Updated: 15 April 2020

Print version

CEE 680: Water Chemistry

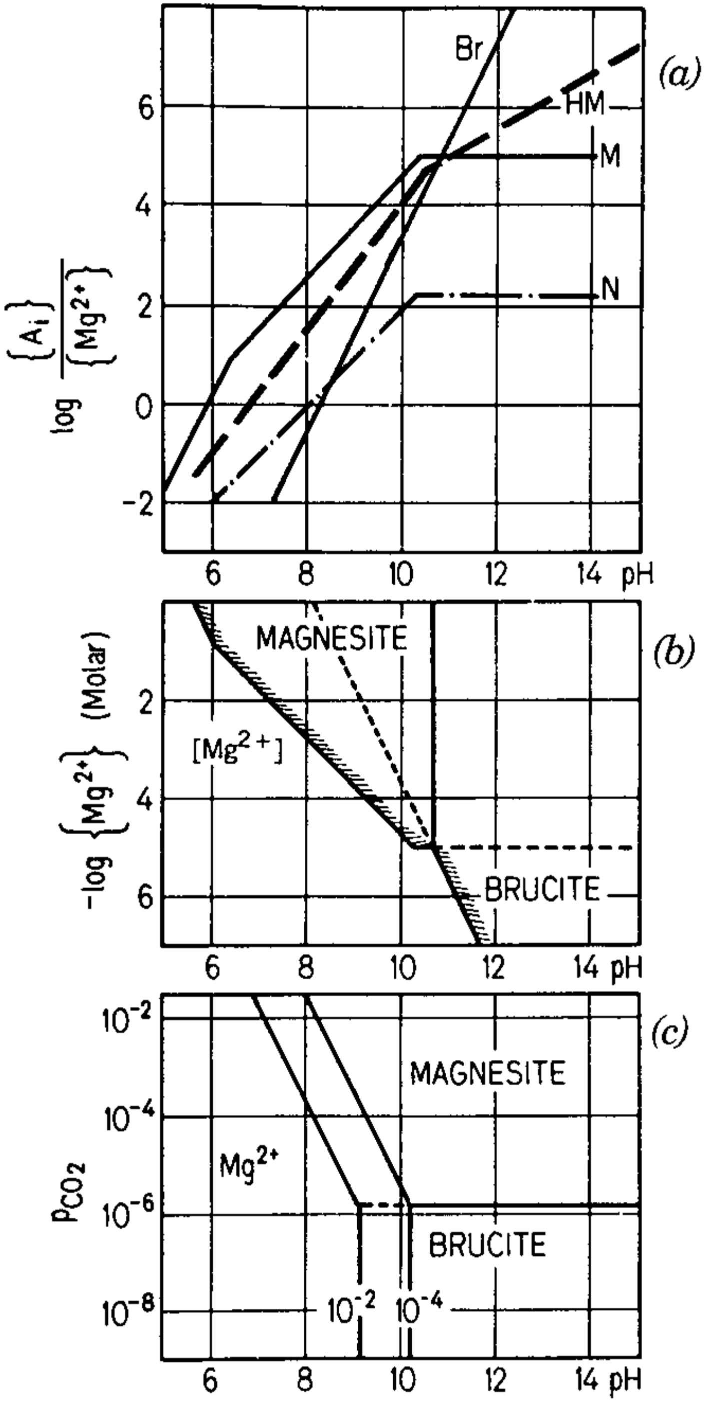
Lecture #44

Precipitation and Dissolution: Application to Mineral Formation

(Stumm & Morgan, Chapt.7)

