

Updated: 15 April 2020 Print version

# CEE 680: Water Chemistry

Lecture #44  
Precipitation and Dissolution: Application to  
 Mineral Formation  
 (Stumm & Morgan, Chapt.7)  
 Benjamin; Chapter 8.7-8.15

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## Mg phases

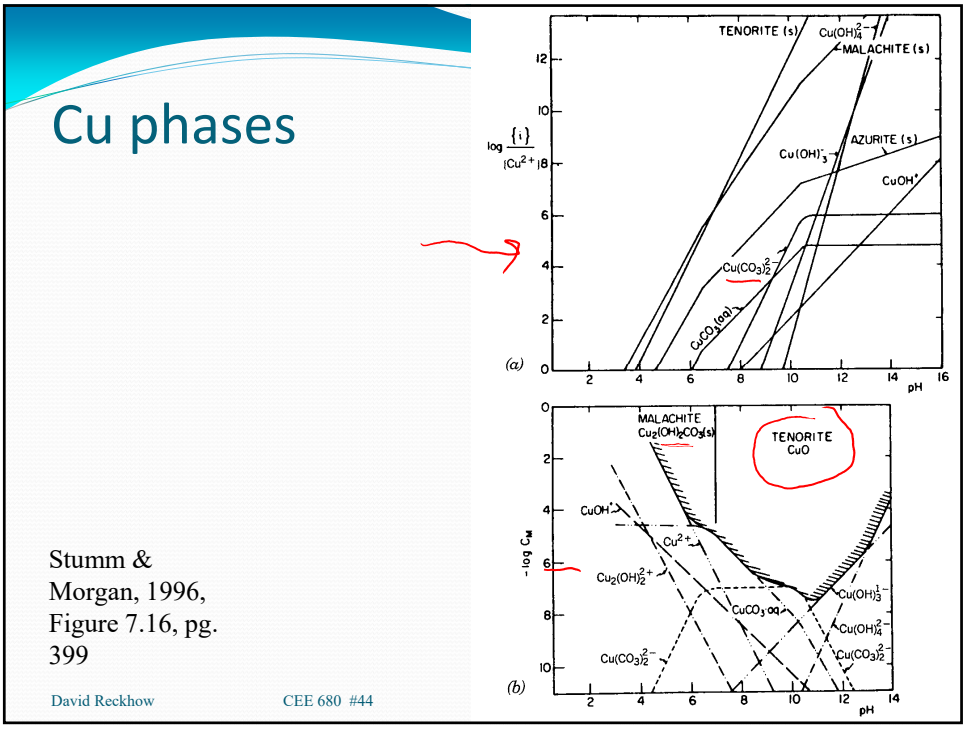
Stumm & Morgan, 1996, Figure 7.15, pg. 396

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(a)  $\log \{A_i\} \text{ (Mg}^{2+}\text{)}$  vs pH. Lines for Br, HM, M, N.

(b)  $-\log \{Mg^{2+}\} \text{ (Molar)}$  vs pH. Regions for MAGNESITE and BRUCITE.

(c)  $P_{CO_2}$  vs pH. Regions for  $Mg^{2+}$ , MAGNESITE, and BRUCITE.



