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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

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## Topics

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

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## 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

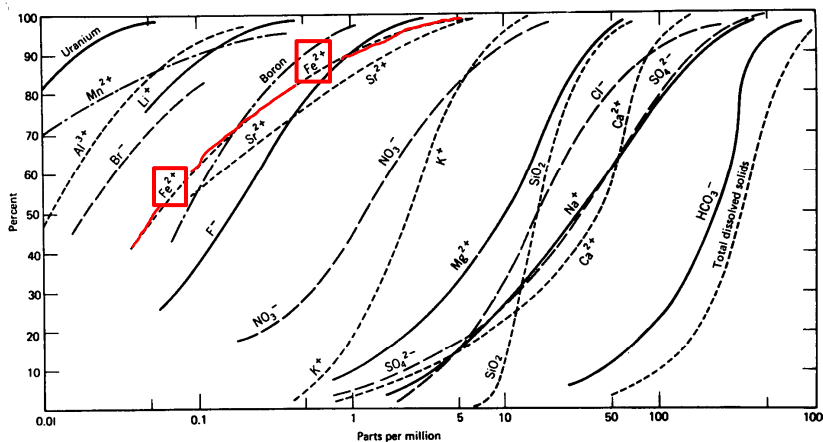
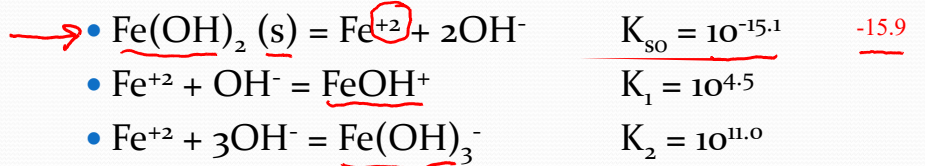


Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)

D:

## Ferrous Hydroxide I

- Thermodynamics



- Mass Balance

$\bullet \underline{\text{Fe}_T = [\text{Fe}^{+2}] + [\text{FeOH}^+] + [\text{Fe(OH)}_3^-]}$

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

## Ferrous Hydroxide II

- Log C vs pH relationships

$\bullet \text{Log } [\text{Fe}^{+2}] = 12.9 - 2\text{pH}$   
 $\bullet \text{Log } [\text{FeOH}^+] = 3.4 - \text{pH}$   
 $\bullet \text{Log } [\text{Fe(OH)}_3^-] = -18 + \text{pH}$

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

# Ferrous Hydroxide III

- Tableaux

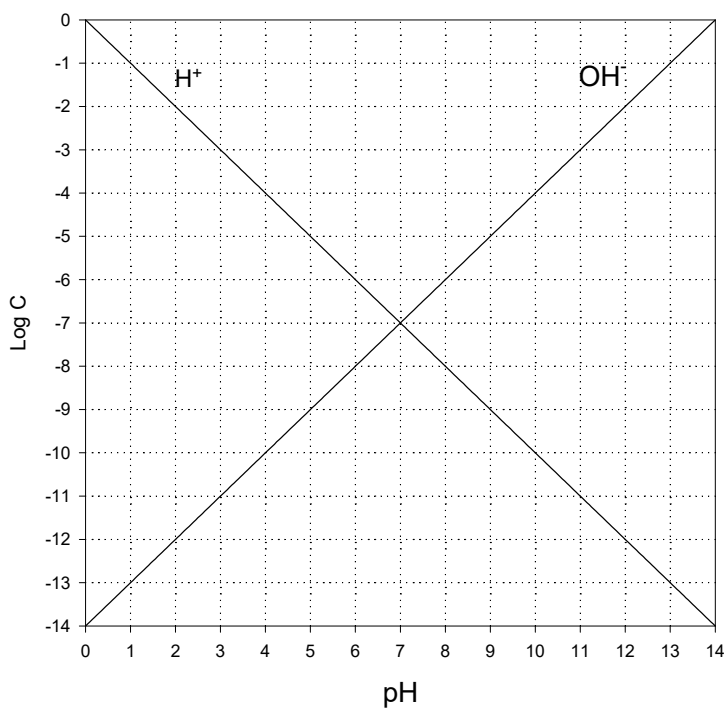
Species	Components		Log K
	Fe(OH) <sub>2</sub> (s)	H <sup>+</sup>	
Fe <sup>2+</sup>	1	2	13.3
FeOH <sup>+</sup>	1	1	4.6
Fe(OH) <sub>3</sub> <sup>-</sup>	1	-1	-19.08
H <sup>+</sup>	0	1	0
OH <sup>-</sup>	0	-1	-14
Log(conc.)	0		