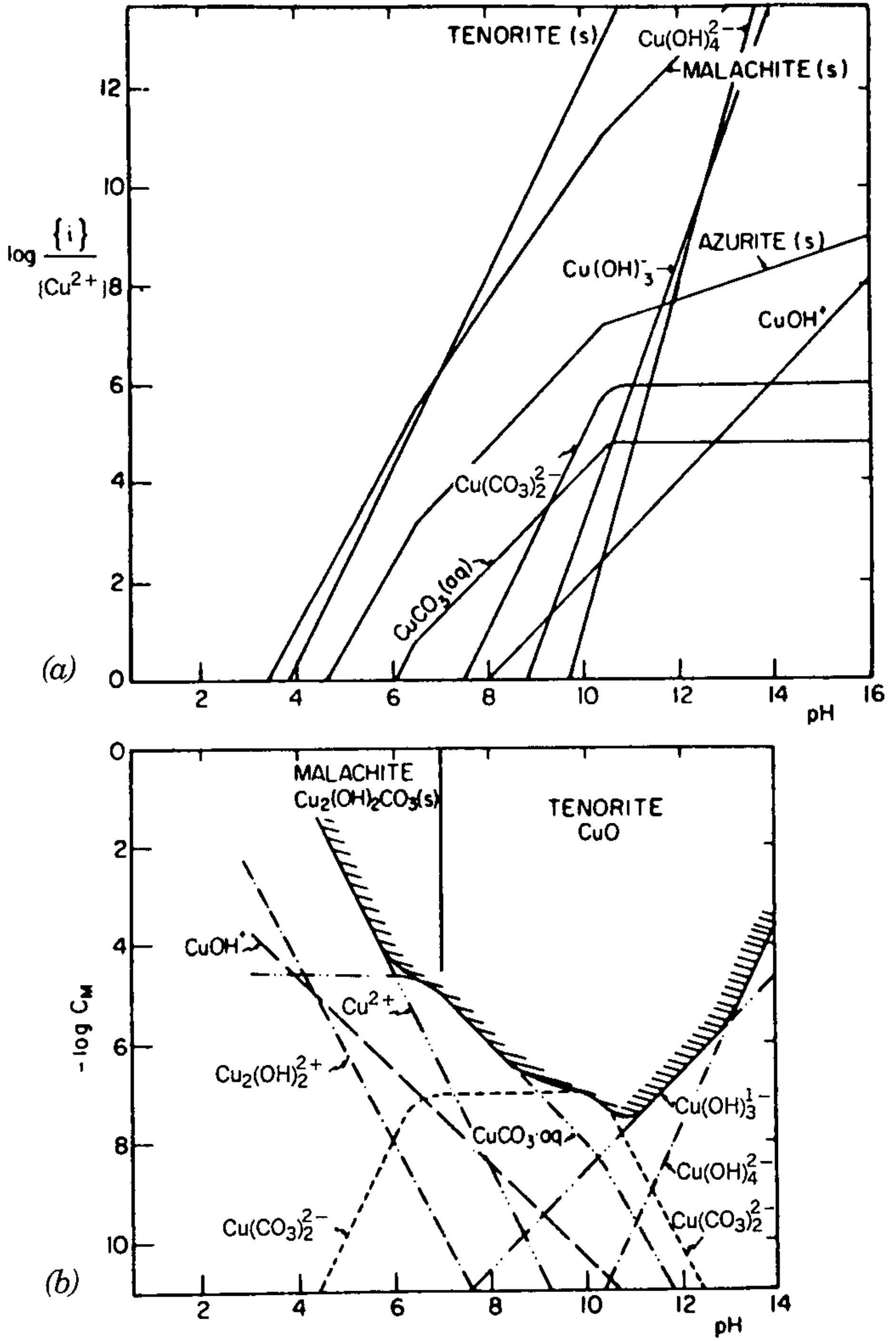
Benjamin; Chapter 8.7-8.15

Mg phases



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

Cu phases



Stumm & Morgan, 1996, Figure 7.16, pg. 399

Clay equilibria

- Stumm & Morgan (2nd ed)
  - Pg 546

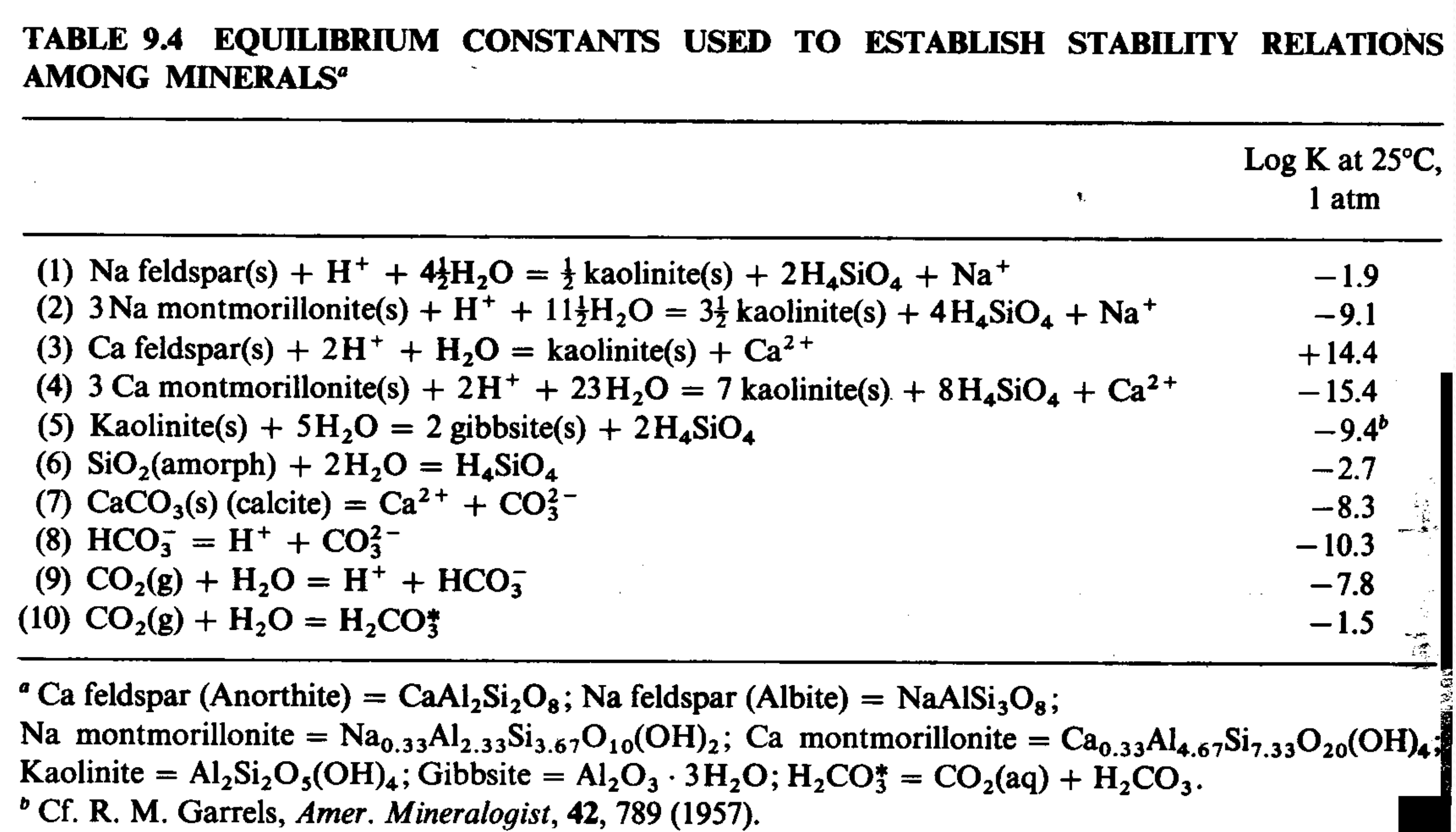


TABLE 9.4 EQUILIBRIUM CONSTANTS USED TO ESTABLISH STABILITY RELATIONS AMONG MINERALS[a]

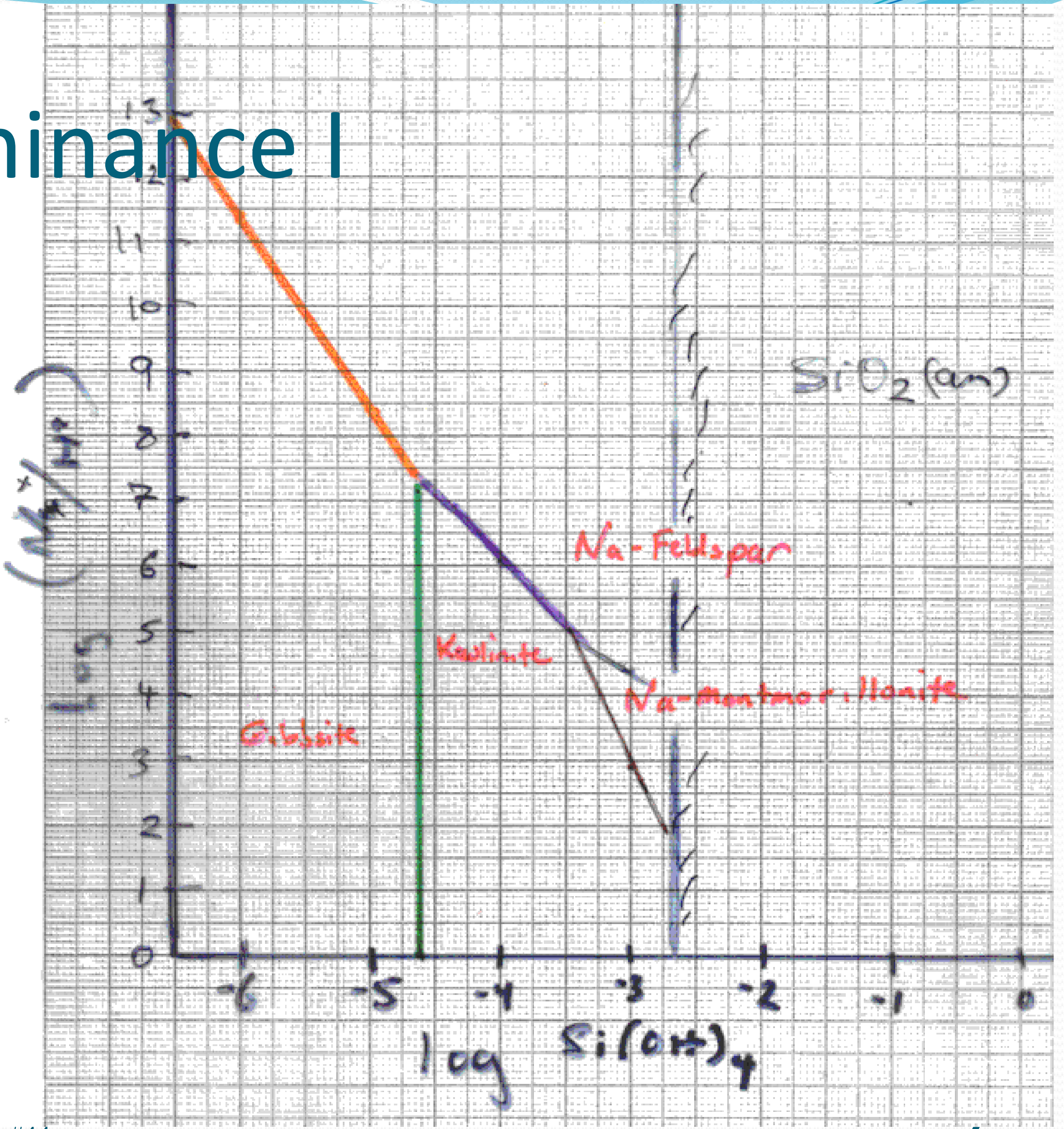
	Log K at 25°C, 1 atm
(1) Na feldspar(s) + H^+ + $4\frac{1}{2}H_2O$ = $\frac{1}{2}$ kaolinite(s) + $2H_4SiO_4$ + Na^+	−1.9
(2) 3 Na montmorillonite(s) + H^+ + $11\frac{1}{2}H_2O$ = $3\frac{1}{2}$ kaolinite(s) + $4H_4SiO_4$ + Na^+	−9.1
(3) Ca feldspar(s) + $2H^+$ + H_2O = kaolinite(s) + Ca^{2+}	+14.4
(4) 3 Ca montmorillonite(s) + $2H^+$ + $23H_2O$ = 7 kaolinite(s) + $8H_4SiO_4$ + Ca^{2+}	−15.4
(5) Kaolinite(s) + $5H_2O$ = 2 gibbsite(s) + $2H_4SiO_4$	−9.4[b]
(6) SiO_2(amorph) + $2H_2O$ = H_4SiO_4	−2.7
(7) $CaCO_3$(s) (calcite) = Ca^{2+} + CO_3^{2-}	−8.3
(8) HCO_3^- = H^+ + CO_3^{2-}	−10.3
(9) CO_2(g) + H_2O = H^+ + HCO_3^-	−7.8
(10) CO_2(g) + H_2O = $H_2CO_3^*$	−1.5

[a] Ca feldspar (Anorthite) = $CaAl_2Si_2O_8$; Na feldspar (Albite) = $NaAlSi_3O_8$; Na montmorillonite = $Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$; Ca montmorillonite = $Ca_{0.33}Al_{4.67}Si_{7.33}O_{20}(OH)_4$; Kaolinite = $Al_2Si_2O_5(OH)_4$; Gibbsite = $Al_2O_3 \cdot 3H_2O$; $H_2CO_3^*$ = $CO_2(aq)$ + H_2CO_3.

[b] Cf. R. M. Garrels, *Amer. Mineralogist*, **42**, 789 (1957).

