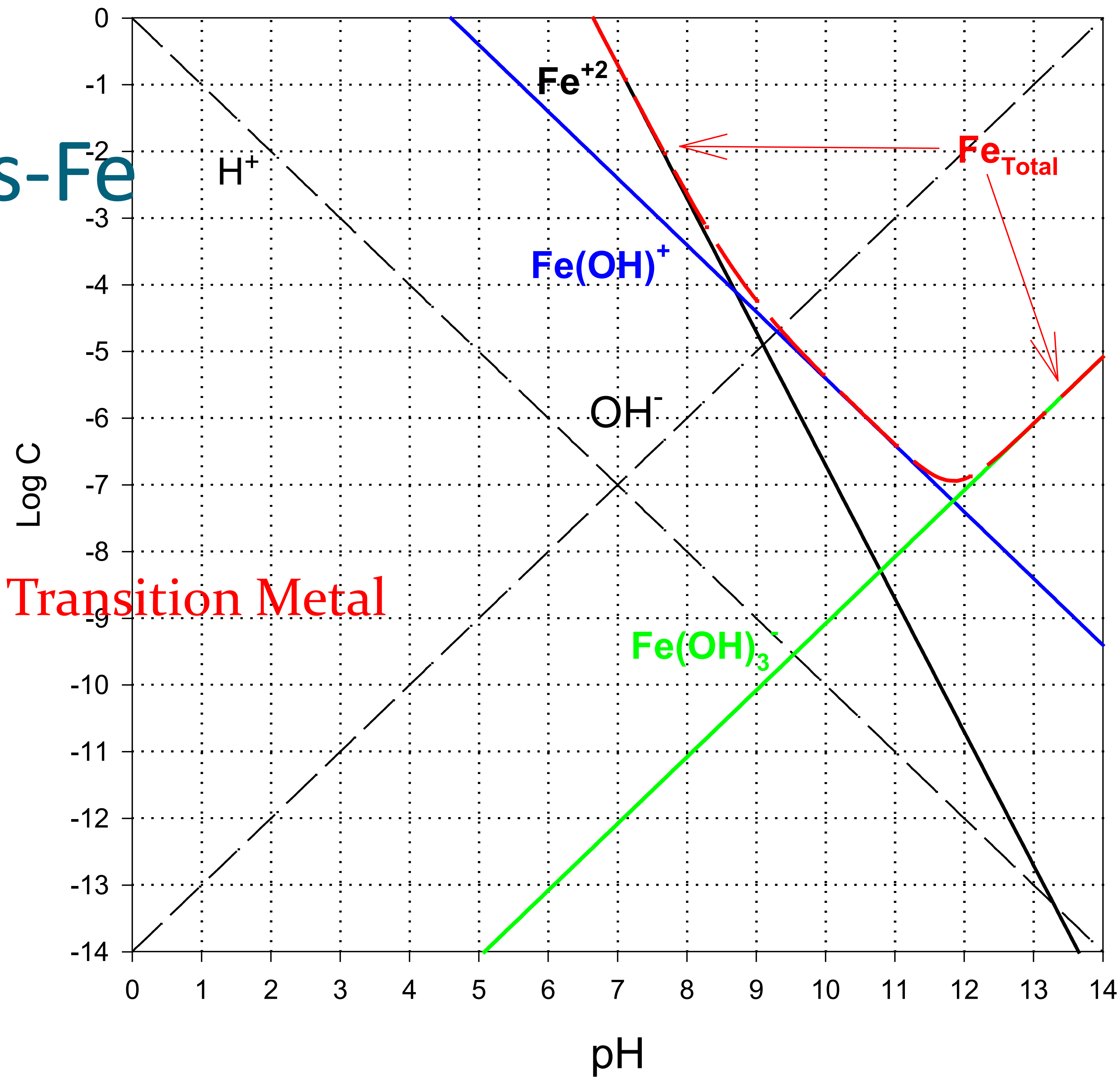
Magnesium



Divalent Alkaline Earth

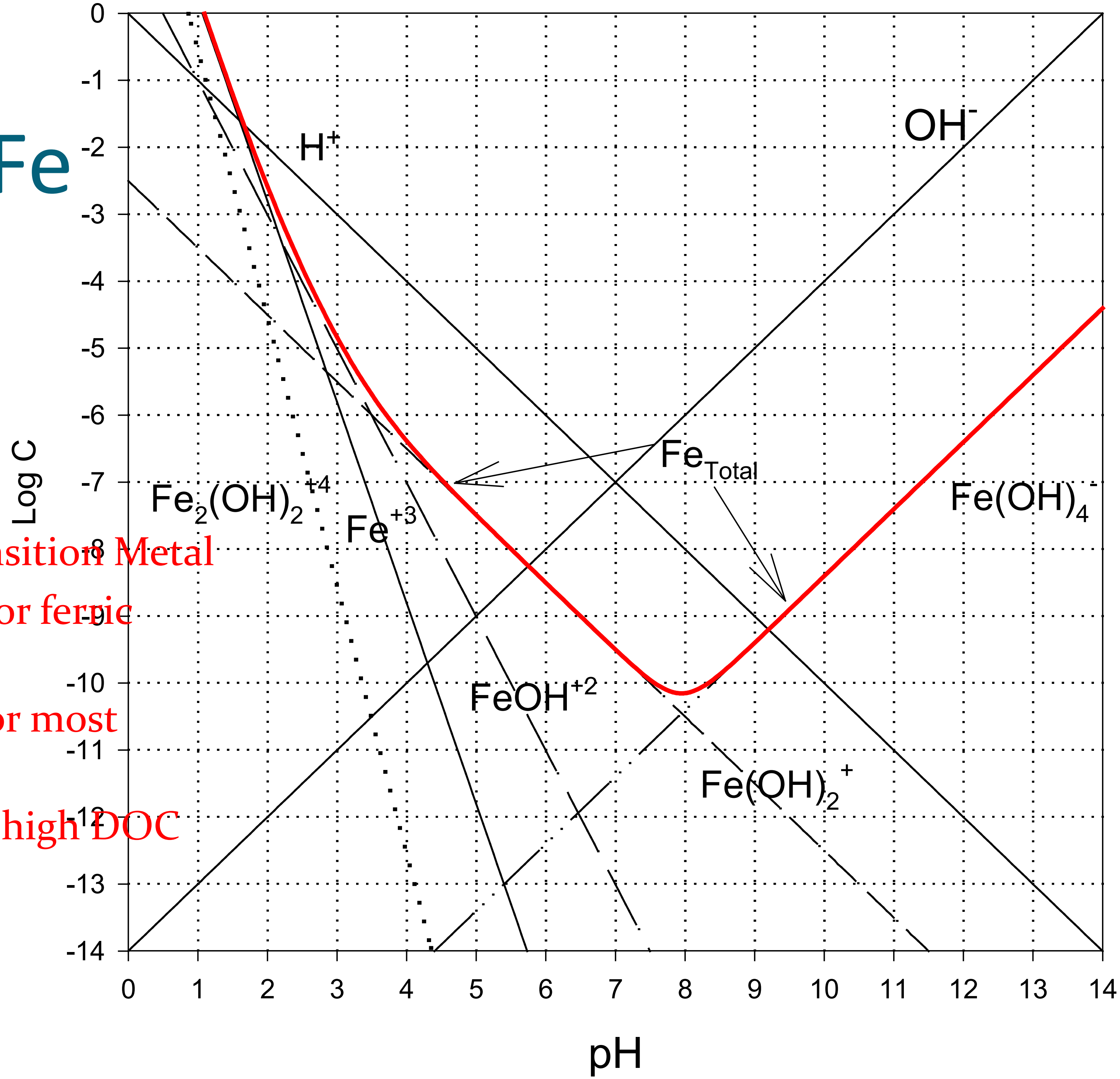
Ferrous-Fe