Log[ Fe <sup>2+</sup> ]	=	13.3	-2 pH
Log[ FeOH <sup>+</sup> ]	=	4.6	-1 pH
Log[ Fe(OH) <sub>3</sub> <sup>-</sup> ]	=	-19.08	1 pH

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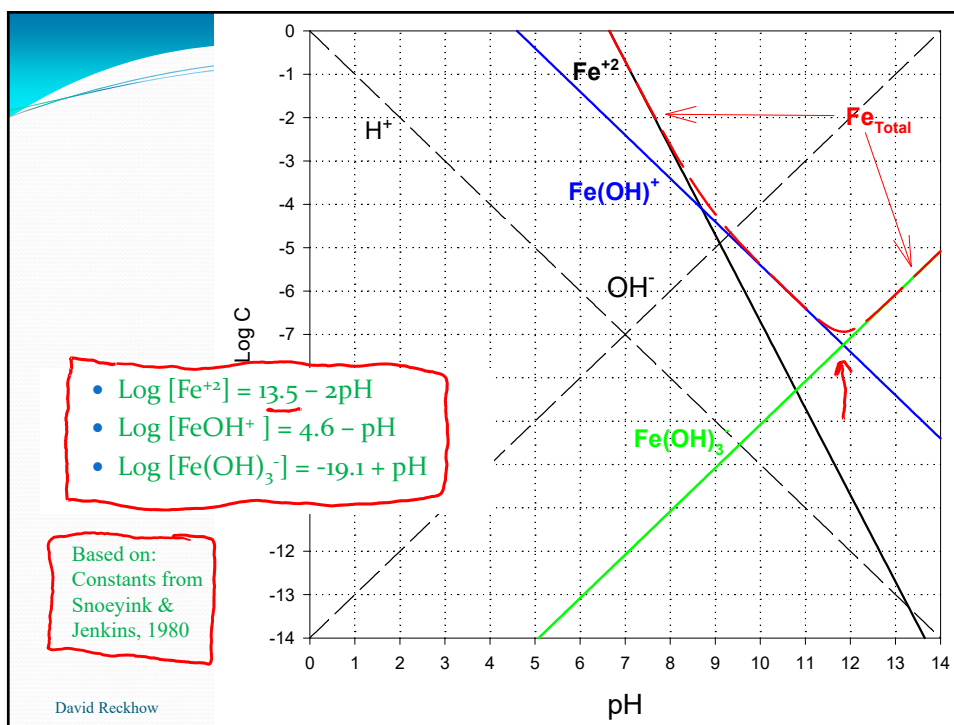
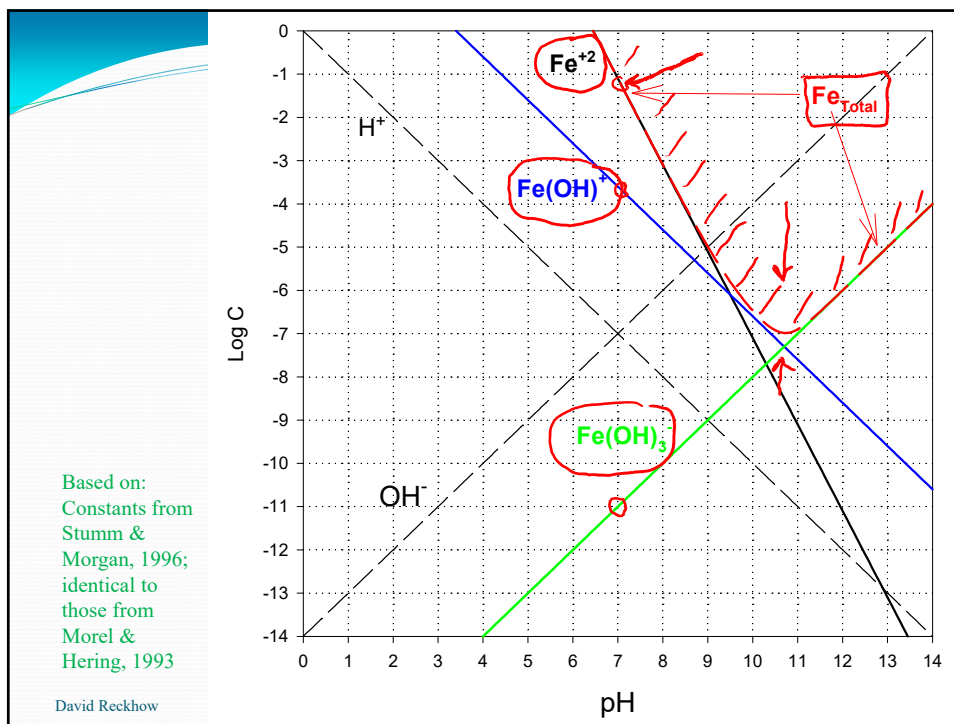
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## Trivalent Metal Hydrolysis