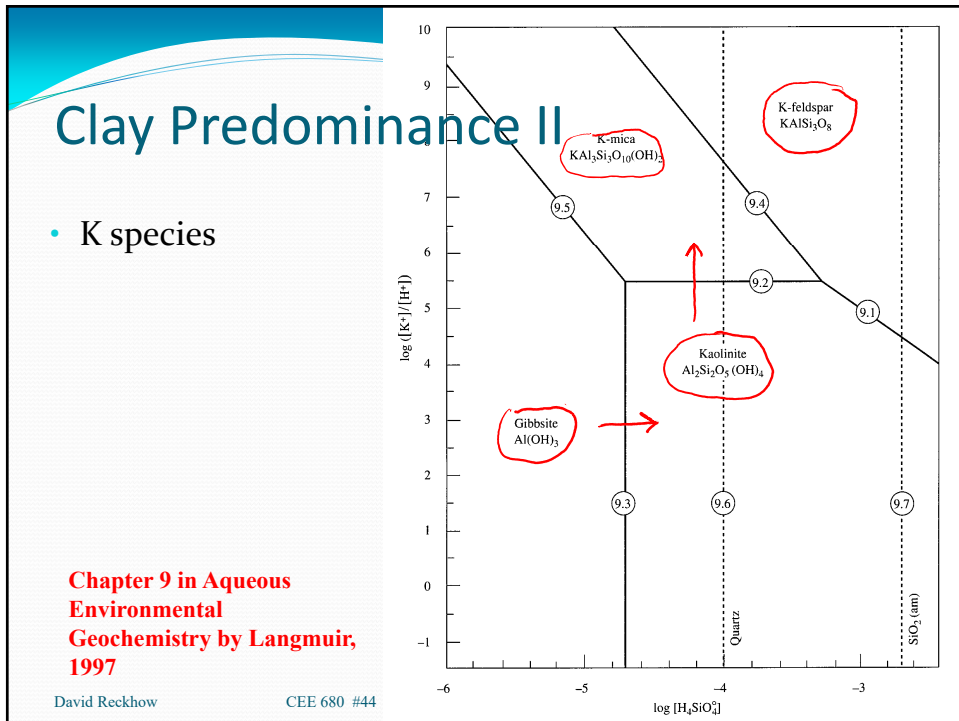
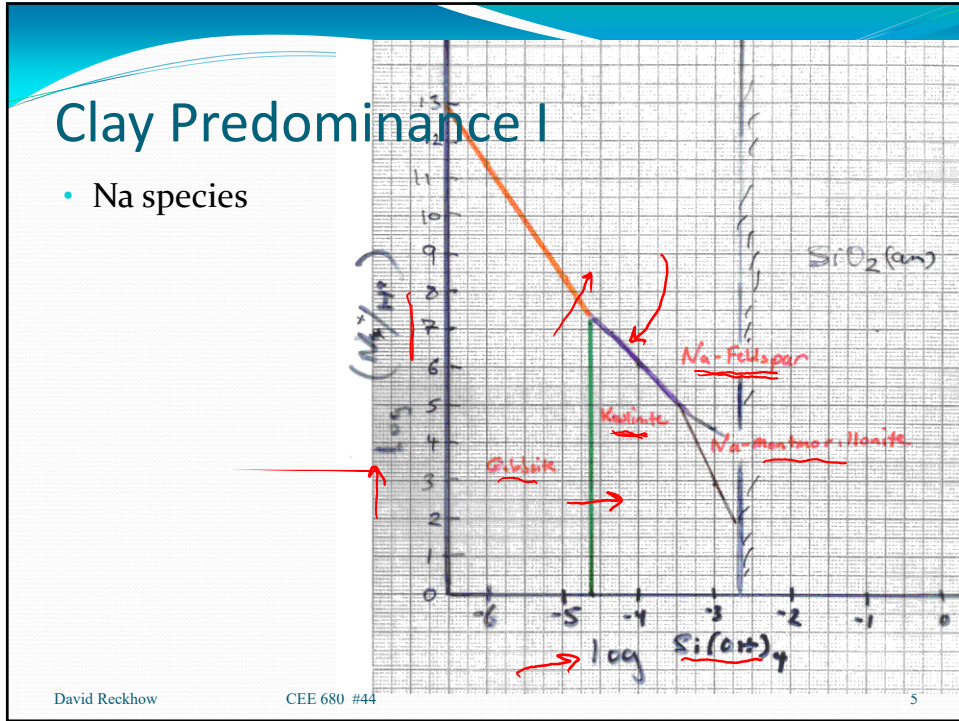
### Clay equilibria

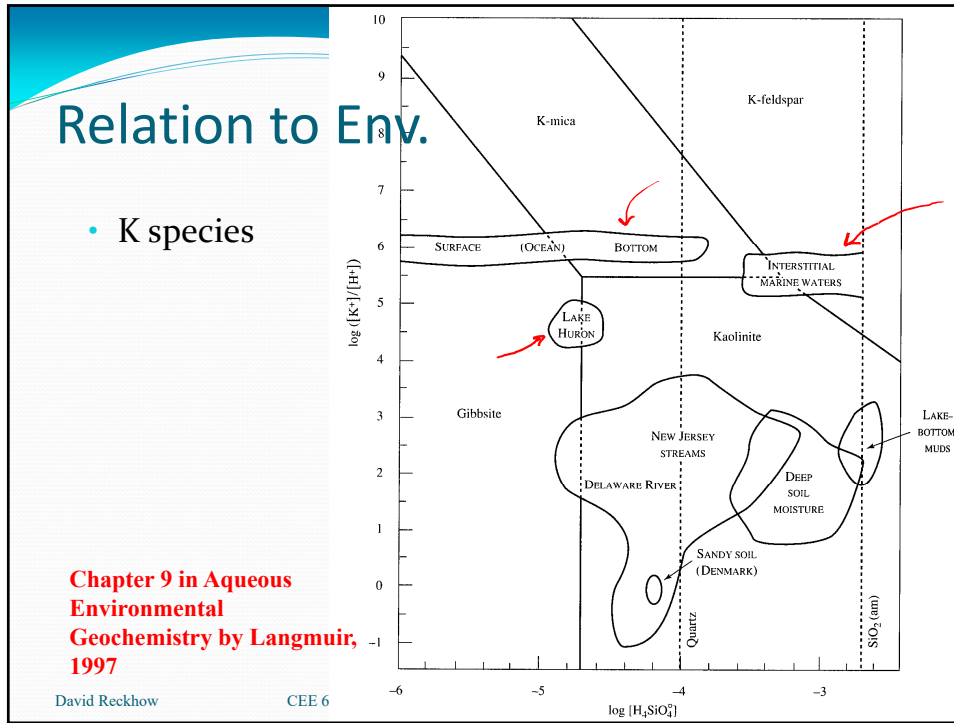
• Stumm & Morgan (2<sup>nd</sup> ed)  
• Pg 546

