TOPIC IV ENSC 4734

SOLID-SOLUTION EQUILIBRIA

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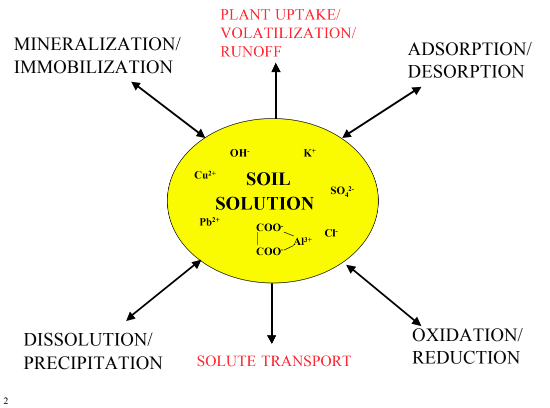

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Solid-Solution Equilibria

- All minerals are soluble to some degree
- Mineral Solubility Principles
  - Elucidate pedogenic processes
  - Predict solution concentrations of elements
  - Predict trace-element bearing phases in both natural and contaminated systems
  - Verify remediation processes

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Complexation/Chelation

- Inorganic/organic ligands are ubiquitous in soils
- Large fraction of soluble metals may be complexed
- Most analytical methods measure total concentrations
  - No difference between free and complexed
- Influence mobility/toxicity

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Complexation/Chelation

- Good estimates of solution chemistry can be obtained with the following info:
  - Concentration of all elements in soil solution influencing speciation of target element
  - Stability constants (K_s) or formation constants (K_f) for all possible soluble complex fromation reactions

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Complexation/Chelation

- Step wise stability constants
  - $M + L = ML$ $K_1 = [ML]/[M][L]$
  - $ML + L = ML_2$ $K_2 = [ML_2]/[ML][L]$
  - $ML_{n-1} + L = ML_n$ $K_n = [ML_n]/ ML_{n-1}][L]$
- Overall stability constant for ML_n
  - $\beta_n = [ML_n]/[M][L]^n$
  - $\beta_n = K_1K_2K_3 .... K_n$

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Complexation/Chelation

- Example: Cd^{2+} complexation by Cl^-

$Cd^{2+} + Cl^- = CdCl^+$	$K_1 = 10^{1.98}$
$Cd^{2+} + 2Cl^- = CdCl^0_2$	$K_2 = 10^{2.68}$
$Cd^{2+} + 3Cl^- = CdCl^-_3$	$K_3 = 10^{2.40}$
$Cd^{2+} + 4Cl^- = CdCl_4^{2-}$	$K_4 = 10^{2.50}$

Overall or cumulative complexation reactions

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Complexation/Chelation

- Example: Cd^{2+} complexation by Cl^-

$$K_n = \frac{[CdCl_n^{(2-n)}]}{[Cd^{+2}][Cl^-]^n}$$

Total Cd =

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Complexation/Chelation

- Example: Cd^{2+} complexation by Cl^-

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Complexation/Chelation

- Example: Speciation of Pb in pH neutral soil leachate (Ion association Model)
- Pertinent ligands are OH^-, Cl^-, SO_4^{2-}, CO_3^{2-} and fulvic acid (Ful^-)
- Assume only a singe ligand complexed to Pb: $PbCl^+$
- $[PbCl^+] = K_{fCl}[Pb^{2+}][Cl^-]$

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Complexation/Chelation

- Mass Balance expression for total Pb
- $Pb_T =$

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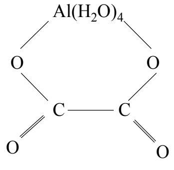
Complexation/Chelation

- Example: oxalic acid-Al hydroxide system



$HOOC\text{--}COOH = HOOC\text{--}COO^-$ $K_{a1}=10^{-1.25}$

$$\frac{(Al(COO^-)_2^+)}{(Al^{3+})((COO^-)_2^{2})} = K_s = 10^{6.1}$$

$HOOC\text{--}COO = {}^-OOC\text{--}COO^-$ $K_{a2}=10^{-4.27}$

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Complexation/Chelation

- Extent of metal complexation is easily calculated
  - pH
  - ligand concentration
  - Al^{3+} concentration

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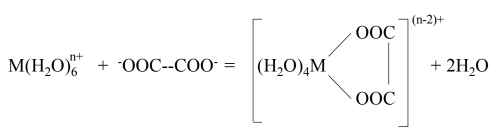
Complexation/Chelation

- Cheletes are favored thermodynamically



CH_3COO^- only bonds weakly to Al^{3+}, Why?