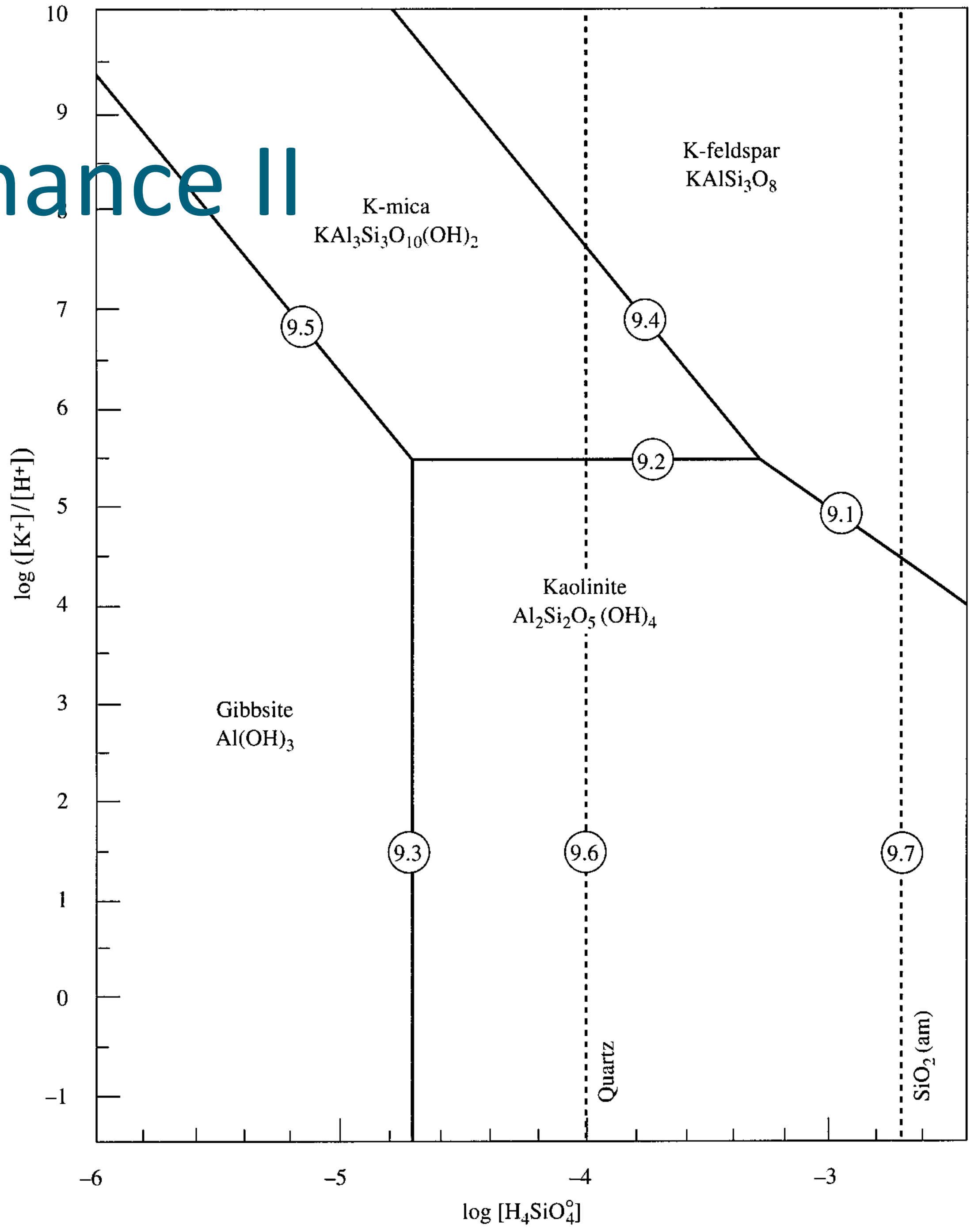
Clay Predominance I

- Na species



Clay Predominance II

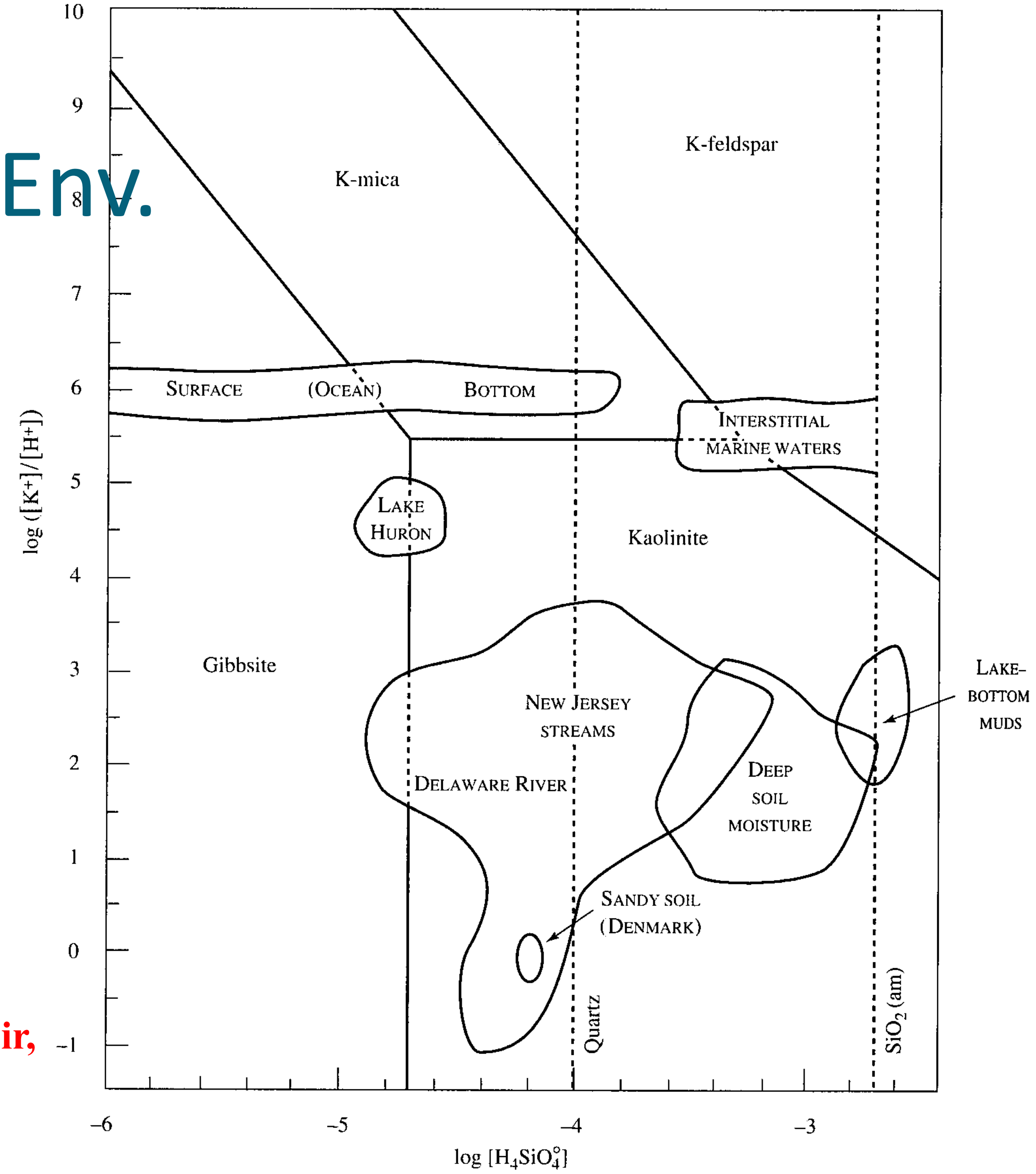
- K species



Chapter 9 in Aqueous Environmental Geochemistry by Langmuir, 1997

Relation to Env.

- K species

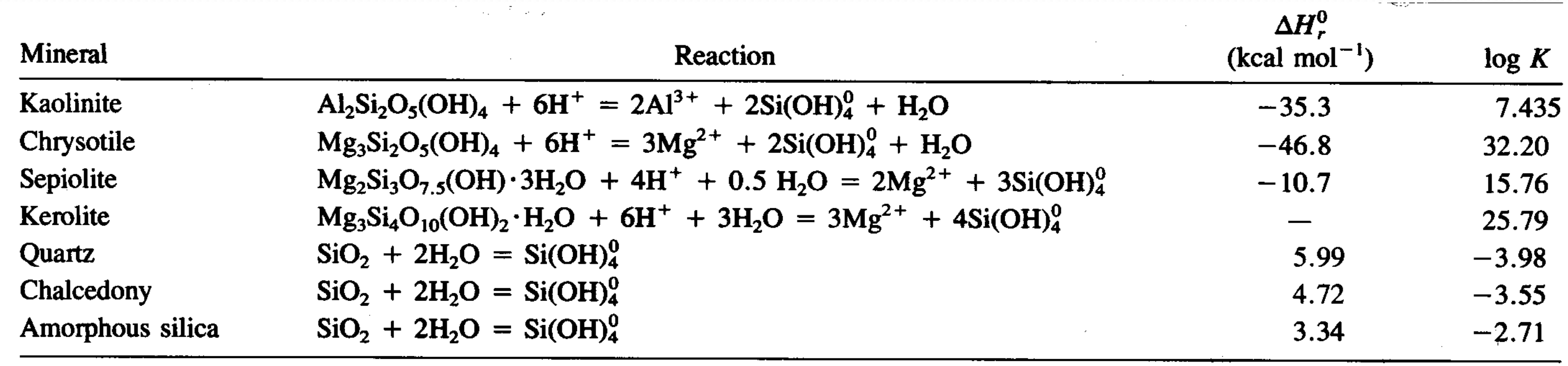


Chapter 9 in Aqueous Environmental Geochemistry by Langmuir, 1997

Practice

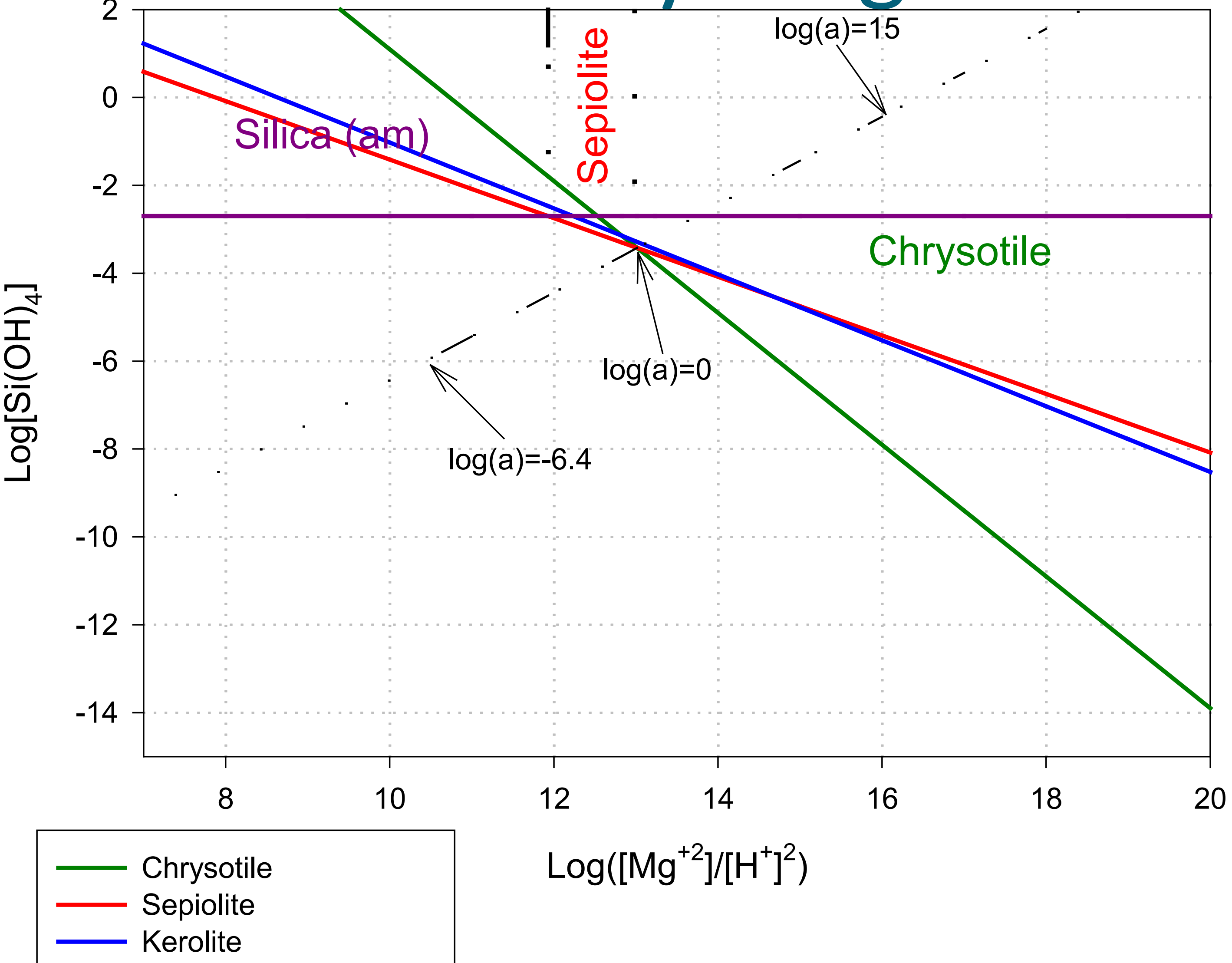
- On a graph with the following axes
  - $\text{Log}([Mg^{+2}]/[H^+]^2)$ vs. $\text{Log}[Si(OH)_4]$
- Prepare a predominance diagram showing regions for:
  - Chrysotile
  - Sepiolite
  - Kerolite
  - Amorphous Silica