**TABLE 9.4 EQUILIBRIUM CONSTANTS USED TO ESTABLISH STABILITY RELATIONS AMONG MINERALS<sup>a</sup>**

	Log K at 25°C, 1 atm
→ (1) Na feldspar(s) + H <sup>+</sup> + 4½H <sub>2</sub> O = ½ kaolinite(s) + 2H <sub>4</sub> SiO <sub>4</sub> + Na <sup>+</sup>	-1.9
(2) 3 Na montmorillonite(s) + H <sup>+</sup> + 11½H <sub>2</sub> O = 3½ kaolinite(s) + 4H <sub>4</sub> SiO <sub>4</sub> + Na <sup>+</sup>	-9.1
(3) Ca feldspar(s) + 2H <sup>+</sup> + H <sub>2</sub> O = kaolinite(s) + Ca <sup>2+</sup>	+14.4
(4) 3 Ca montmorillonite(s) + 2H <sup>+</sup> + 23H <sub>2</sub> O = 7 kaolinite(s) + 8H <sub>4</sub> SiO <sub>4</sub> + Ca <sup>2+</sup>	-15.4
(5) Kaolinite(s) + 5H <sub>2</sub> O = 2 gibbsite(s) + 2H <sub>4</sub> SiO <sub>4</sub>	-9.4 <sup>b</sup>
(6) SiO <sub>2</sub> (amorph) + 2H <sub>2</sub> O = H <sub>4</sub> SiO <sub>4</sub>	-2.7
(7) CaCO <sub>3</sub> (s) (calcite) = Ca <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup>	-8.3
(8) HCO <sub>3</sub> <sup>-</sup> = H <sup>+</sup> + CO <sub>3</sub> <sup>2-</sup>	-10.3
(9) CO <sub>2</sub> (g) + H <sub>2</sub> O = H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>	-7.8
(10) CO <sub>2</sub> (g) + H <sub>2</sub> O = H <sub>2</sub> CO <sub>3</sub> <sup>*</sup>	-1.5

<sup>a</sup> Ca feldspar (Anorthite) = CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>; Na feldspar (Albite) = NaAlSi<sub>3</sub>O<sub>8</sub>;  
 Na montmorillonite = Na<sub>0.33</sub>Al<sub>2.33</sub>Si<sub>3.67</sub>O<sub>10</sub>(OH)<sub>2</sub>; Ca montmorillonite = Ca<sub>0.33</sub>Al<sub>4.67</sub>Si<sub>7.33</sub>O<sub>20</sub>(OH)<sub>4</sub>;  
 Kaolinite = Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>; Gibbsite = Al<sub>2</sub>O<sub>3</sub> · 3H<sub>2</sub>O; H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> = CO<sub>2</sub>(aq) + H<sub>2</sub>CO<sub>3</sub>.  
<sup>b</sup> Cf. R. M. Garrels, *Amer. Mineralogist*, **42**, 789 (1957).





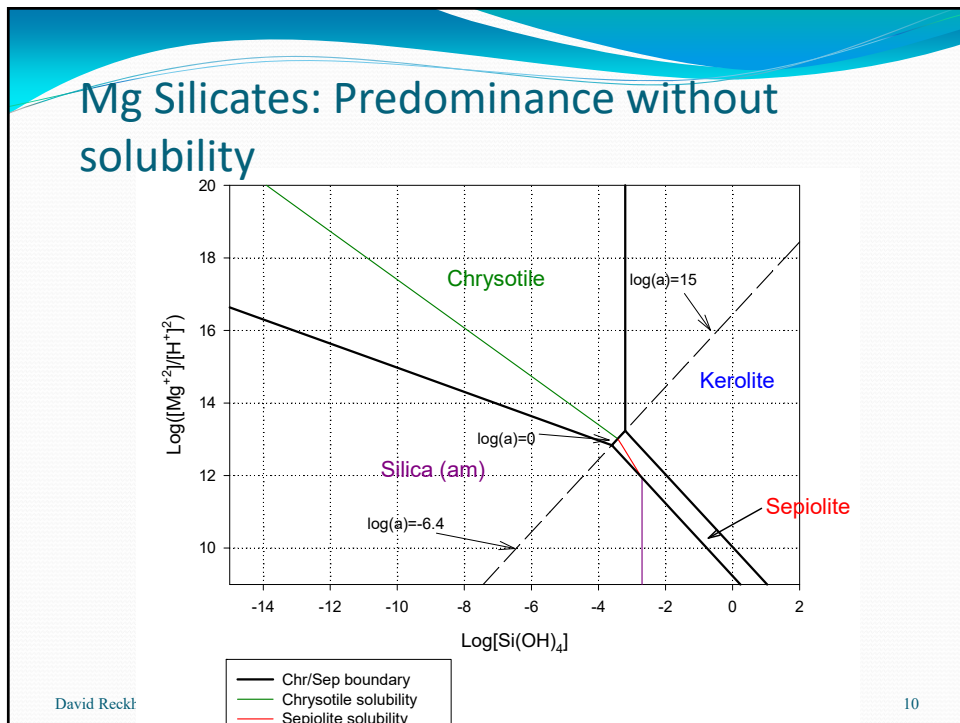
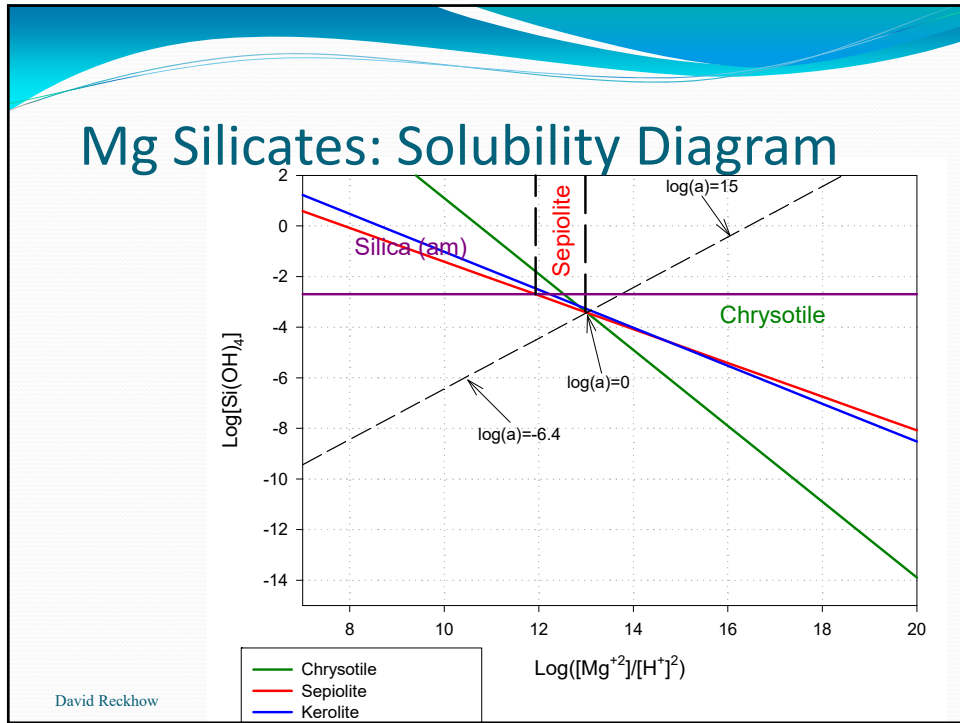
### Practice

