THE GEOCHEMISTRY OF COPPER LEACHING

SME COPPER HEAP LEACH SHORT COURSE SEATTLE WA FEB. 18TH AND 19TH, 2012

JOHN E. DREIER

JEDREIERGEO@COMCAST.NET

Mineral Dissolution Rates

- The ore and gangue are composed of discrete mineral species.

- Each mineral species has its own unique dissolution kinetics and solubility in the leach solution.

- The degree to which the ore and gangue minerals are soluble in the leach solution and the rates at which they dissolve determine copper leach kinetics and acid consumption.

- *Of the common rock-forming minerals, only quartz, rutile, and zircon are insoluble in leach solutions.*

Flow Through Mineral Reactor

Over the past 50 years thousands of rate measurements have been made. Mineral dissolution rates are reported as moles of mineral dissolved per sq. meter of mineral surface area per second (r). Mineral dissolution data shows that mineral dissolution kinetics depend on the following:

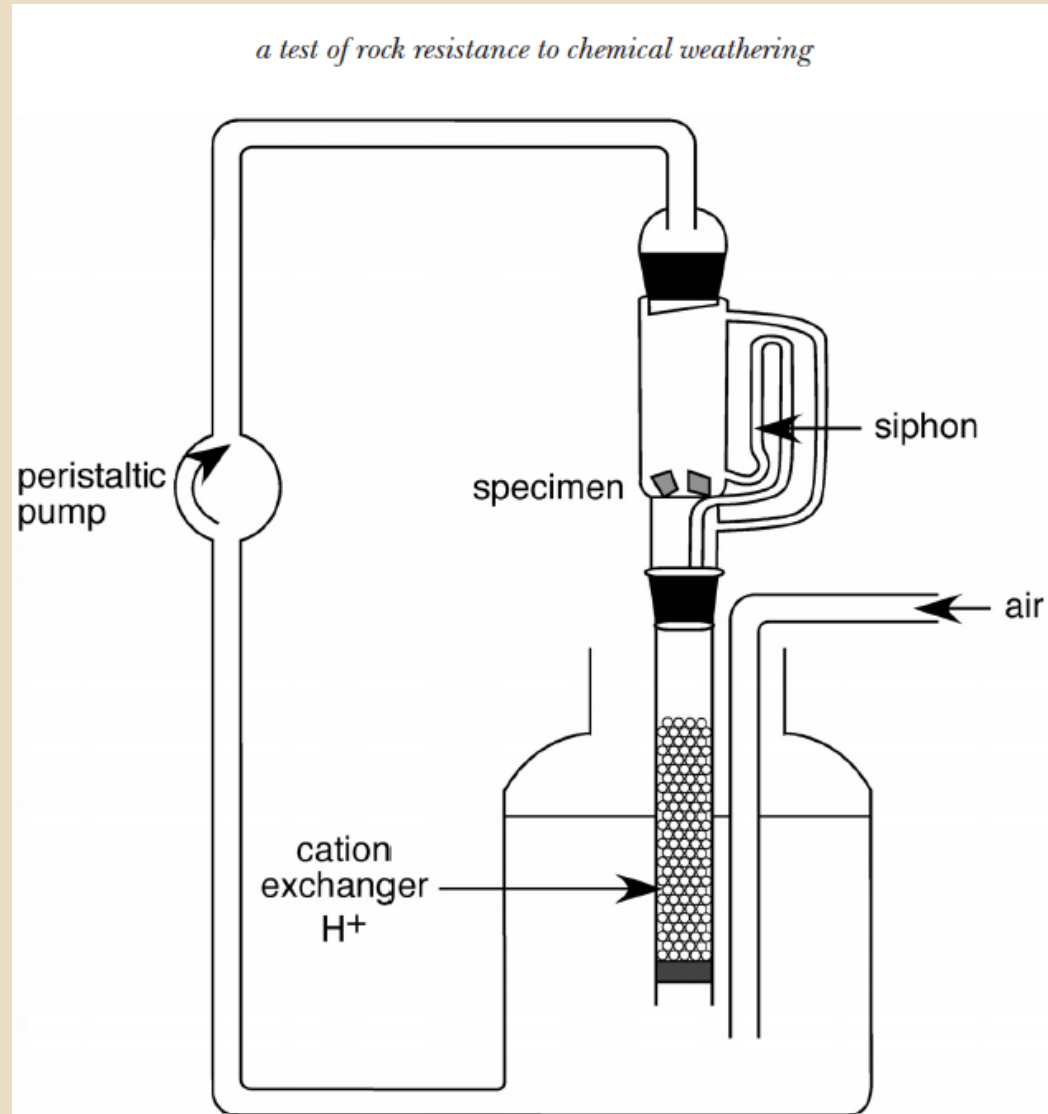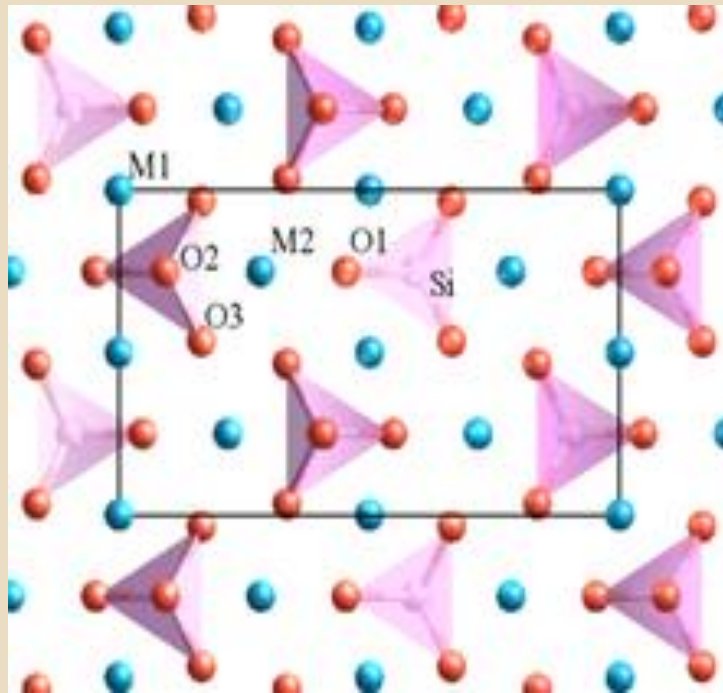*a test of rock resistance to chemical weathering*