From: Table 1D in S&M, 3rd ed.

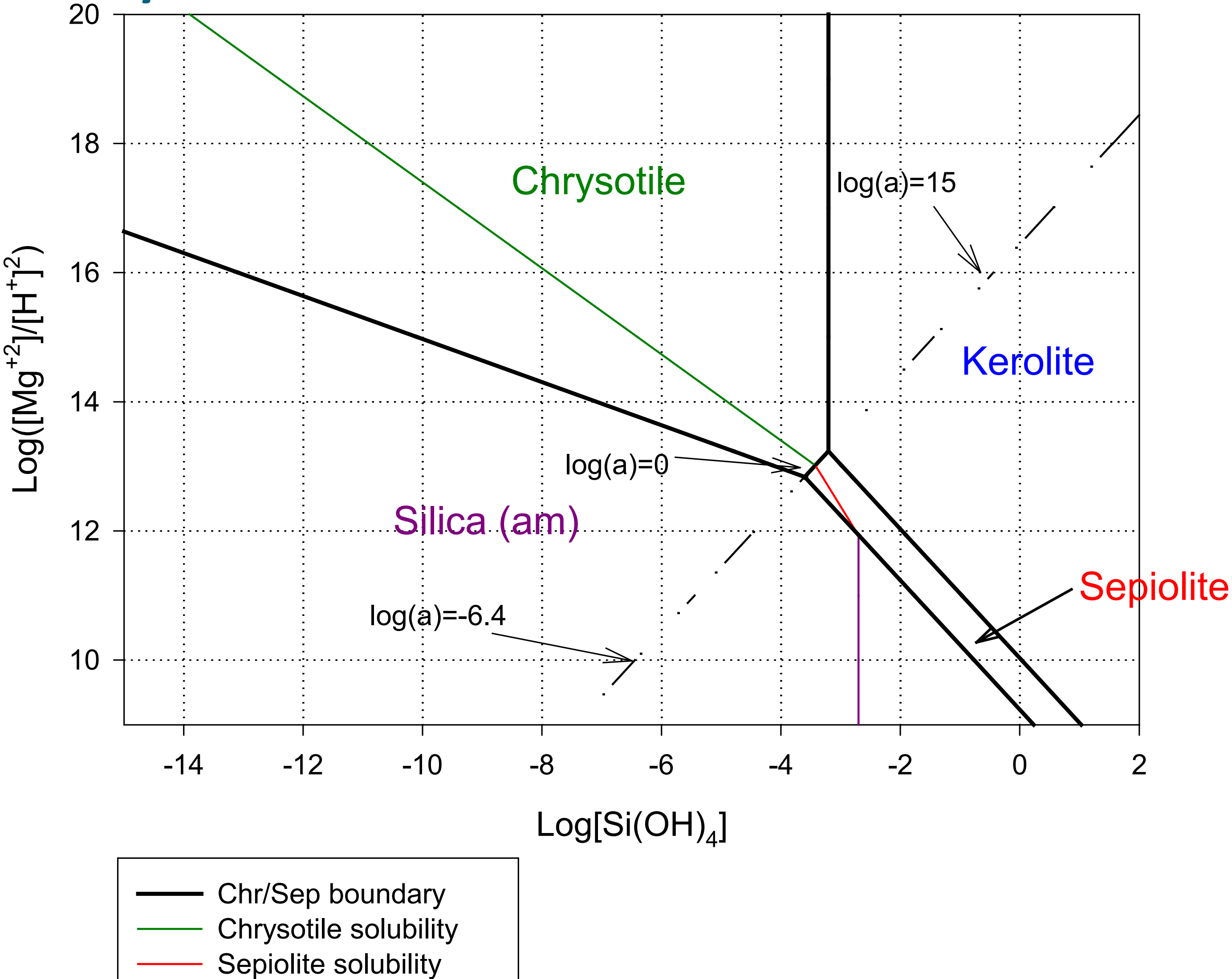


Mineral	Reaction	ΔH_r^0 (kcal mol^{-1})	log K
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2Si(OH)_4^0 + H_2O$	−35.3	7.435
Chrysotile	$Mg_3Si_2O_5(OH)_4 + 6H^+ = 3Mg^{2+} + 2Si(OH)_4^0 + H_2O$	−46.8	32.20
Sepiolite	$Mg_2Si_3O_{7.5}(OH)\cdot 3H_2O + 4H^+ + 0.5\ H_2O = 2Mg^{2+} + 3Si(OH)_4^0$	−10.7	15.76
Kerolite	$Mg_3Si_4O_{10}(OH)_2\cdot H_2O + 6H^+ + 3H_2O = 3Mg^{2+} + 4Si(OH)_4^0$	—	25.79
Quartz	$SiO_2 + 2H_2O = Si(OH)_4^0$	5.99	−3.98
Chalcedony	$SiO_2 + 2H_2O = Si(OH)_4^0$	4.72	−3.55
Amorphous silica	$SiO_2 + 2H_2O = Si(OH)_4^0$	3.34	−2.71

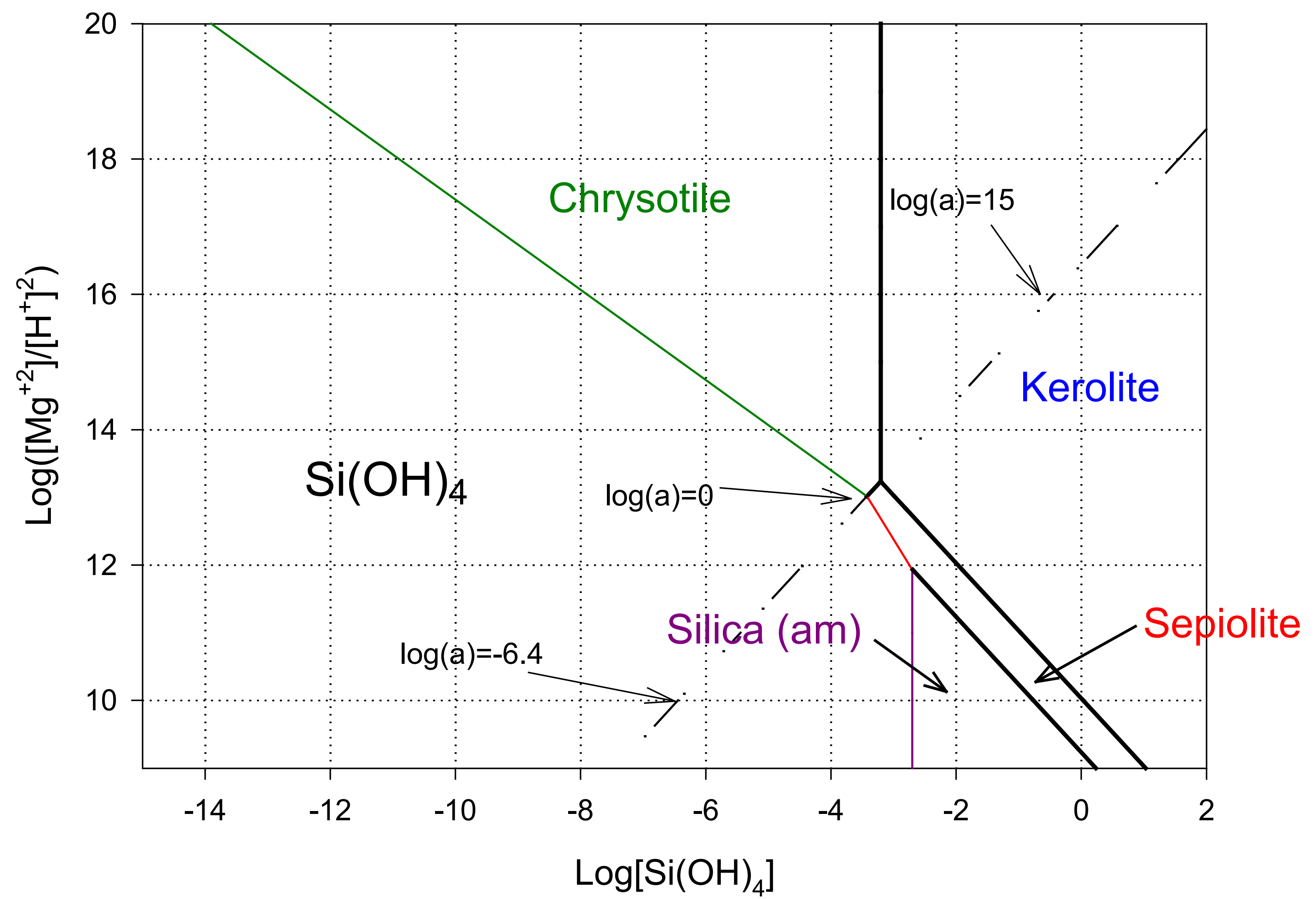
Mg Silicates: Solubility Diagram



Mg Silicates: Predominance without solubility



Mg-silicates: predominance



Topics

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

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 KH_2PO_4 and 0.025 M Na_2HPO_4

Ionic Strength Effects (cont.)