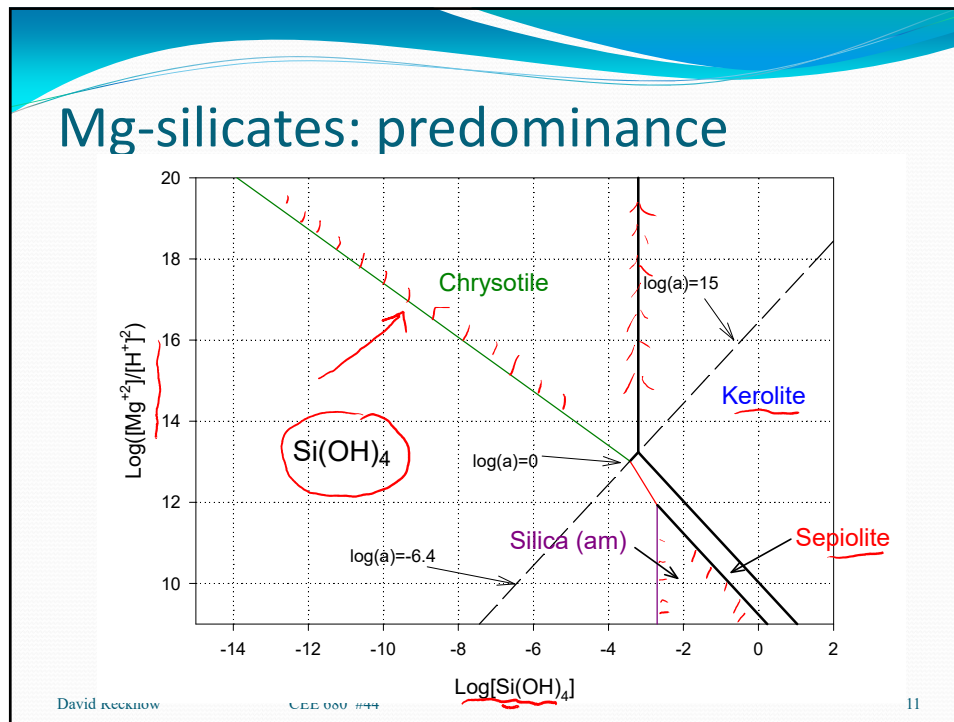
- On a graph with the following axes
  - $\text{Log}([\text{Mg}^{+2}]/[\text{H}^+]^2)$  vs.  $\text{Log}[\text{Si}(\text{OH})_4]$
- Prepare a predominance diagram showing regions for:
  - Chrysotile
  - Sepiolite
  - Kerolite
  - Amorphous Silica

From: Table 1D in S&M, 3<sup>rd</sup> ed.