- Divalent Transition Metal



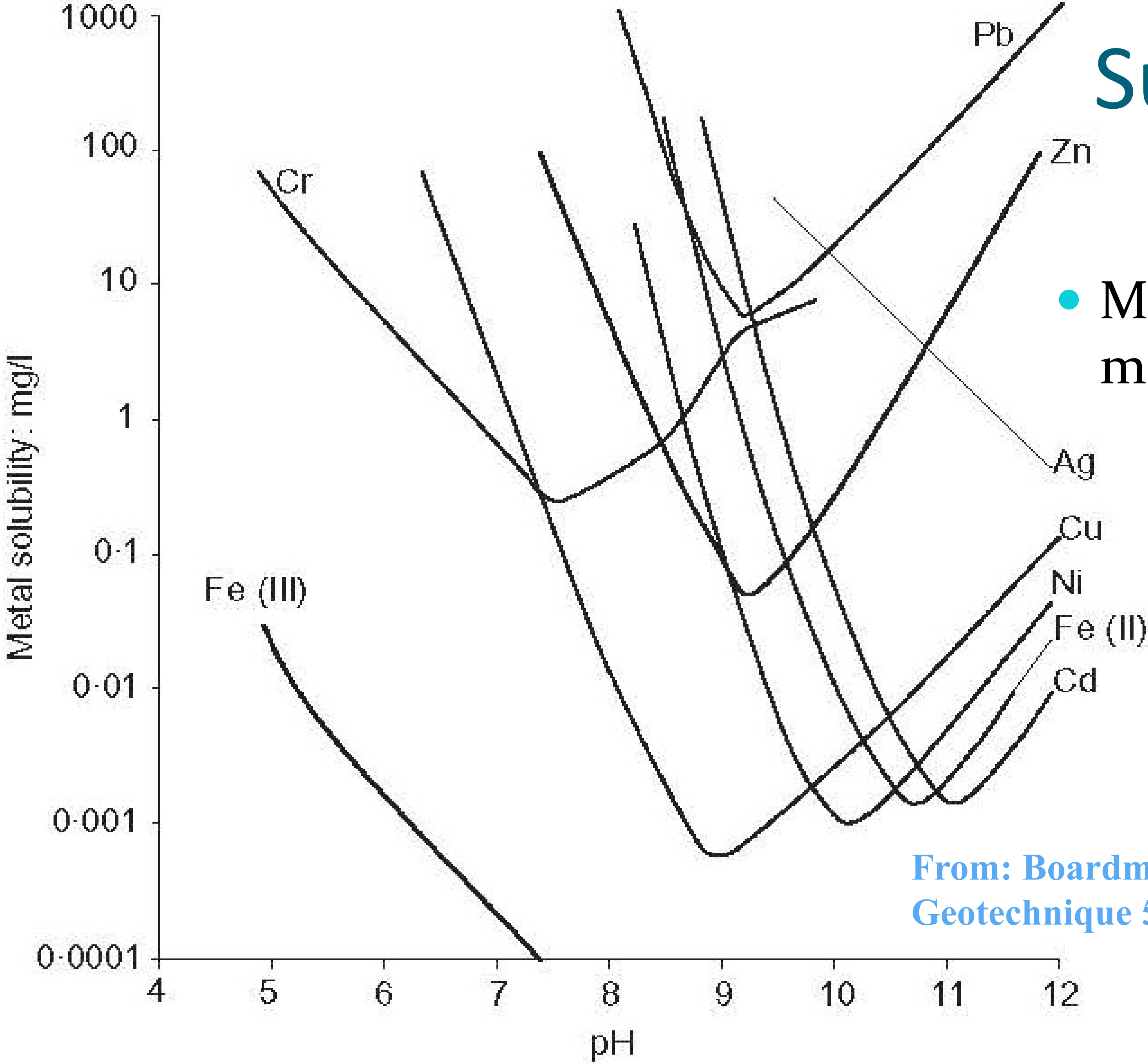
Based on:
Constants from
Snoeyink &
Jenkins, 1980

Ferric-Fe



- Trivalent Transition Metal
- Optimal pH for ferric coagulation
  - 5.0 to 6s for most waters
  - 5.0-5.5 for high DOC waters