- Example
  - calculate: I=0.1 M
  - use Guntelberg approximation to get γ

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

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

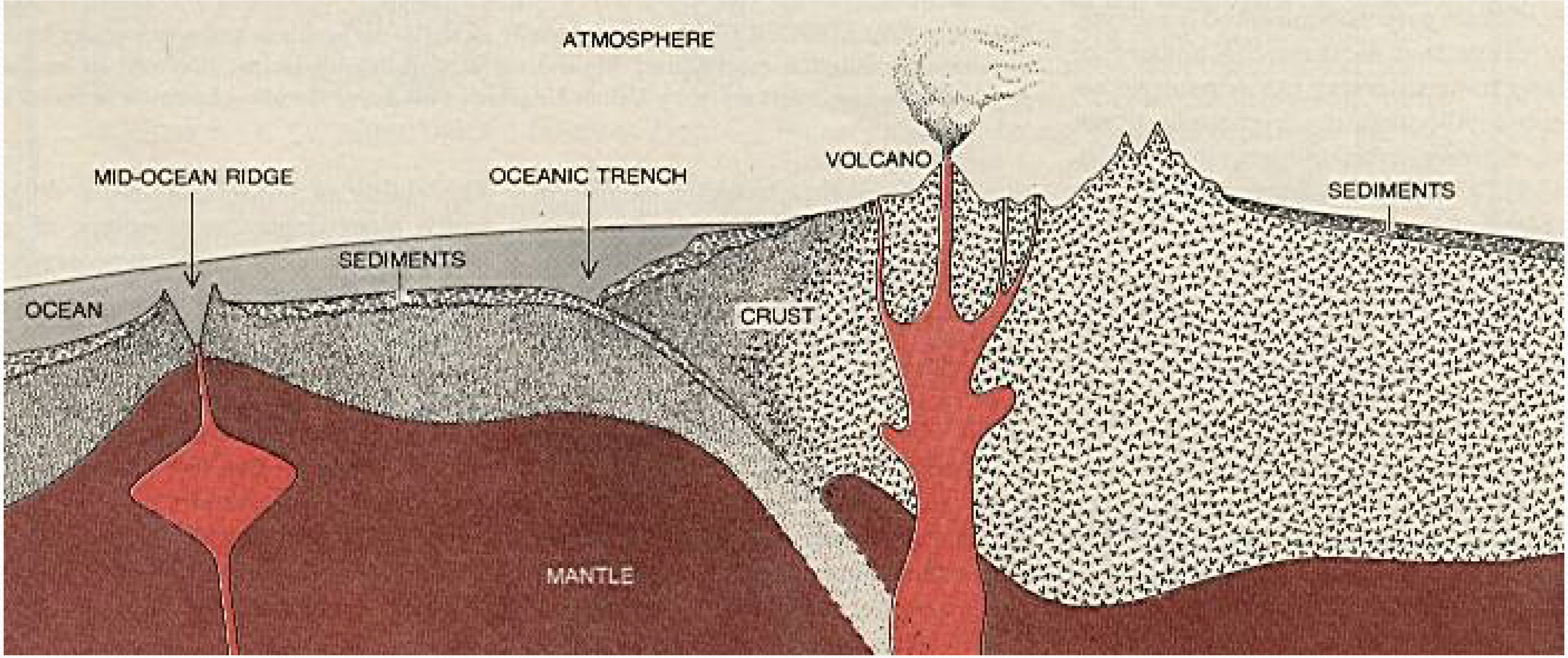
Ionic Strength Effects (cont.)

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

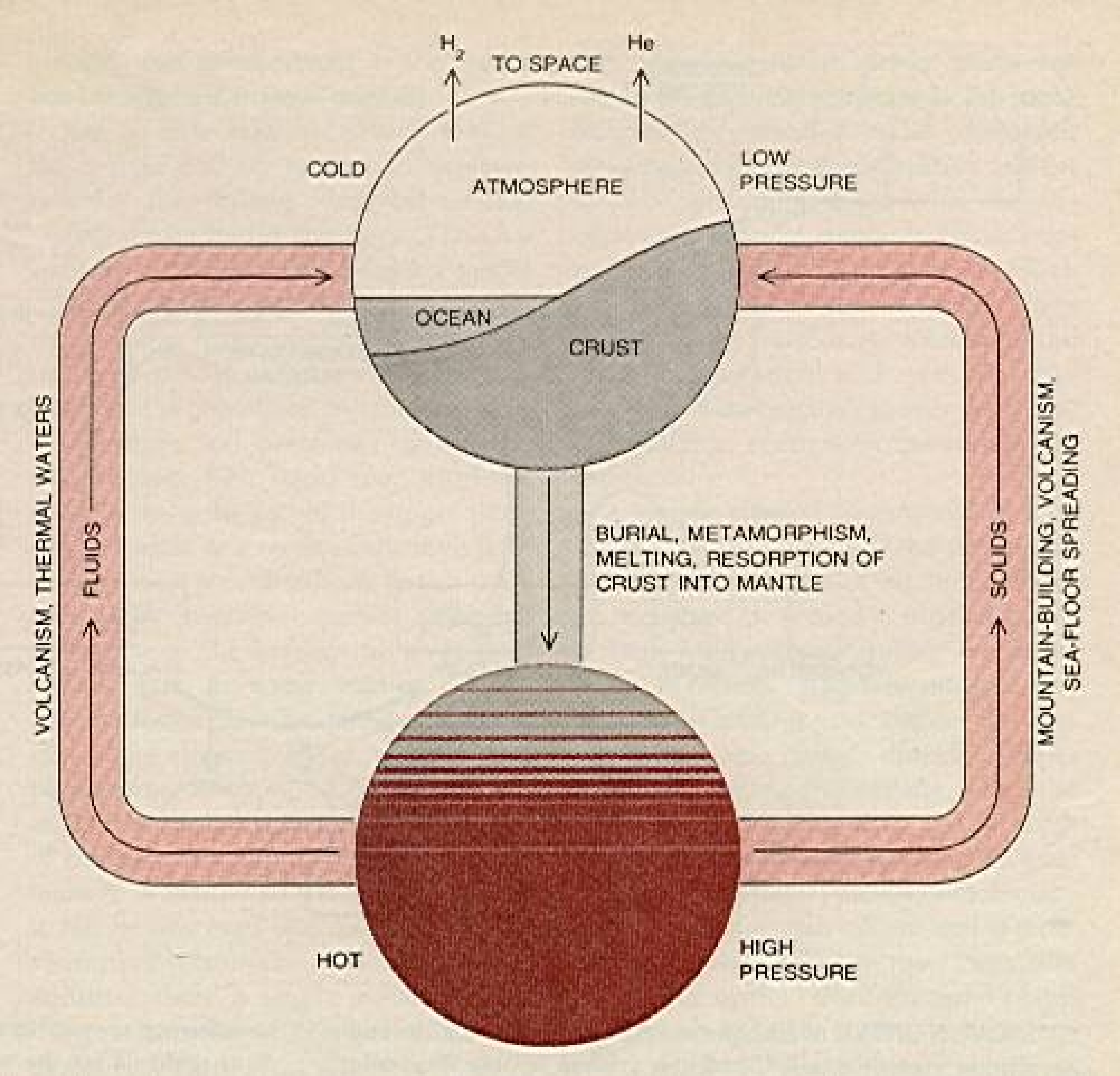
$$ {}^cK_{so} = \frac{K_{so}}{\gamma_A^m \gamma_B^n} = \left[A^{+n}\right]^m \left[B^{-m}\right]^n $$