Mineral	Reaction	$\Delta H_f^\circ$ (kcal mol <sup>-1</sup> )	log K
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{3+} + 2\text{Si}(\text{OH})_4^\circ + \text{H}_2\text{O}$	-35.3	7.435
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3\text{Mg}^{2+} + 2\text{Si}(\text{OH})_4^\circ + \text{H}_2\text{O}$	-46.8	32.20
Sepiolite	$\text{Mg}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 3\text{H}_2\text{O} + 4\text{H}^+ + 0.5 \text{H}_2\text{O} = 2\text{Mg}^{2+} + 3\text{Si}(\text{OH})_4^\circ$	-10.7	15.76
Kerolite	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O} + 6\text{H}^+ + 3\text{H}_2\text{O} = 3\text{Mg}^{2+} + 4\text{Si}(\text{OH})_4^\circ$	-	25.79
Quartz	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^\circ$	5.99	-3.98
Chalcedony	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^\circ$	4.72	-3.55
Amorphous silica	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^\circ$	3.34	-2.71

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### Topics

- Ionic Strength Considerations
  - buffer equation
  - solubility
- Mixed carbonate/hydroxide diagrams
  - Log C vs pH
  - Predominance diagrams

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## Ionic Strength Effects

- Buffer Equation

- recall our earlier derivation:  $pH = pK_a + \log \frac{C_B}{C_A}$

- but because of high I with many buffers:

$$pH = pK'_a + \log \frac{C_B}{C_A}$$

- where:  $K'_a = K_a \left( \frac{\gamma_{HA}}{\gamma_{A^-}} \right)$

- example with phosphate buffer

- composition

- 0.025 M  $\text{KH}_2\text{PO}_4$  and 0.025 M  $\text{Na}_2\text{HPO}_4$

## Ionic Strength Effects (cont.)

- Example

- calculate:  $I=0.1$  M

- use Guntelberg approximation to get  $\gamma$

$$K'_a = K_a \left( \frac{\gamma_{HA}}{\gamma_{A^-}} \right) = 10^{-7.2} \left( \frac{0.76}{0.33} \right) = 10^{-6.84}$$

$$\begin{aligned} pH &= pK'_a + \log \frac{C_B}{C_A} \\ &= 6.84 + \log \frac{0.025}{0.025} \\ &= 6.84 \end{aligned}$$

## Ionic Strength Effects (cont.)

- Precipitation/Dissolution
  - recall that for the equilibrium:  $A_m B_n \leftrightarrow mA + nB$   
we had defined:  $K_{so} = [A^{+n}]^m [B^{-m}]^n$
  - But some relatively soluble solids will result in a high I, so we must:  $\rightarrow K_{so} = \{A^{+n}\}^m \{B^{-m}\}^n$   
 $\rightarrow = [A^{+n}]^m \gamma_A^m [B^{-m}]^n \gamma_B^n$
  - And then we define the conditional constant

$${}^c K_{so} = \frac{K_{so}}{\gamma_A^m \gamma_B^n} = [A^{+n}]^m [B^{-m}]^n$$

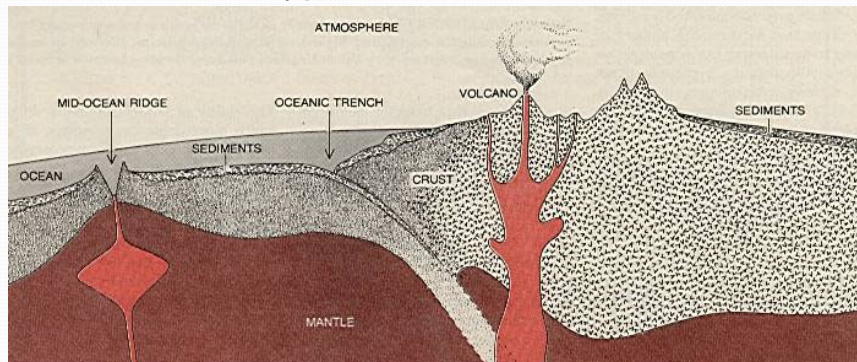
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## SciAm I

- The Steady State of the Earth's Crust, Atmosphere and Oceans
  - Siever, June 1974