- Case for iron

$$\begin{array}{ccccc}
 & + \text{H}^+ & & + 2\text{H}^+ & \\
 \text{Fe}(\text{H}_2\text{O})_6^{+3} & \longleftrightarrow & \text{FeOH}(\text{H}_2\text{O})_5^{+2} & \longleftrightarrow & \text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4^+ \\
 & & & & \\
 & + 3\text{H}^+ & & + 4\text{H}^+ & \\
 & \text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3 & \longleftrightarrow & \text{Fe}(\text{OH})_4(\text{H}_2\text{O})_2^- & \\
 & \downarrow & & & \\
 & \text{Fe}(\text{OH})_3(\text{s}) & & & 
 \end{array}$$

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## Ferric Hydroxide I

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

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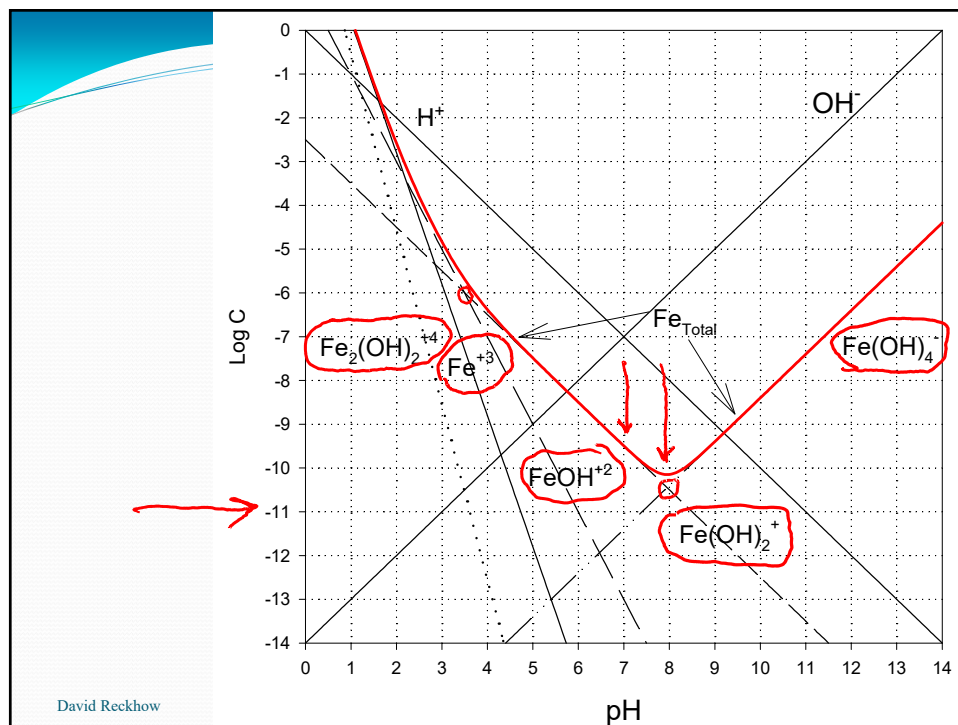
## Ferric Hydroxide II