SciAm I

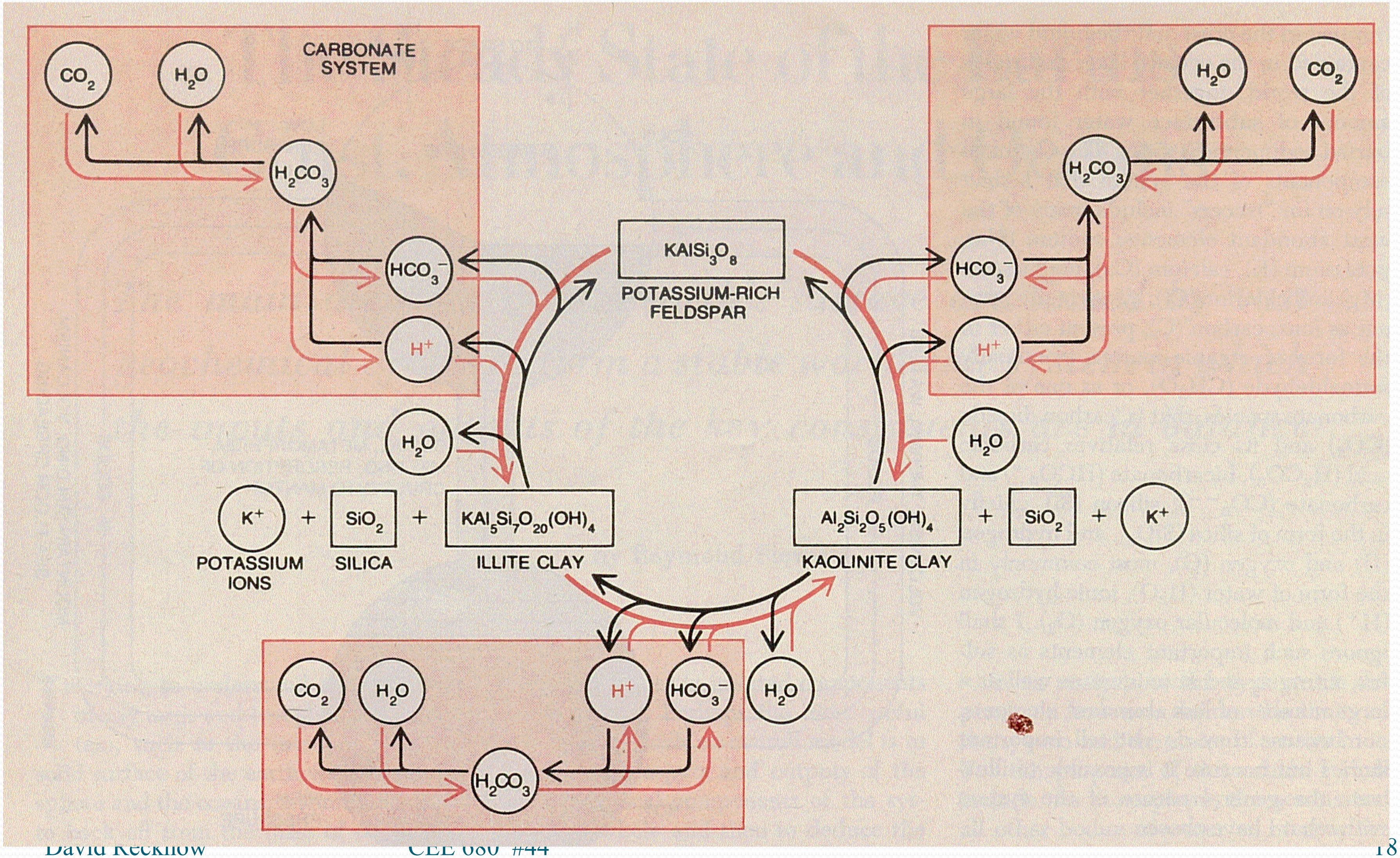
- The Steady State of the Earth's Crust, Atmosphere and Oceans
  - Siever, June 1974



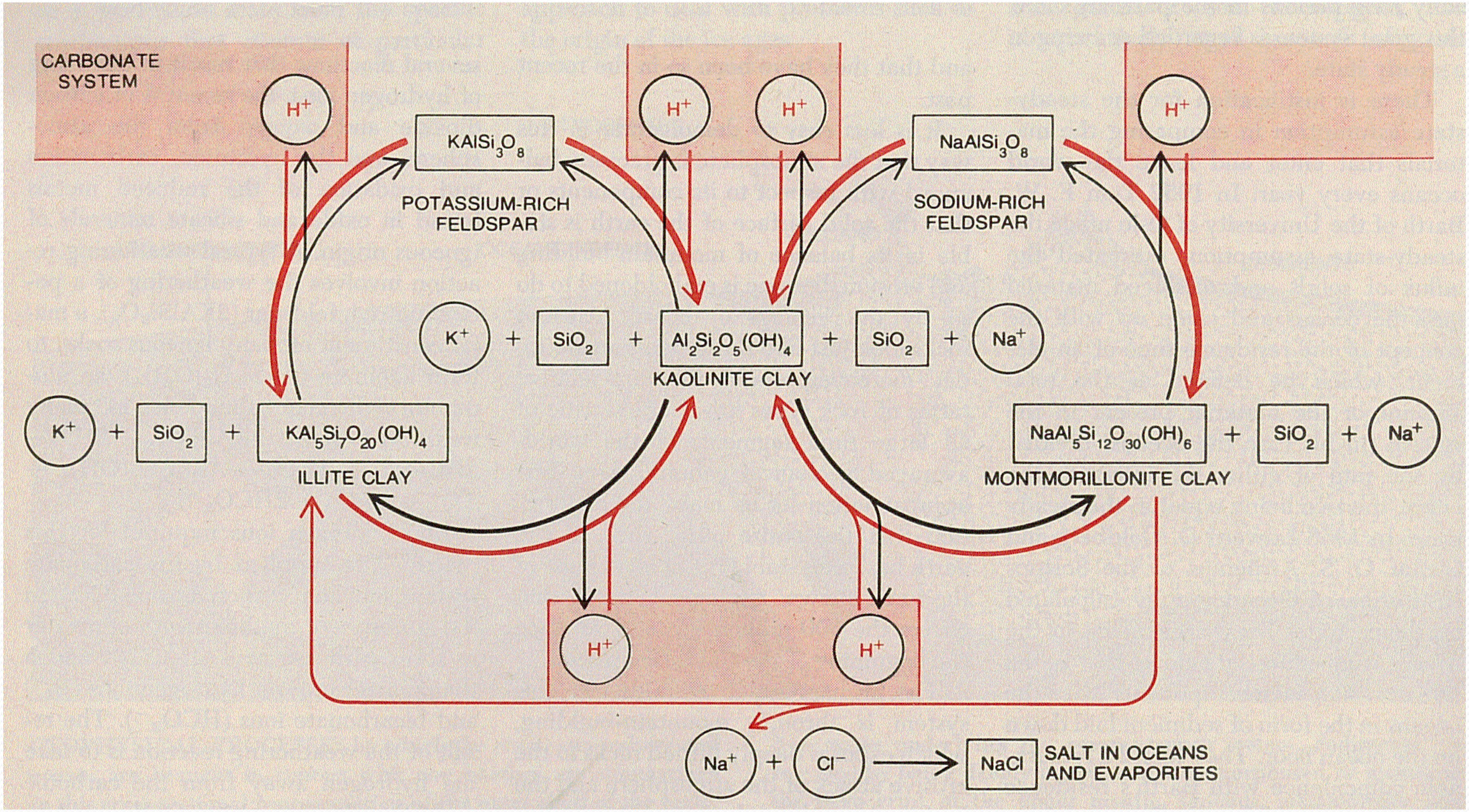
SciAm II


H_2
TO SPACE
He
COLD
ATMOSPHERE
LOW PRESSURE
OCEAN
CRUST
BURIAL, METAMORPHISM, MELTING, RESORPTION OF CRUST INTO MANTLE
VOLCANISM, THERMAL WATERS
FLUIDS
SOLIDS
MOUNTAIN-BUILDING, VOLCANISM, SEA-FLOOR SPREADING
HOT
HIGH PRESSURE

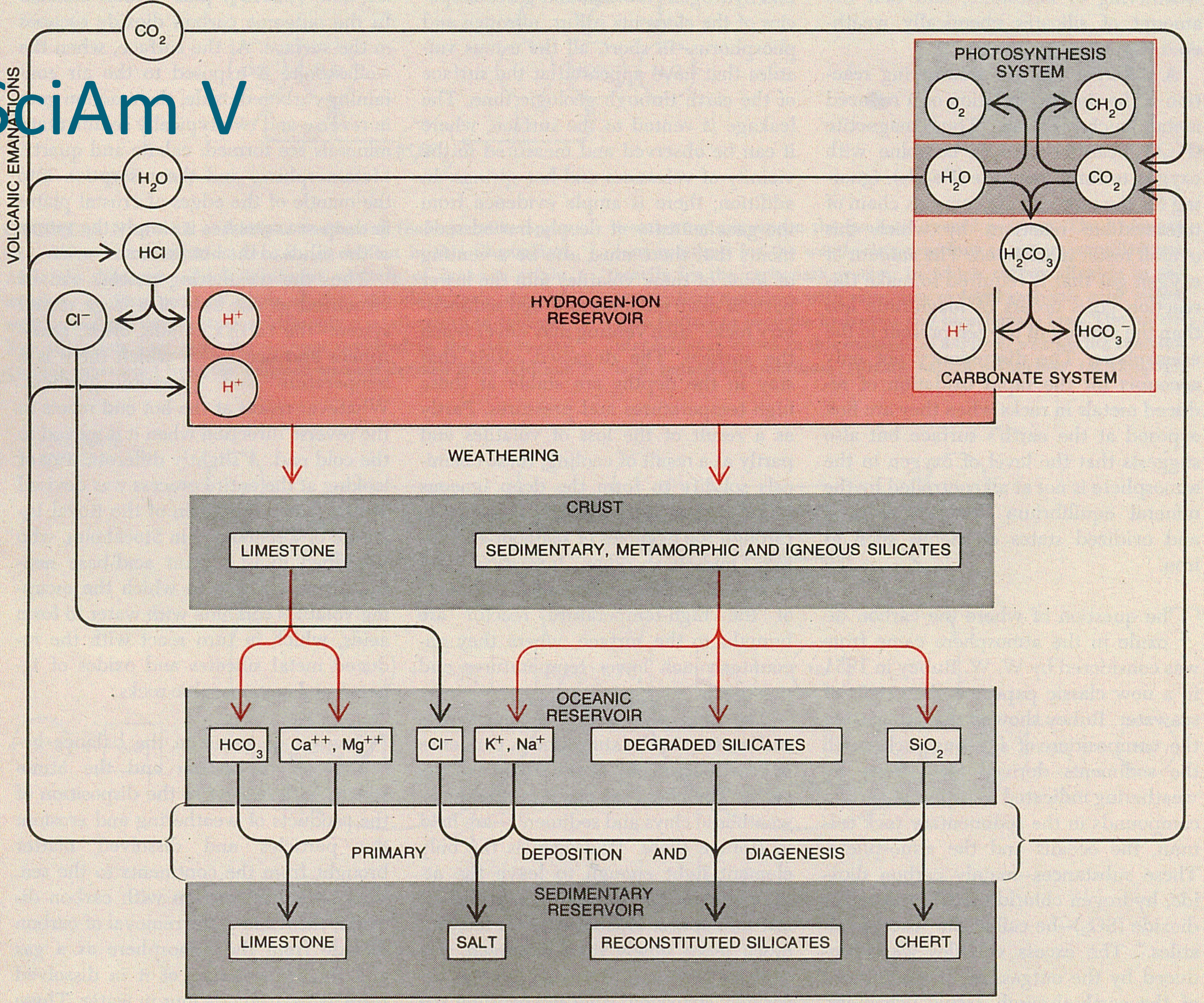
SciAm III


CARBONATE SYSTEM
CO_2
H_2O
H_2CO_3
HCO_3^-
H^+
$KAlSi_3O_8$
POTASSIUM-RICH FELDSPAR
K^+ + SiO_2 + $KAl_5Si_7O_{20}(OH)_4$
POTASSIUM IONS
SILICA
ILLITE CLAY
$Al_2Si_2O_5(OH)_4$ + SiO_2 + K^+
KAOLINITE CLAY