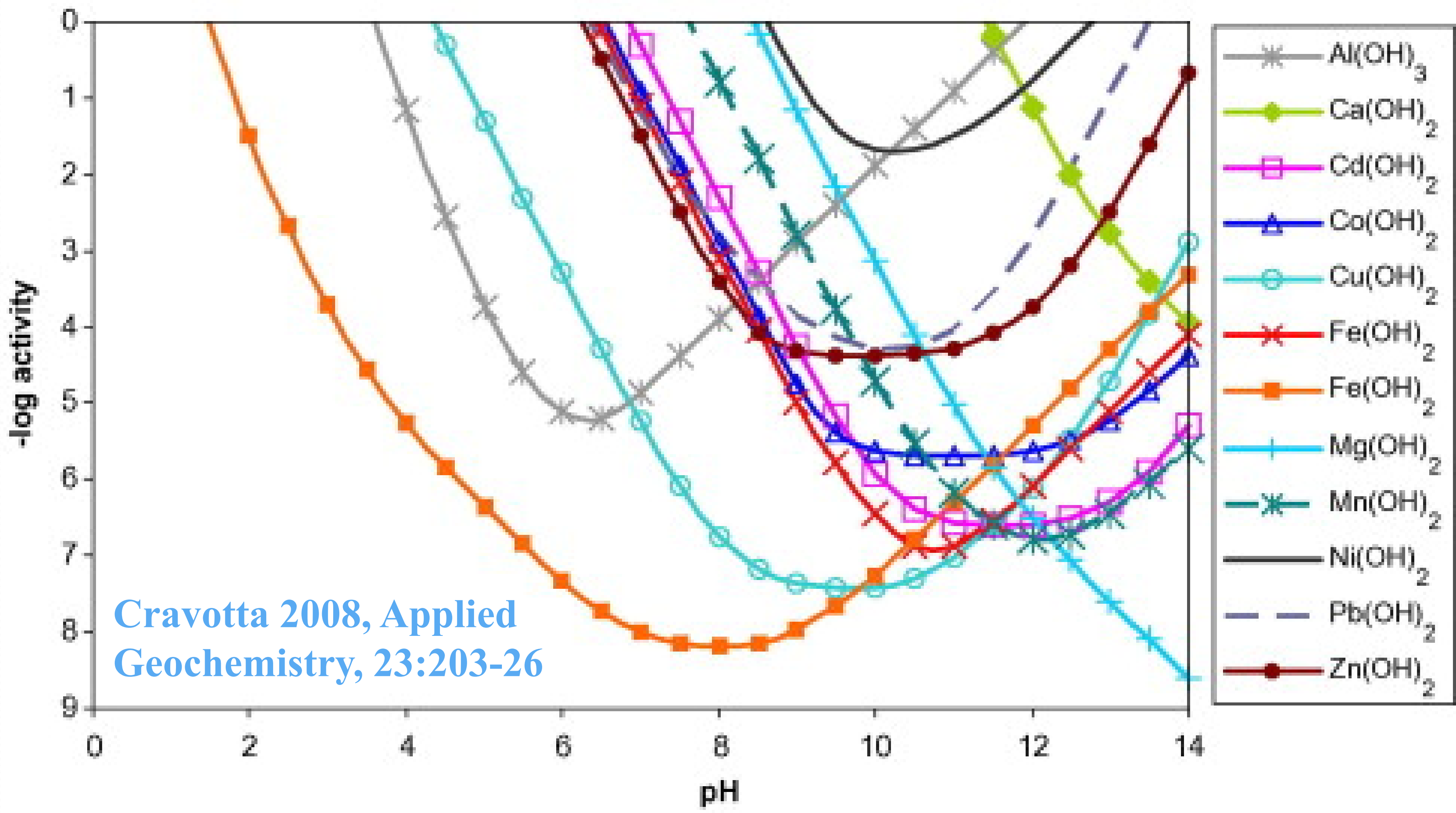
Summary



- Multiple metals

From: Boardman et al., 2004, Geotechnique 54:7:467-486

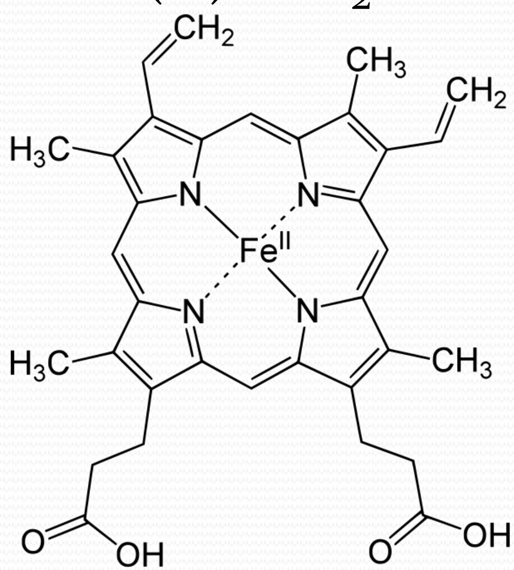
Summary II

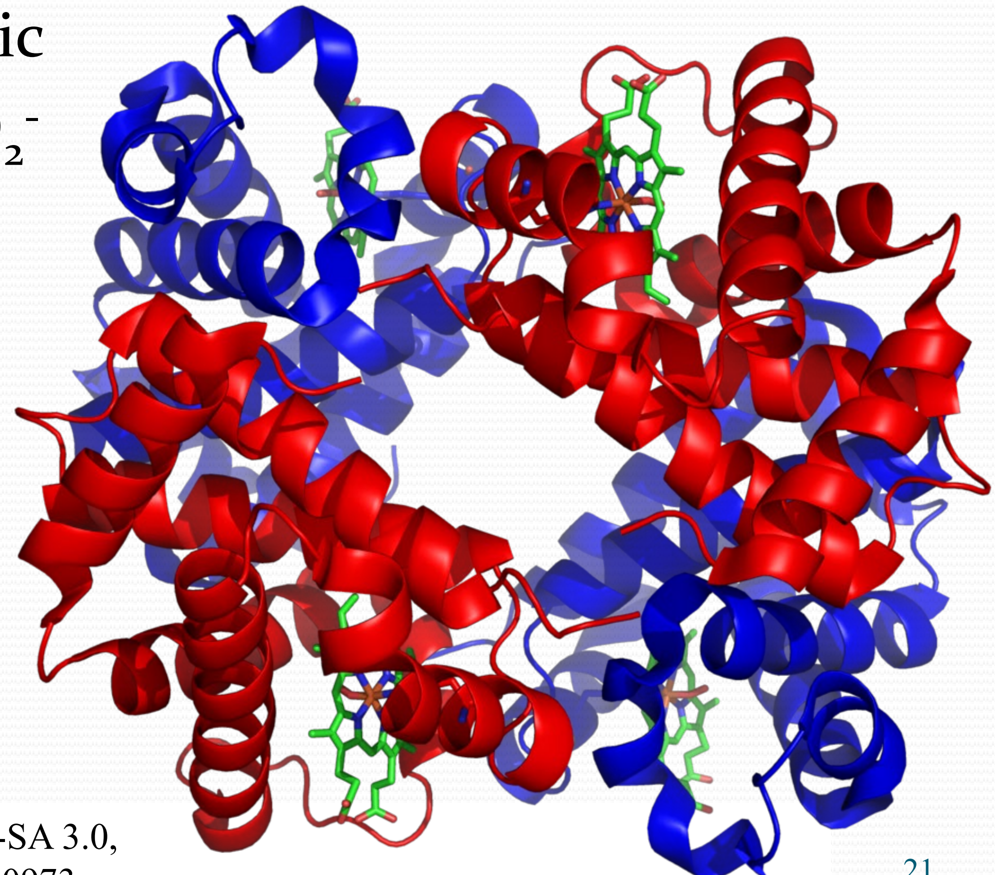