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Complexation/Chelation

- Previous calculations are laborious
- More difficult in soil solutions (multiple ligands and metals)
- Simplified using computer speciation models
  - GEOCHEM-PC (Parker et al., 1994)
  - MINTEQA2 (Allison et al., 1991)
  - SOILCHEM (Sposito and Coves, 1988)

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Solubility Relationships

- Ksp allows one to predict chemical composition of soil solution in equilibrium with particular mineral phase
- Example Cu^{2+} solubility controlled by malachite dissolution
- $Cu_2(OH)_2CO_{3(s)} + 2H^+ \rightarrow 2Cu^{2+} + CO_3^{2-} + 2H_2O$

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Solubility Relationships

- Equilibrium Expression

$$K_{diss} = \frac{(Cu^{2+})^2(CO_3^{2-})(H_2O)^2}{(Cu_2(OH)_2CO_3)(H^+)^2}$$

- Equilibrium constant for malachite dissolution can be determined from standard Gibbs free energy of formation (ΔG_f°)

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Solubility Relationships

- $\Delta G^\circ_r = m\Delta G^\circ_f \text{products} - n\Delta G^\circ_f \text{reactants}$
- $\Delta G^\circ_r = 2\Delta G^\circ_{f,Cu} + \Delta G^\circ_{f,CO3} + 2\Delta G^\circ_{f,H2O} - \Delta G^\circ_{f,mal}$
- $\Delta G^\circ_r = 2(65.52) + (-527.9) + 2(-237.114) - (-903.7) = 32.56$ kJ mol^{-1}

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Solubility Relationships

- $-RT \ Ln \ K = \Delta G^{\circ}_{r}$
- At 298.15 K (25ºC) and R=8.314 J K^{-1} mol^{-1}
- $K = 10^{-5.70}$

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Solubility Relationships

- Next step is to determine CO_3^{2-} and proton concentration
- Proton measured with pH meter, 7.5
- Carbonate:
  - $CO_2(g) + H_2O \dashrightarrow CO_3^{2-} + 2H^+$
- $K = 10^{-18.17} = \dfrac{(CO_3^{2-})(H^+)^2}{P_{CO2}}$

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Solubility Relationships

- $Log(CO_3^{2-}) = -18.17 + \log P_{CO2} + 2pH$
- Use $P_{CO2} = 10^{-2.5}$
- $Log(CO_3^{2-}) = -18.17 + -2.5 + 2(7.5) = -5.67$

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Solubility Relationships

- $(Cu^{2+})^2 = \frac{10^{-5.70}(H^+)^2}{CO_3^{2-}}$
- $(Cu^{2+}) = \frac{10^{-2.85}(H^+)}{(CO_3^{2-})^{0.5}}$
- $\log(Cu^{2+}) = -2.85 - 1/2\log(CO_3^{2-}) - pH$
- $\log(Cu^{2+}) = -2.85 - 1/2(-5.67) - 7.5 = -7.52$

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Solubility Relationships

- Ion Activity Product and Relative Saturation
- Previous example determine activity of a component based on controlling solid phase
- Procedure can work in reverse
- Difficult to determine spectroscopically

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Solubility Relationships

- Ksp describes activity ratio of products to reactants that will exist in soln at equilibrium with a mineral
- Ksp is mineral specific
- Solution values called the IAP
- IAP=Ksp if a specific mineral present and in equilibrium with soil components

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Solubility Relationships

- IAP is a property of the soil solution
  - Very difficult to accurately determine in soils
- Detail characterization of chemical composition of soil solution
  - Ion association model
  - Commercially available computer codes

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Solubility Relationships

- Example: lead contaminated soil
- SEM indicates lead associated with P
- Potentially 3 lead bearing phosphates
  - Lead phosphate ($Pb(PO_4)_{0.67}$)
  - Hydroxypyromorphite ($Pb(PO_4)_{0.6}(OH)_{0.2}$)
  - Plumbogummite ($PbAl_3(PO_4)_2(OH)_5$)

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Solubility Relationships

- Lead Phosphate
- $Pb(PO_4)_{0.67}$ ---> $Pb^{2+} + 0.67PO_4^{3-}$
- $Ksp = (Pb^{2+})(PO_4^{3-}) = 10^{-14.79}$

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Solubility Relationships

- Hydroxypyromorphite
- $Pb(PO_4)_{0.6}(OH)_{0.2} + 0.2H^+ \dashrightarrow Pb^{2+} + 0.6PO_4^{3-} + 0.2H_2O$
- $Ksp = \frac{(Pb^{2+})(PO_4^{3-})}{(H^+)^{0.2}} = 10^{-12.56}$

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Solubility Relationships

- Plumbogummite
- $PbAl_3(PO_4)(OH)_5 \bullet H_2O + 5H^+ \dashrightarrow Pb^{2+} + 3Al^{3+} + 2PO_4^{3-} + 6\ H_2O$
- $Ksp = \frac{(Pb^{2+})(Al^{3+})^3(PO_4^{3-})^2}{(H^+)^5} = 10^{-32.79}$

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Solubility Relationships

- Detailed chemical analysis and GEOCHEM-PC yielded:
  - $[Pb^{2+}] = 10^{-7.25}$
  - $[PO_4^{3-}] = 10^{-13.13}$
  - $[Al^{3+}] = 10^{-9.86}$
  - pH = 5.97