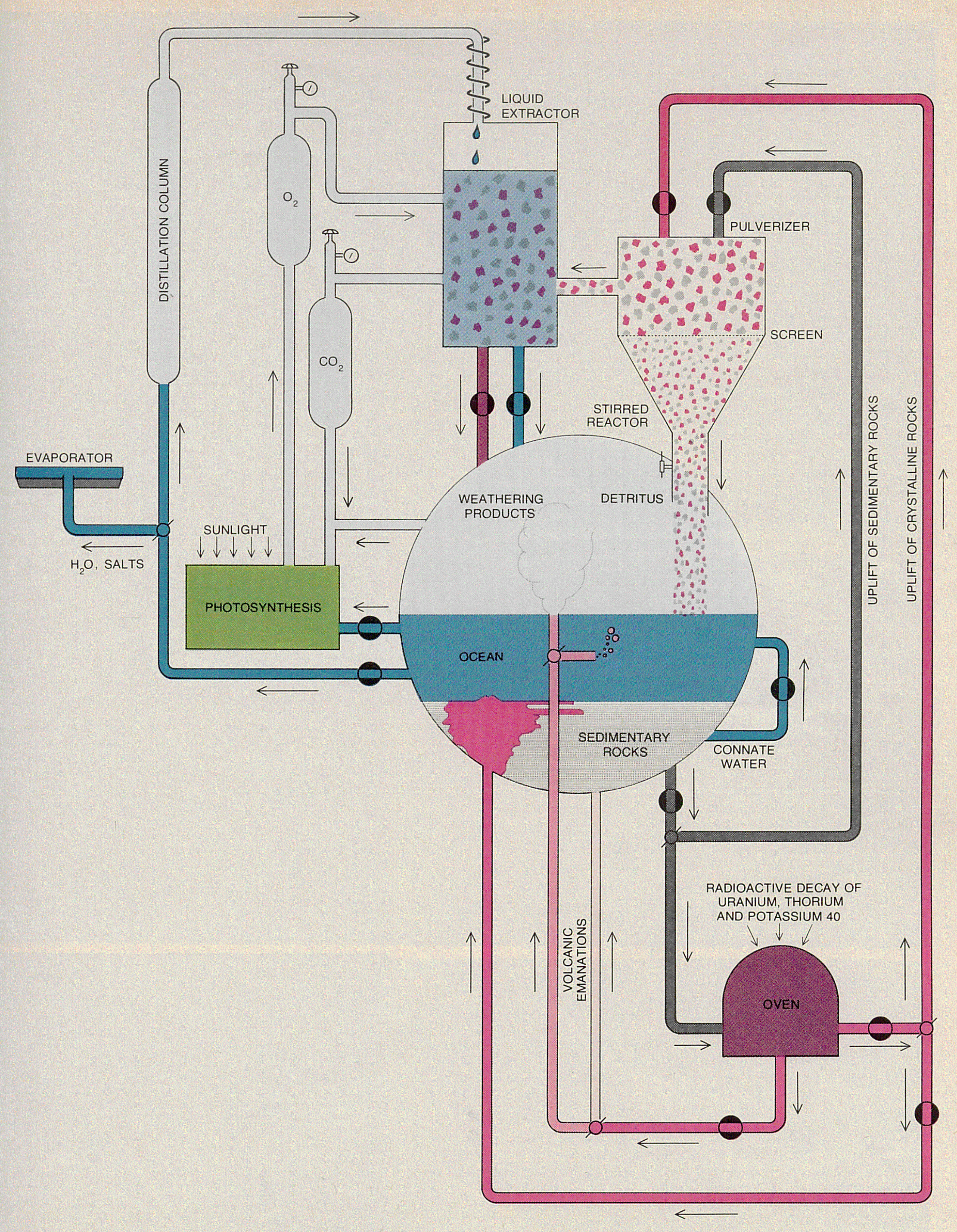
SciAm IV


CARBONATE SYSTEM
H^+
H^+
H^+
H^+
$KAlSi_3O_8$
POTASSIUM-RICH FELDSPAR
$NaAlSi_3O_8$
SODIUM-RICH FELDSPAR
$K^+ + SiO_2 + Al_2Si_2O_5(OH)_4 + SiO_2 + Na^+$
KAOLINITE CLAY
$K^+ + SiO_2 + KAl_5Si_7O_{20}(OH)_4$
ILLITE CLAY
$NaAl_5Si_{12}O_{30}(OH)_6 + SiO_2 + Na^+$
MONTMORILLONITE CLAY
H^+
H^+
$Na^+ + Cl^- \rightarrow NaCl$
SALT IN OCEANS AND EVAPORITES

SciAm V


VOLCANIC EMANATIONS
CO_2
H_2O
HCl
Cl^-
H^+
H^+
HYDROGEN-ION RESERVOIR
PHOTOSYNTHESIS SYSTEM
O_2
CH_2O
H_2O
CO_2
H_2CO_3
H^+
HCO_3^-
CARBONATE SYSTEM
WEATHERING
CRUST
LIMESTONE
SEDIMENTARY, METAMORPHIC AND IGNEOUS SILICATES
OCEANIC RESERVOIR
HCO_3
Ca^{++}, Mg^{++}
Cl^-
K^+, Na^+
DEGRADED SILICATES
SiO_2
PRIMARY DEPOSITION AND DIAGENESIS
SEDIMENTARY RESERVOIR
LIMESTONE
SALT
RECONSTITUTED SILICATES
CHERT

SciAm VI


LIQUID EXTRACTOR
DISTILLATION COLUMN
O_2
CO_2
PULVERIZER
SCREEN
STIRRED REACTOR
EVAPORATOR
SUNLIGHT
H_2O, SALTS
PHOTOSYNTHESIS
WEATHERING PRODUCTS
DETRITUS
OCEAN
SEDIMENTARY ROCKS
CONNATE WATER
UPLIFT OF SEDIMENTARY ROCKS
UPLIFT OF CRYSTALLINE ROCKS
RADIOACTIVE DECAY OF URANIUM, THORIUM AND POTASSIUM 40
OVEN
VOLCANIC EMANATIONS

Question

- Are solubility product values (K_{so} or K_{sp}) independent of pH?
  1. Yes
  2. No

Struvite

- Magnesium Ammonium Phosphate mineral
  - $NH_4MgPO_4 \cdot 6H_2O$
- 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/

Equilibrium equation	**p*K***
NH+4↔NH3+H+	9.0
HPO2−4↔PO3−4+H+	12.3
H2PO−4↔HPO2−4+H+	7.2
H3PO4↔H2PO−4+H+	2.14
H2O↔OH−+H+	14.0
MgOH+↔Mg2++OH−	2.56
MgPO−4↔Mg2++PO3−4	4.8
MgHPO4↔Mg2++HPO2−4	5.7
MgH2PO+4↔Mg2++H2PO−4	0.45
Mg3(PO4)2.8H2O↓↔3Mg2++2PO3−4+8H2O	23.98
Mg3(PO4)2.22H2O↓↔3Mg2++2PO3−4+22H2O	22.89
MgHPO4↓↔MgHPO4	0.15
Mg(OH)2.6H2O↓↔Mg2++2OH−+6H2O	10.7
MgNH4PO4.6H2O↓↔Mg2++NH+4+PO3−4+6H2O	12.7