Al(OH)3
Ca(OH)2
Cd(OH)2
Co(OH)2
Cu(OH)2
Fe(OH)2
Fe(OH)2
Mg(OH)2
Mn(OH)2
Ni(OH)2
Pb(OH)2
Zn(OH)2
-log activity
pH
Cravotta 2008, Applied Geochemistry, 23:203-26

Hemoglobin

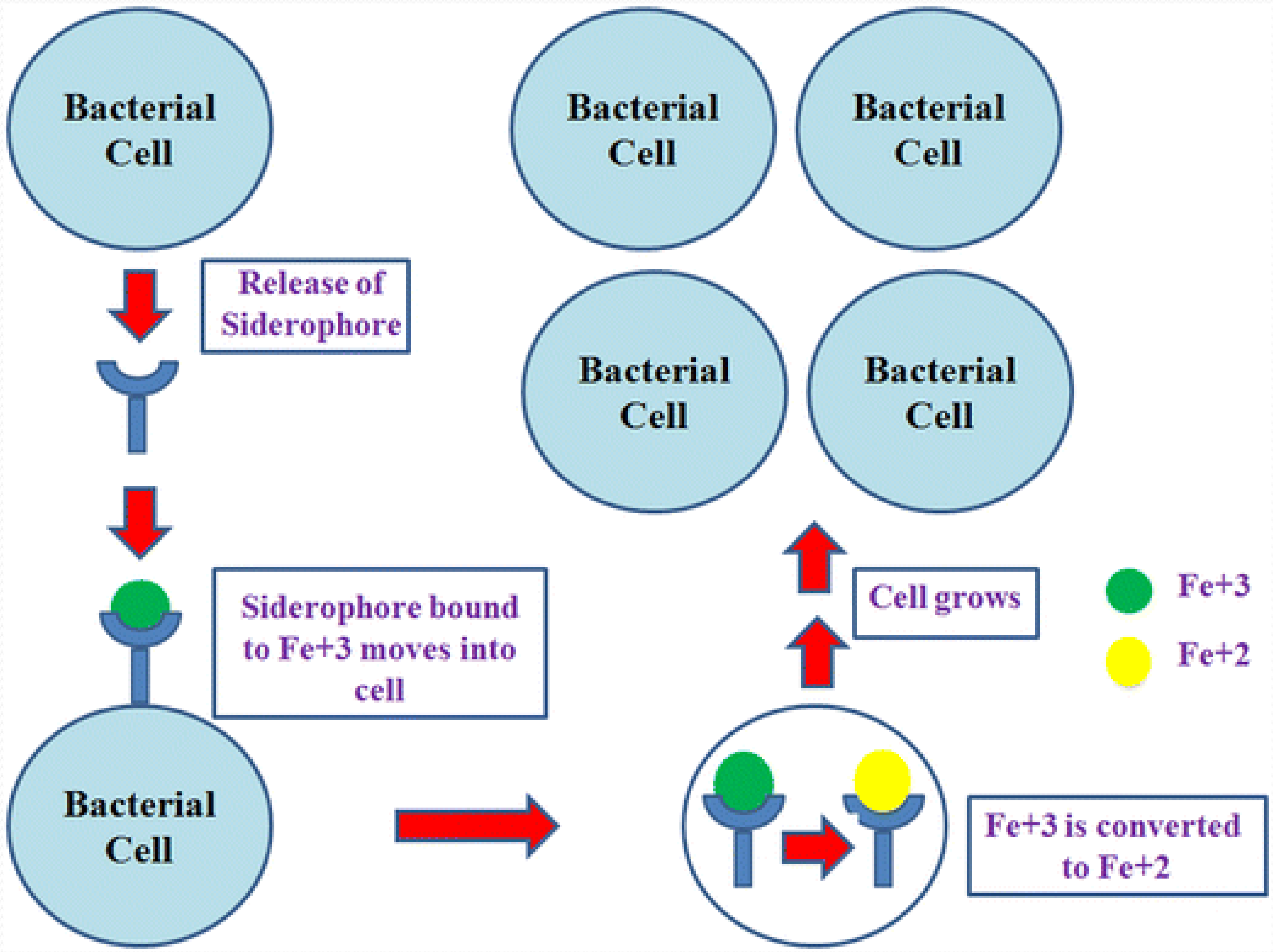
- One essential use of iron
  - Electron transfer in the heme, forming superoxide ion that binds with the ferric
  - $Fe(II) + O_2 \Leftrightarrow Fe(III)\text{-}O_2^-$