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

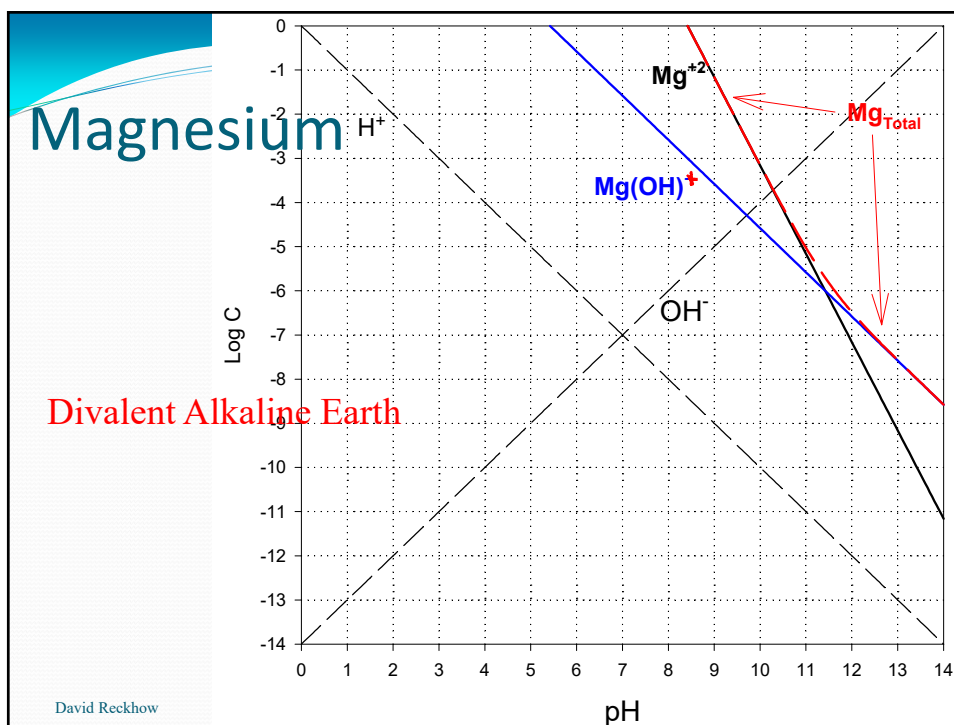
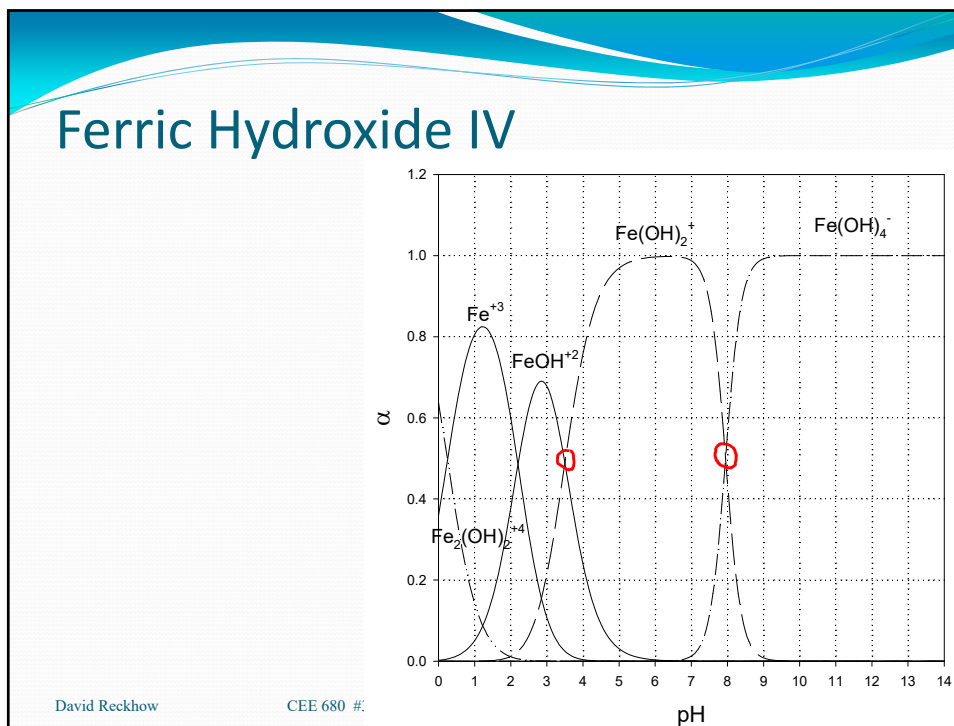