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Solubility Relationships

- IAP compared to Ksp
- Relative saturation: $\Omega = \frac{IAP}{Ksp}$
- Saturation index = logIAP - Log Ksp

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Solubility Relationships

- IAP is between Ksp and 0.1 Ksp ($0.1 < \Omega < 1$ and $-1 < SI < 0$) saturated
- IAP < 0.1Ksp ($\Omega < 0.1$ and $SI < -1$) undersaturated
- IAP > Ksp ($\Omega > 1$ and $SI > 0$) supersaturated

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Solubility Relationships

- Plumbogummite present assuming the following:
  - Equilbrium exists
  - Mineral activities unity
  - Soil water activity is unity
  - STP
  - All significant components in soil solution determined and modeled

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Solubility Relationships

- Deviations from solubility relationships
  - Metastability and the step rule
  - Poorly and microcrystalline solids
  - Solid solutions

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Stability diagrams

- Used to determine which solid phase(s) control the conc. of an element in the soil solution
- Constructed by converting solubility relationships into log terms and rearranging to form straight lines
- Advantage - several different solid phases can be compared at one time
  - Comparing IAP to K_{sp} for each possible mineral phase extremely tedious

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Stability diagrams

- Example: Gibbsite Dissolution

Calculate K from standard ΔG values

$Al(OH)_3 + 3H^+ \text{--->} Al^{3+} + 3H_2O$

$\Delta G_{rxn} = [(-491.61) + 3(-237.52)] - [(1158.24) + 3(0)]$
$= -45.92 \text{ kJ mole}^{-1}$

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Stability diagrams

- Example: Gibbsite Dissolution

ΔG_{rxn} = -RTlnK =
-(0.00831 kJ K^{-1} $mole^{-1}$)(298K)(2.303)log(K)

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Stability diagrams

- $Al(OH)_{3gibbsite}$ + $3H^+$ = Al^{3+} + 3 H_2O
- $(Al^{3+})/(H^+)^3 = 10^{8.04}$

  or
- log Al^{3+} = 8.04 -3pH

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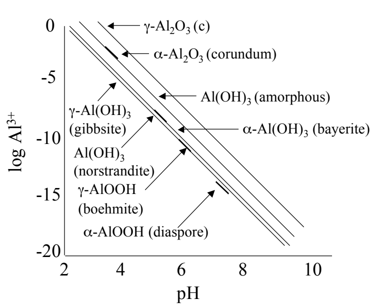
Stability diagrams



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Stability diagrams

- Line nearest the axis the most insoluble
- Solubility Al-oxides>corundum>bayerite>boehimite>nostrandite>gibbsite>diaspore
- Activity of Al^{3+} very pH dependent
  - decrease 100 fold for each unit increase in pH

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Stability diagrams

- Mineralogical characterization of sewage sludge: Pb associated with either silica or phosphate
- Two plausible mineral phases
  - Hydroxypyromorphite [$Pb_5(PO_4)_3OH$]
  - Alamosite [$PbSiO_3$]

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Stability diagrams

- Hydroxypyromorphite
  - $Pb_5(PO_4)_3(OH)_{(s)} + 7\ H^+ \text{-->} 5Pb^{2+} + 3H_2PO_4^- + H_2O$
- Alamosite
  - $PbSiO_3(s) + 2H^+ + H_2O \text{-->} Pb^{2+} + H_4SiO_4$

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Stability diagrams

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Stability diagrams

- Aluminosilicate minerals
- Can be expressed in terms of Al^{3+}, H^+, H_4SiO_4(e.g. kaolinite)

$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O$

Equilibrium Constant: $K = 10^{5.45}$

$$\frac{(Al^{3+})_2(H_4SiO_4)_2}{(H^+)^6} = 10^{5.45}$$

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Stability diagrams

- $2 \log Al^{3+} + 6\ pH = 5.45 - 2 \log H_4SiO_4$
- $\log Al^{3+} + 3pH = 2.73 - \log H_4SiO_4$
- Plot $\log Al^{3+} + 3\ pH$ on y-axis and $\log H_4SiO_4$ on x-axis
- Selecting diff values for $\log H_4SiO_4$

Log H_4SiO_4	$\log Al^{3+} + 3pH$
-2.5	5.23
-4.0	6.73
-5.5	8.23

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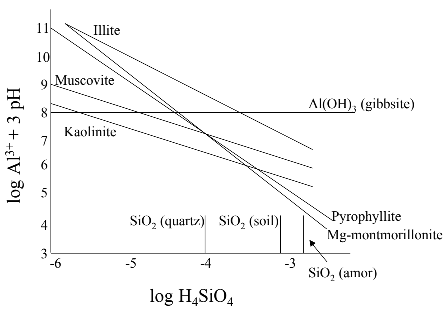
Stability diagrams



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Stability diagrams

- Soils are in a general state of dis-equilibrium
  - steady states only locally extablished
- Dis-equilibrium due to
  - slow rates of mineral neoformation/alteration
  - incongruent and slow dissolution rates
  - open system (leaching)
- Thermodynamics vs. kinetics

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