Siderophores

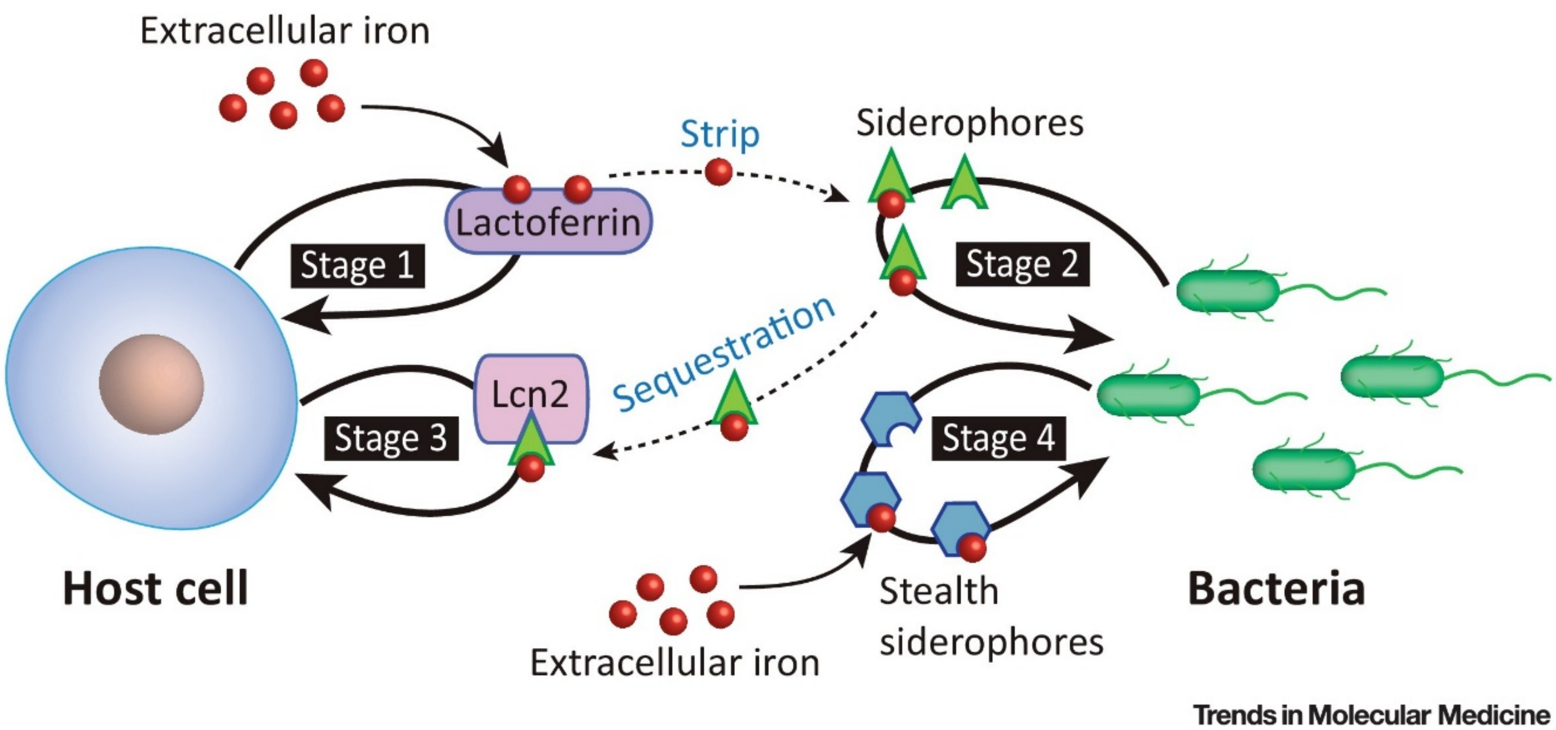
- Mining Iron for Bacteria



Saha et al., 2016

Siderophores

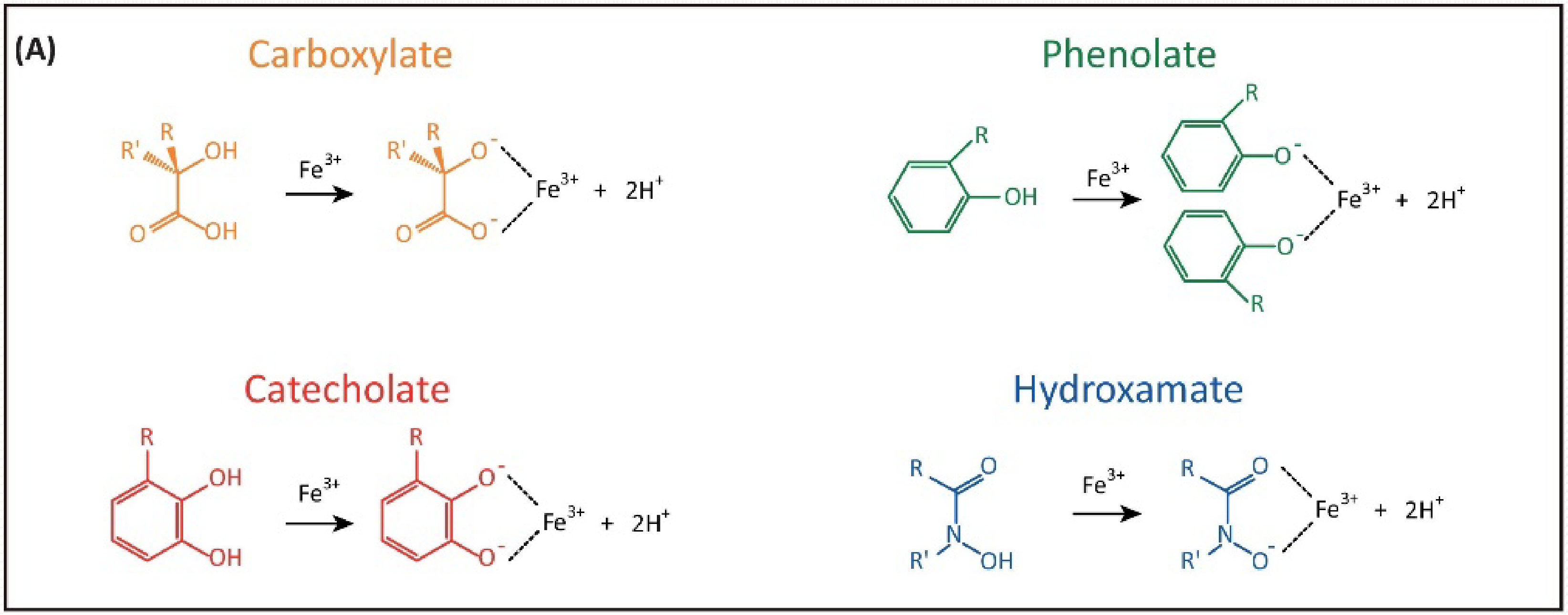
- Fighting for Iron between host cells and bacteria