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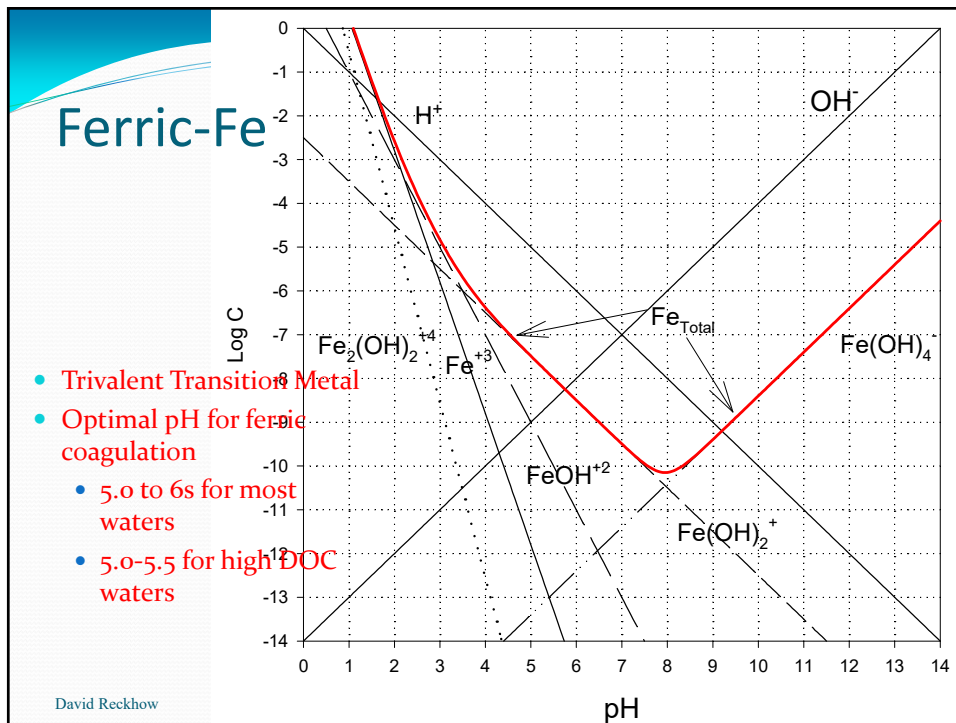
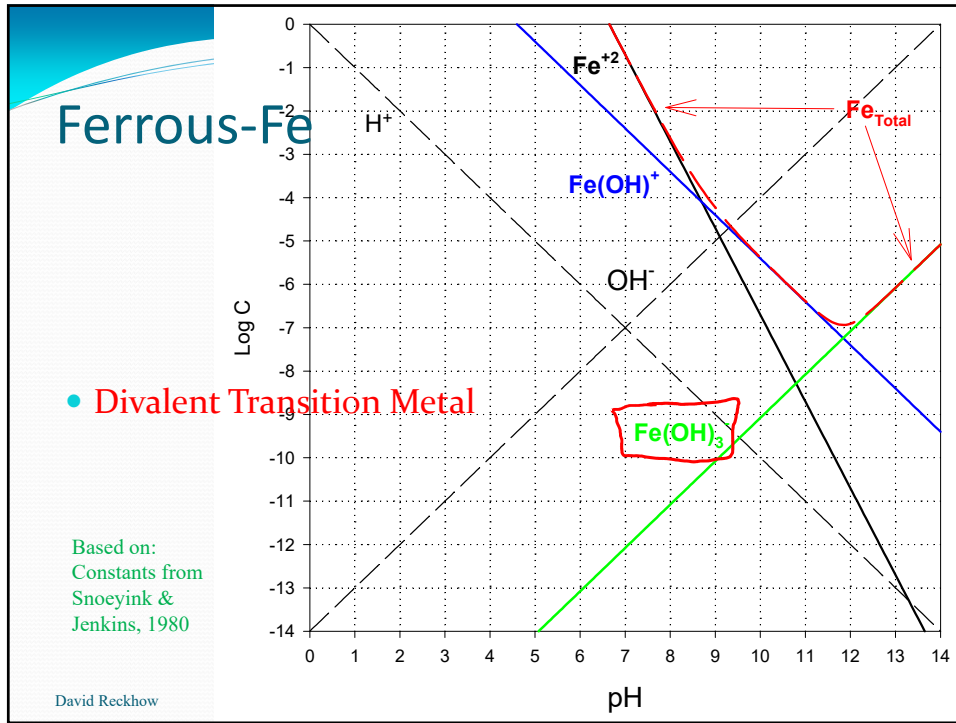