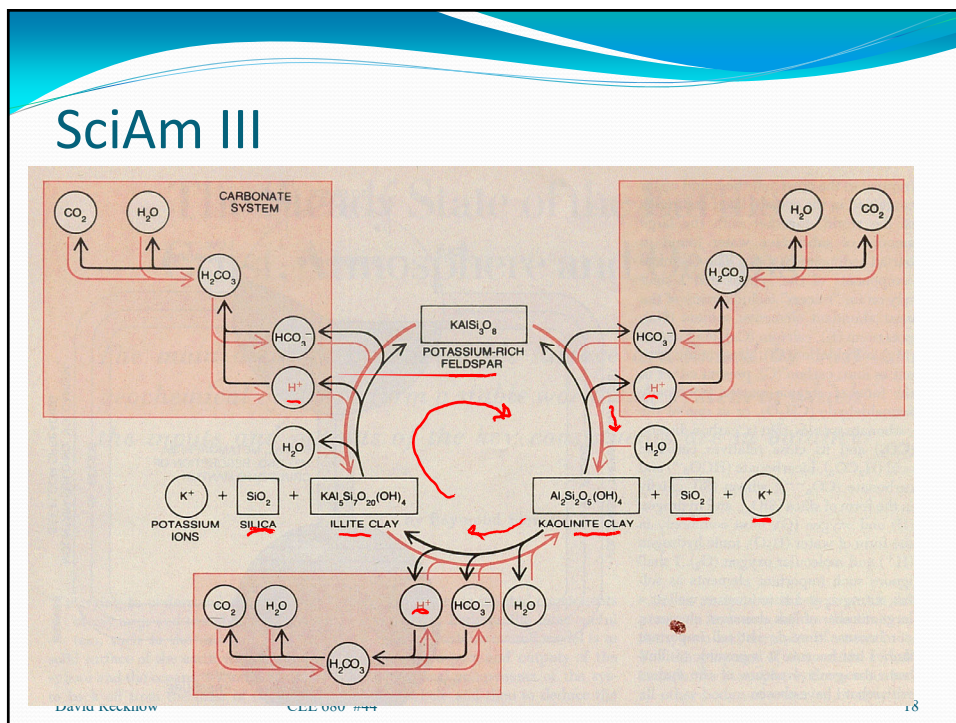
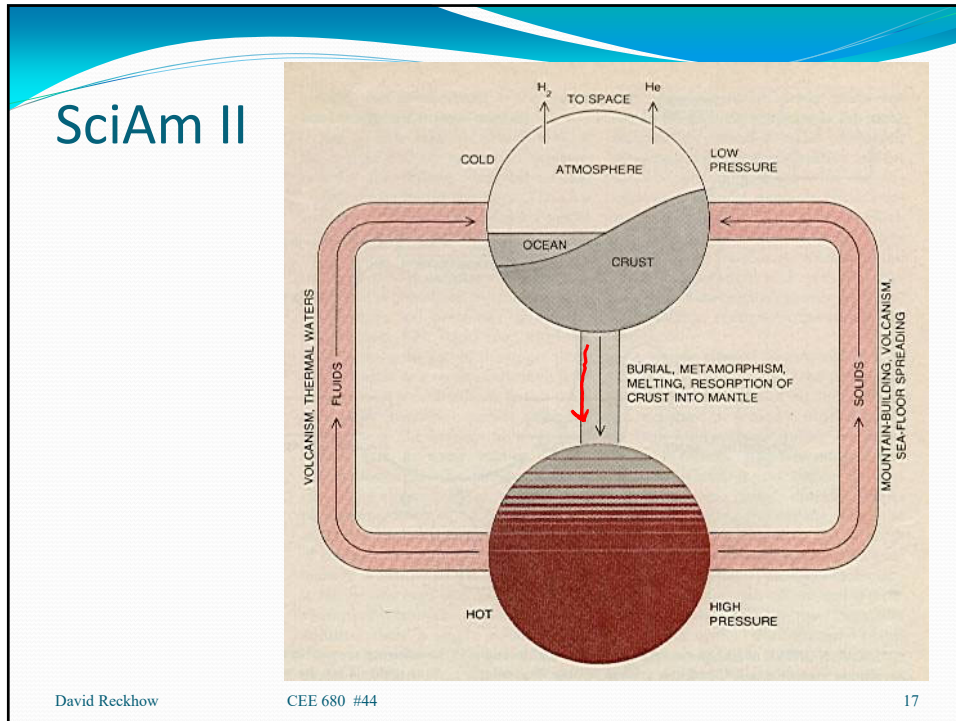


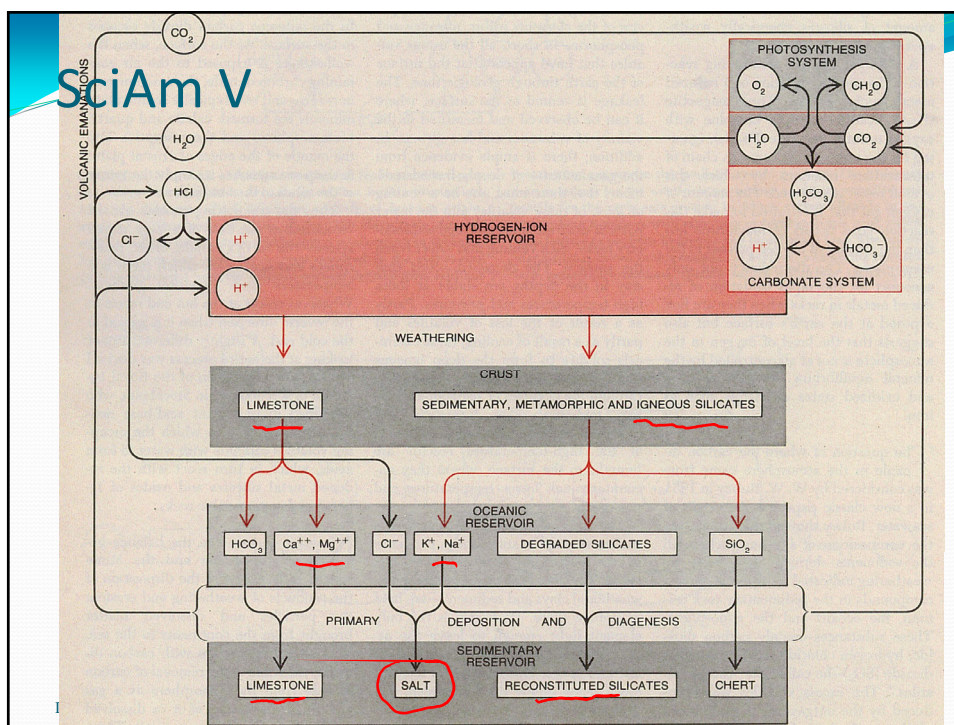
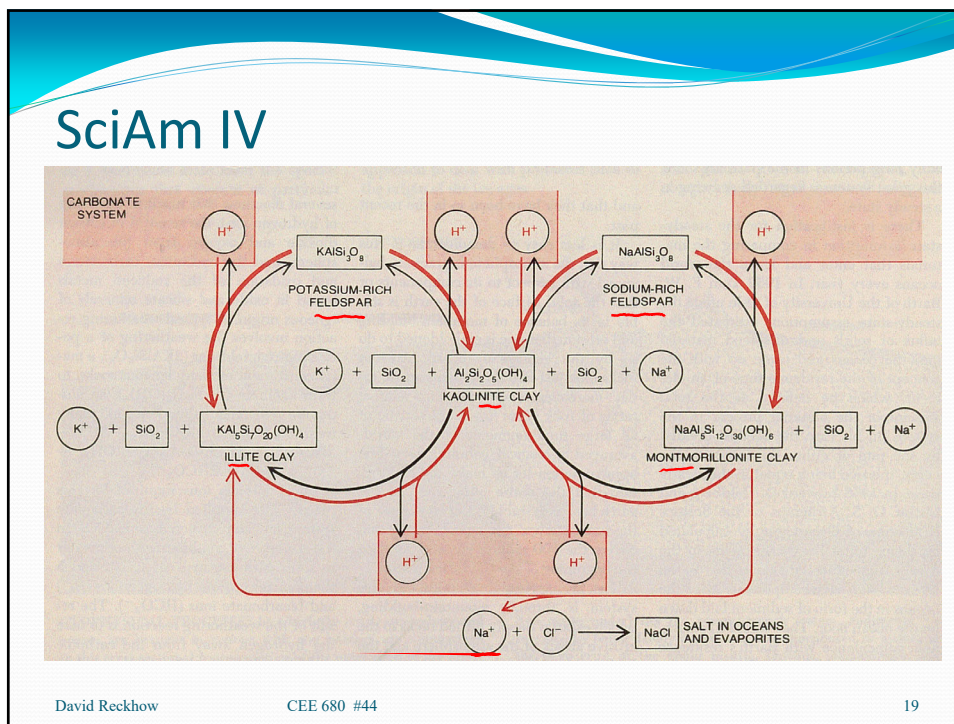
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## Struvite