Equilibria #1

From Ohlinger's 1998 Wat Res paper

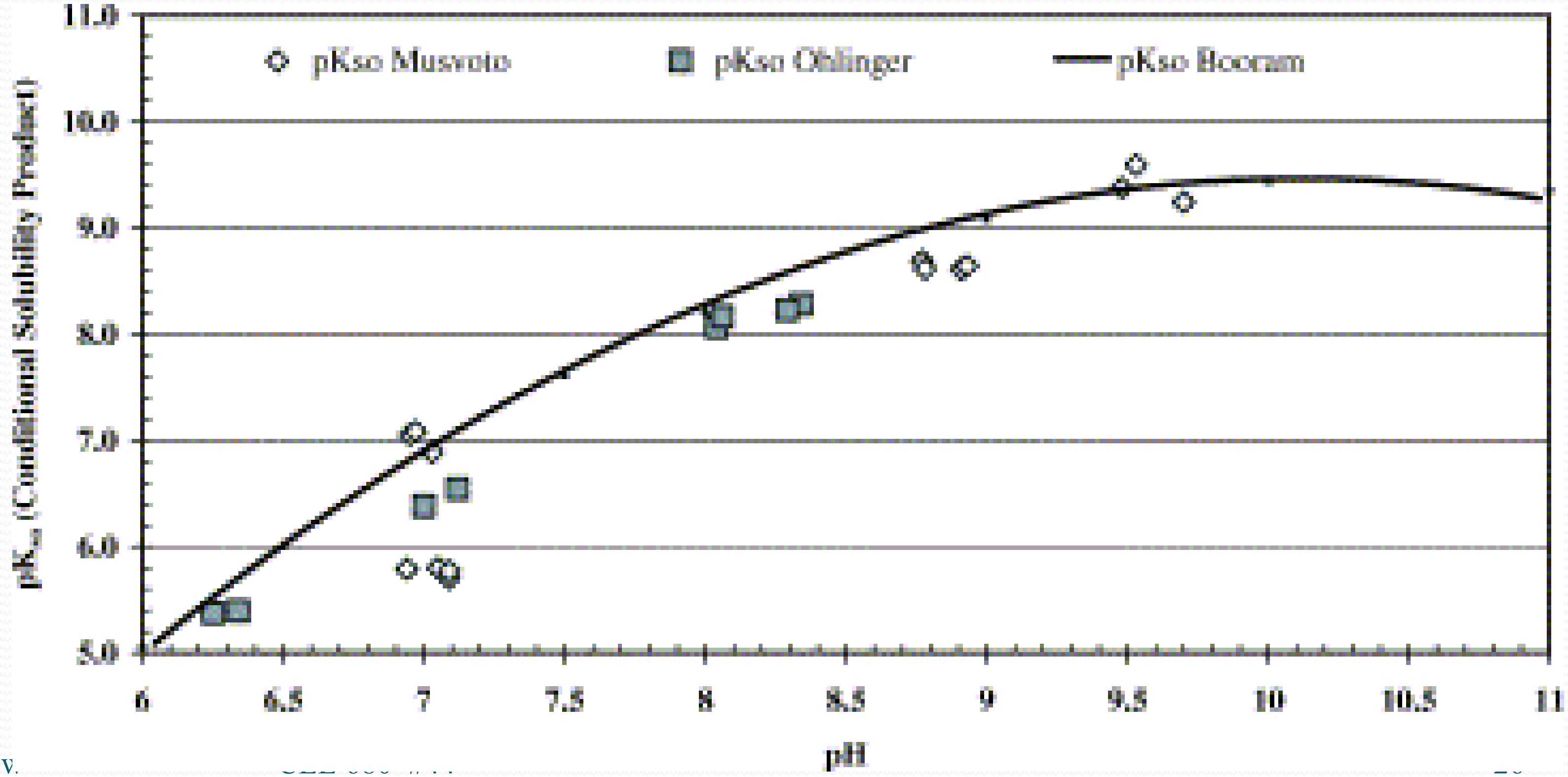
Ohlinger, K.N., T.M. Young, and E.D. Schroeder. 1998. Predicting struvite formation in digestion. Water Research 32:3607-3614.

Equilibrium relationship	p*K*	Ref.
$MgPO_4^{-} \Leftrightarrow Mg^{2+} + PO_4^{3-}$	4.80	Childs (1970)
$MgHPO_4 \Leftrightarrow Mg^{2+} + HPO_4^{2-}$	2.91	Taylor et al. (1963b)
$MgH_2PO_4^{+} \Leftrightarrow Mg^{2+} + H_2PO_4^{-}$	0.45	Morel and Hering (1993)
$MgOH^{++} \Leftrightarrow Mg^{2+} + OH^{-}$	2.56	Morel and Hering (1993)
$HPO_4^{2-} \Leftrightarrow H^{+} + PO_4^{3-}$	12.35	Martell and Smith (1989)
$H_2PO_4^{-} \Leftrightarrow H^{+} + HPO_4^{2-}$	7.20	Martell and Smith (1989)
$H_3PO_4 \Leftrightarrow H^{+} + H_2PO_4^{-}$	2.15	Martell and Smith (1989)
$MgNH_4PO_4 \cdot 6H_2O \Leftrightarrow Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O$	13.26	Ohlinger et al., 1998

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



Kinetic ppt/diss model

- Roncal-Herraro, 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:
- $r = r_+\left(1 - exp\left(\frac{2.303*SI}{2}\right)\right)$
  - where r_+ symbolizes the forward dissolution rate. Values of r_+ are found to be independent of pH and equal to $10^{-12.85\pm0.15}$ mol/cm^2/s in initially NH_4-free reactive fluids.
  - SI is the saturation index
    - $SI = log\left(\frac{\alpha_{Mg+2}\alpha_{NH4+}\alpha_{PO4-3}}{K_{so-struvite}}\right)$

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

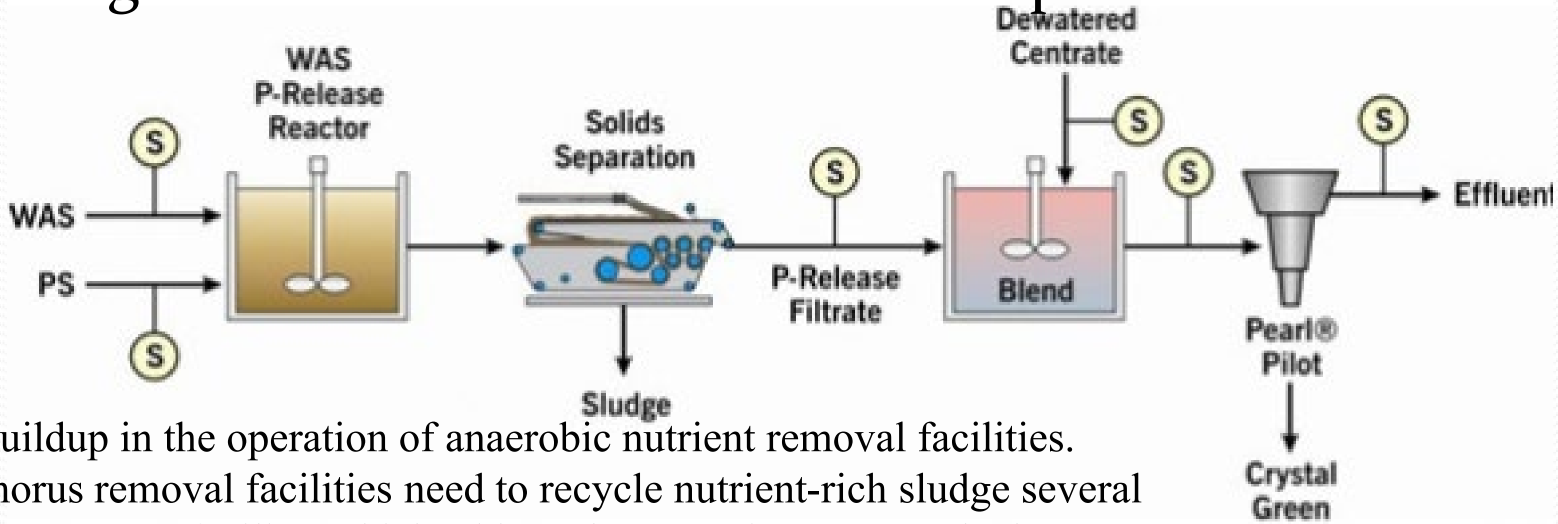
- FWHWRC is a 60-mgd advanced WWTP facility that utilizes 3 and 5-stage BNR secondary treatment and an array of tertiary treatment methods including: chemical clarification, granular media filtration, chemical flocculation/clarification, ultrafiltration membrane filtration, granular activated carbon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

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.

Waste Activated Sludge Stripping to Remove Internal Phosphorous

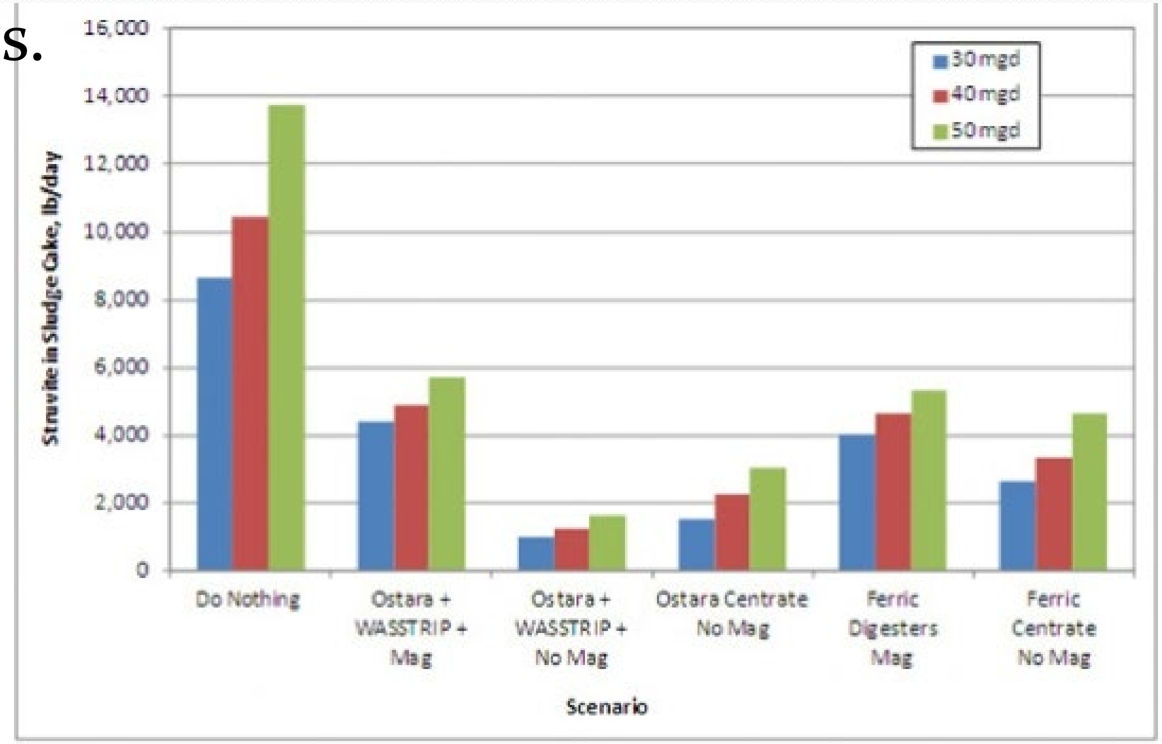
- In the WASSTRIP Process, primary sludge and waste activated sludge are anaerobically reacted to induce phosphorus release from phosphate accumulating bacteria. Filtrate from the reacted sludge blend is mixed with dewatering centrate and treated in Ostara's process.



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

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.



- To next lecture