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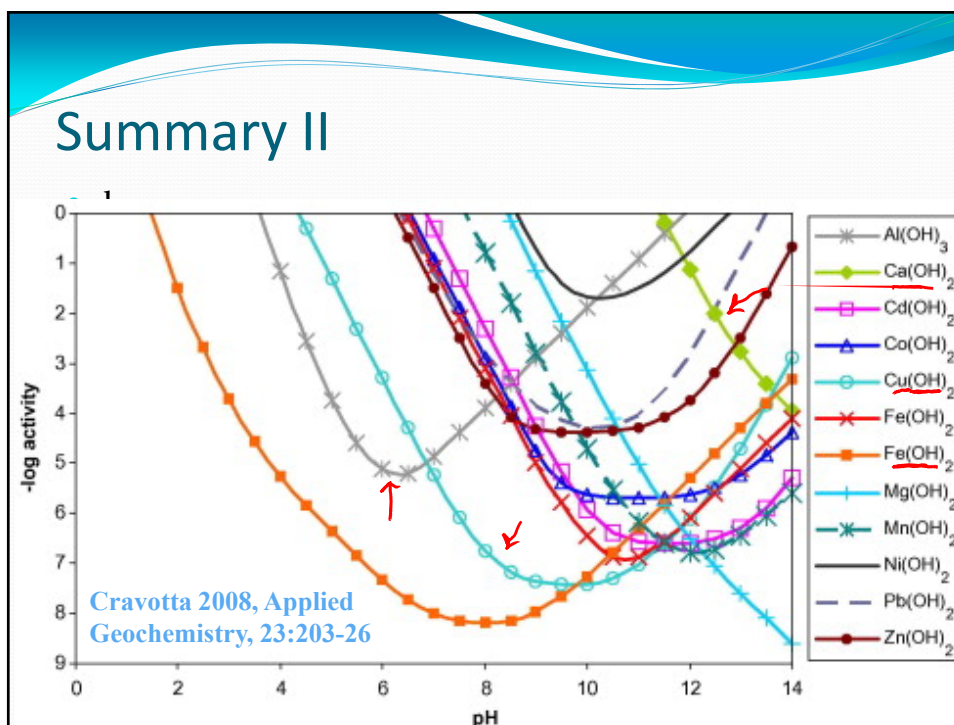
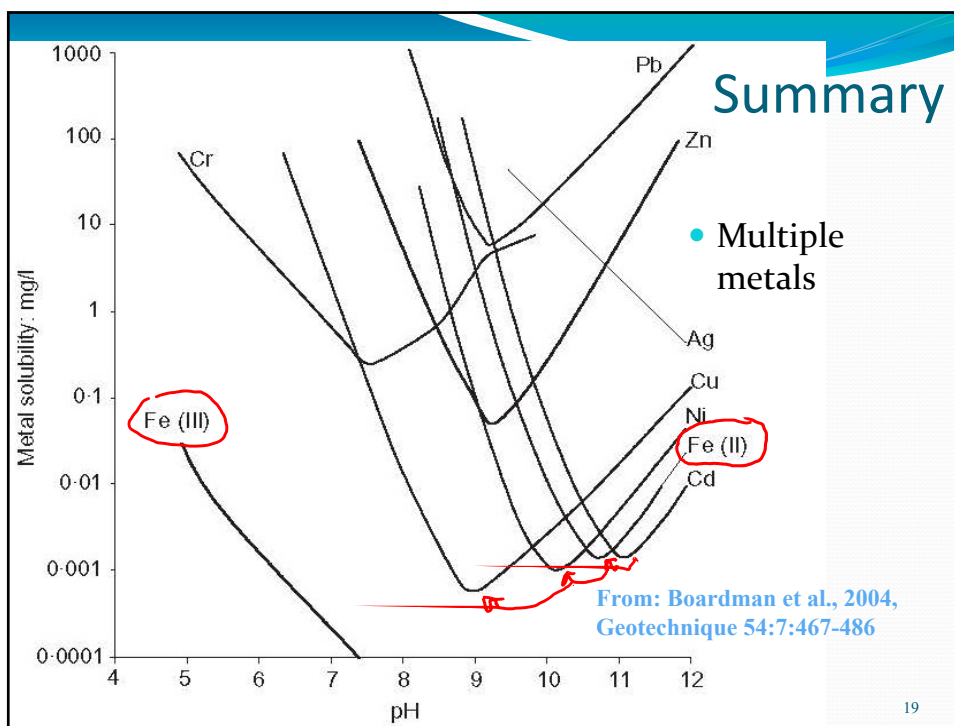