- Magnesium Ammonium Phosphate mineral
  - $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$
- Environmental Relevance
  - Formation in Sewers and Anaerobic Digesters
    - Reduces hydraulic capacity
  - Use in Municipal WWT
    - Gwinnett County WWTP
      - <http://www.hazenandsawyer.com/work/projects/nutrient-recovery-using-ostara-with-wasstrip-multiform-harvest/>

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Equilibrium equation	pK
$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$	9.0
$\text{HPO}_4^{2-} \leftrightarrow \text{PO}_4^{3-} + \text{H}^+$	12.3
$\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-} + \text{H}^+$	7.2
$\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+$	2.14
$\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}^+$	14.0
$\text{MgOH}^+ \leftrightarrow \text{Mg}^{2+} + \text{OH}^-$	2.56
$\text{MgPO}_4 \leftrightarrow \text{Mg}^{2+} + \text{PO}_4^{3-}$	4.8
$\text{MgHPO}_4 \leftrightarrow \text{Mg}^{2+} + \text{HPO}_4^{2-}$	5.7
$\text{MgH}_2\text{PO}_4 \leftrightarrow \text{Mg}^{2+} + \text{H}_2\text{PO}_4^-$	0.45
$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \downarrow \leftrightarrow 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$	23.98
$\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O} \downarrow \leftrightarrow 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 22\text{H}_2\text{O}$	22.89
$\text{MgHPO}_4 \downarrow \leftrightarrow \text{MgHPO}_4$	0.15
$\text{Mg}(\text{OH})_2 \cdot 6\text{H}_2\text{O} \downarrow \leftrightarrow \text{Mg}^{2+} + 2\text{OH}^- + 6\text{H}_2\text{O}$	10.7
$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \downarrow \leftrightarrow \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O}$	12.7

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# Equilibria #1

From Ohlinger's 1998 Wat Res paper

Ohlinger, K.N., T.M. Young, and E.D. Schroeder. 1998. Predicting struvite formation in digestion. Water Research 32:3607-3614.

Equilibrium relationship	pK	Ref.
$MgPO_4^- \rightleftharpoons Mg^{2+} + PO_4^{3-}$	4.80	<a href="#">Childs (1970)</a>
$MgHPO_4 \rightleftharpoons Mg^{2+} + HPO_4^{2-}$	2.91	<a href="#">Taylor et al. (1963b)</a>
$MgH_2PO_4^+ \rightleftharpoons Mg^{2+} + H_2PO_4^-$	0.45	<a href="#">Morel and Hering (1993)</a>
$MgOH^{++} \rightleftharpoons Mg^{2+} + OH^-$	2.56	<a href="#">Morel and Hering (1993)</a>
$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	12.35	<a href="#">Martell and Smith (1989)</a>
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	7.20	<a href="#">Martell and Smith (1989)</a>
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	2.15	<a href="#">Martell and Smith (1989)</a>
→ $MgNH_4PO_4 \cdot 6H_2O \rightleftharpoons Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O$	13.26	Ohlinger et al., 1998