Wilson et al., 2016

Siderophores

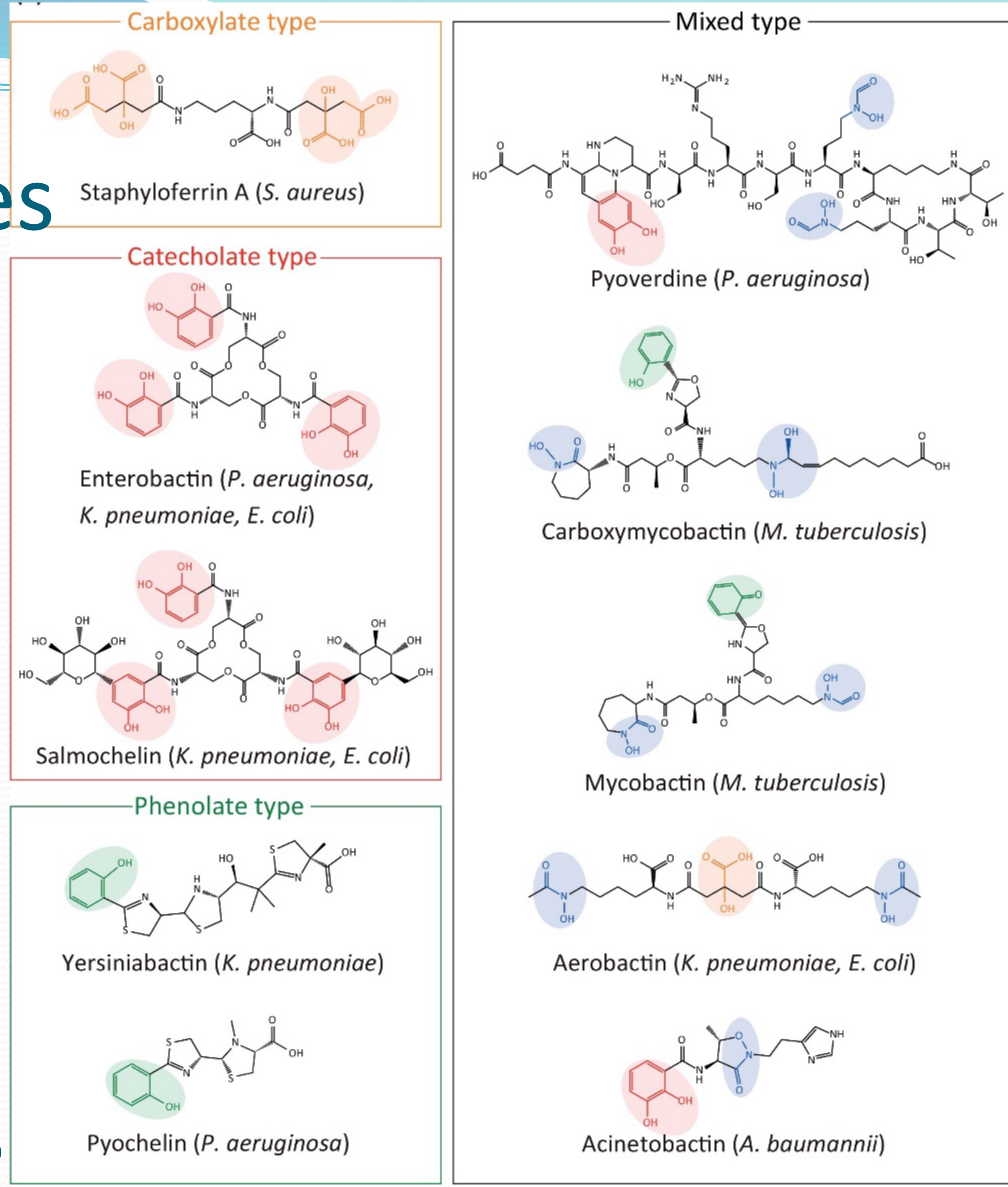
- Ligand Atoms and immediate environment



Wilson et al., 2016

Siderophores

- Full Molecules



Wilson et al., 2016

- To next lecture

Charge Balance & Alk

- Major Cation Charge = Major Anion Charge

$$\underbrace{Na^{+} + K^{+} + 2Ca^{+2} + 2Mg^{+2}}_{C_B} + H^{+} = \underbrace{Cl^{-} + NO_3^{-} + 2\,SO_4^{-2}}_{C_A} + HCO_3^{-} + 2\,CO_3^{-2} + OH^{-}$$

- And simplifying:

$$C_B - C_A = \underbrace{HCO_3^{-} + 2\,CO_3^{-2} + OH^{-} - H^{+}}_{\equiv \text{Alkalinity}}$$

- Now combining with equilibria

$$C_B - C_A \equiv Alk \equiv (\alpha_1 + 2\alpha_2)C_T + K_w/[H^{+}] - H^{+}$$

$$Alk_{blend} = \frac{\sum Q_i Alk_i}{\sum Q_i}$$

Closed & Open

- Closed system
  - Most common, especially in treatment systems

C_T is fixed (from mass balance)

- Open System
  - Requires full equilibrium with bulk atmosphere or large volume of headspace

H_2CO_3 is fixed (from fixed pCO2)

Alkalinity is fixed or "conservative" (from mass balance)

Calculate pH (and other carbonate species)