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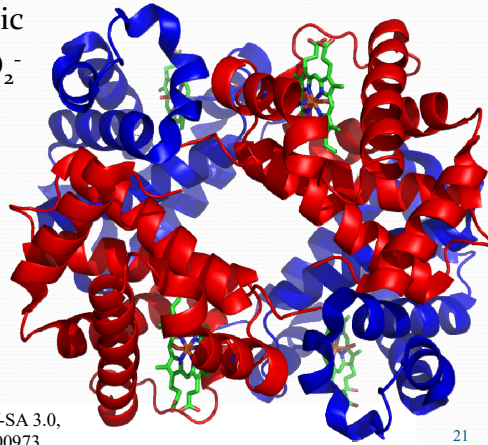
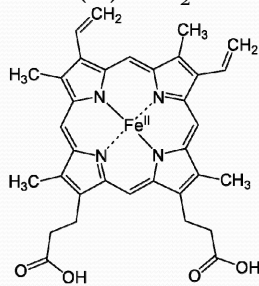






# Hemoglobin

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

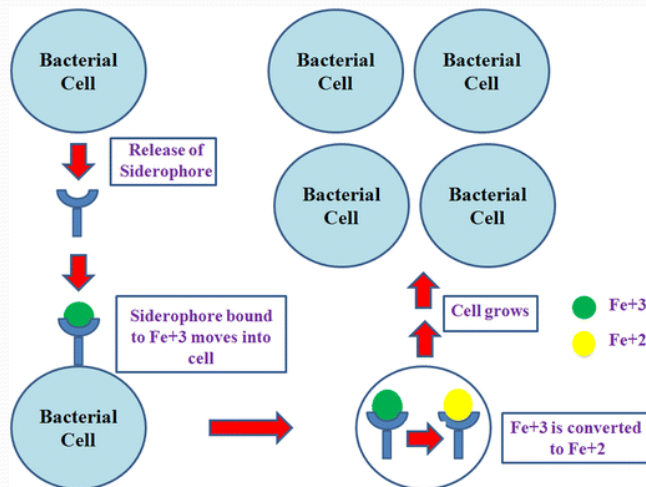


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# Siderophores

- Mining Iron for Bacteria



Saha et al., 2016

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## Siderophores

- Fighting for Iron between host cells and bacteria

The diagram shows a cycle of iron acquisition and sequestration. In Stage 1, extracellular iron (red dots) binds to Lactoferrin on the host cell. In Stage 2, bacteria release siderophores (green triangles) that strip iron from Lactoferrin. In Stage 3, Lcn2 on the host cell sequesters iron. In Stage 4, bacteria release stealth siderophores (blue pentagons) that sequester iron from Lcn2.