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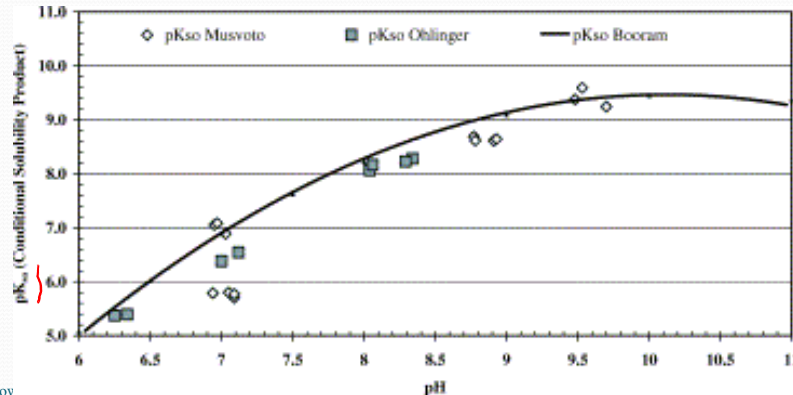
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Doyle, J.D., and S.A. Parsons. 2002. Struvite formation, control and recovery. Water Research 36:3925-3940.

# Conditional Stability Constants

- Doyle & Parsons, 2002
- A comparison of  $pK_{so}$  data for struvite over a range of pH values



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## Kinetic ppt/diss model

- Roncal-Herrero, 2011
  - Roncal-Herrero, T., and E.H. Oelkers. 2011. Experimental determination of struvite dissolution and precipitation rates as a function of pH. Applied Geochemistry 26:921-928.
  - Model for rate of precipitation and dissolution:
  - $r = r_+ \left( 1 - \exp \left( \frac{2.303 \cdot SI}{2} \right) \right)$  ←
  - where  $r_+$  symbolizes the forward dissolution rate. Values of  $r_+$  are found to be independent of pH and equal to  $10^{-12.85 \pm 0.15}$  mol/cm<sup>2</sup>/s in initially NH<sub>4</sub>-free reactive fluids.
  - SI is the saturation index ←
  - $SI = \log \left( \frac{\alpha_{Mg+2} \alpha_{NH4} + \alpha_{PO4-3}}{K_{so-struvite}} \right)$  ←

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## F. Wayne Hill Water Resources Center, Gwinnett County, GA

- FWHWRC is a 60-mgd advanced WWTP facility that utilizes 3 and 5-stage BNR secondary treatment and an array of tertiary treatment methods including: chemical clarification, granular media filtration, chemical flocculation/clarification, ultrafiltration membrane filtration, granular activated carbon (GAC) filtration and ozone disinfection.



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## Struvite

- As a result of a decision to switch to  $Mg(OH)_2$  in the collection system for odor and corrosion control, struvite ( $NH_4MgPO_4 \cdot 6H_2O$ ) formation in the solids handling facilities has become an operations and maintenance concern. The piece of struvite above was taken from a dewatering centrifuge during cleaning.



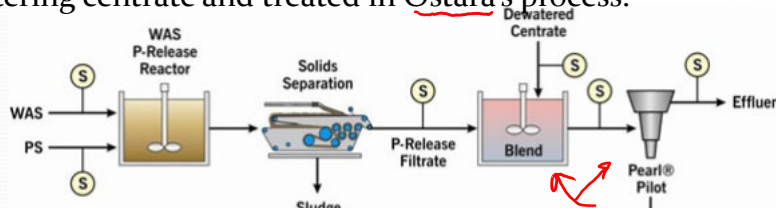
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## Waste Activated Sludge Stripping to Remove Internal Phosphorous

- In the WASSTRIP Process, primary sludge and waste activated sludge are anaerobically reacted to induce phosphorus release from phosphate accumulating bacteria. Filtrate from the reacted sludge blend is mixed with dewatering centrate and treated in Ostara's process.



reduces struvite buildup in the operation of anaerobic nutrient removal facilities. Biological phosphorus removal facilities need to recycle nutrient-rich sludge several times within the wastewater facility, which adds to the operating costs and takes up plant capacity. Phosphorus, ammonia, and magnesium become highly concentrated when this happens. Struvite formation coats pipes, valves, and other equipment which reduces flow capacities and increases maintenance requirements

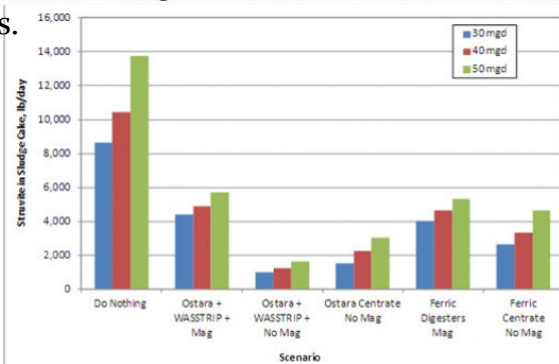
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## Controlling Struvite Formation

- BioWin® modeling results show that nutrient recovery (Ostara) + WASSTRIP offers similar struvite reduction potential to ferric addition in the digesters, which a traditional method of treating struvite formation in anaerobic digesters.



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- To next lecture

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