Wilson et al., 2016

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## Siderophores

- Ligand Atoms and immediate environment

(A) Chemical reactions showing the coordination of Fe<sup>3+</sup> with various ligands:

- Carboxylate:** R1C(OH)(R2)C(=O)OH + Fe3+ -> R1C(OH)(R2)C(=O)[O-]O-Fe3+ + 2H+
- Phenolate:** c1ccc(O)c(R)c1 + Fe3+ -> c1ccc(O[O-])c(R)c1 + Fe3+ + 2H+
- Catecholate:** c1ccc(O)c(O)c(R)c1 + Fe3+ -> c1ccc(O[O-])c(O[O-])c(R)c1 + Fe3+ + 2H+
- Hydroxamate:** R2C(=O)N(OH)R1 + Fe3+ -> R2C(=O)N(O[O-])R1 + Fe3+ + 2H+

Wilson et al., 2016

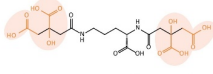
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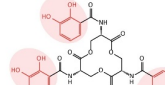
# Siderophores

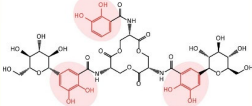
- Full Molecules

**Carboxylate type**

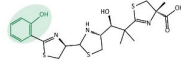
  
Staphyloferrin A (*S. aureus*)

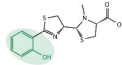
**Catecholate type**

  
Enterobactin (*P. aeruginosa*,  
*K. pneumoniae*, *E. coli*)

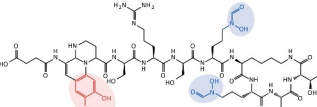
  
Salmochelin (*K. pneumoniae*, *E. coli*)

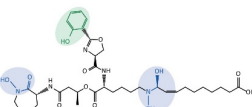
**Phenolate type**

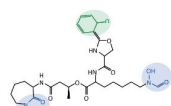
  
Yersiniabactin (*K. pneumoniae*)

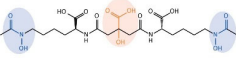
  
Pyochelin (*P. aeruginosa*)

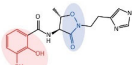
**Mixed type**

  
Pyoverdine (*P. aeruginosa*)

  
Carboxymycobactin (*M. tuberculosis*)

  
Mycobactin (*M. tuberculosis*)

  
Aerobactin (*K. pneumoniae*, *E. coli*)

  
Acinetobactin (*A. baumannii*)

**Wilson et al., 2016**

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## • To next lecture

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## Charge Balance & Alk

- Major Cation Charge = Major Anion Charge

$$C_B \left\{ \begin{array}{l} \text{Na}^+ + \text{K}^+ + 2\text{Ca}^{+2} + 2\text{Mg}^{+2} \\ + \text{H}^+ \end{array} \right. = \left. \begin{array}{l} \text{Cl}^- + \text{NO}_3^- + 2 \text{SO}_4^{-2} \\ + \text{HCO}_3^- + 2 \text{CO}_3^{-2} + \text{OH}^- \end{array} \right. C_A$$

- And simplifying:

$$C_B - C_A = \underbrace{\text{HCO}_3^- + 2 \text{CO}_3^{-2} + \text{OH}^- - \text{H}^+}_{\equiv \text{Alkalinity}}$$

- Now combining with equilibria

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

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## Closed & Open

$$\text{Alk}_{blend} = \frac{\sum Q_i \text{Alk}_i}{\sum Q_i}$$

- Closed system**
  - Most common, especially in treatment systems

↓

$C_T$  is fixed (from mass balance)

↓

Alkalinity is fixed or “conservative” (from mass balance)

↓

Calculate pH (and other carbonate species)

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

↓

$\text{H}_2\text{CO}_3$  is fixed (from fixed  $p\text{CO}_2$ )

↓

Alkalinity is fixed or “conservative” (from mass balance)

↓

Calculate pH (and other carbonate species)

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