Fig. 1. Experimental setup for the determination of the weathering rates of carbonates.

For Silicate Minerals, the connectivity of Oxygen in Si-O and Al-O tetrahedra

Rapid dissolution kinetics
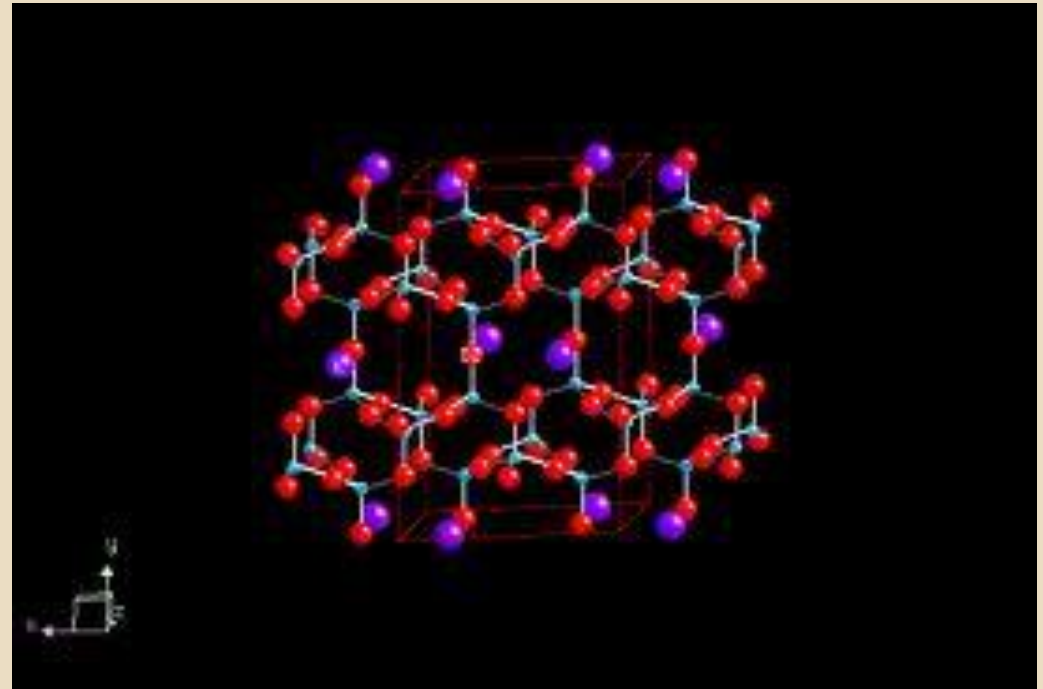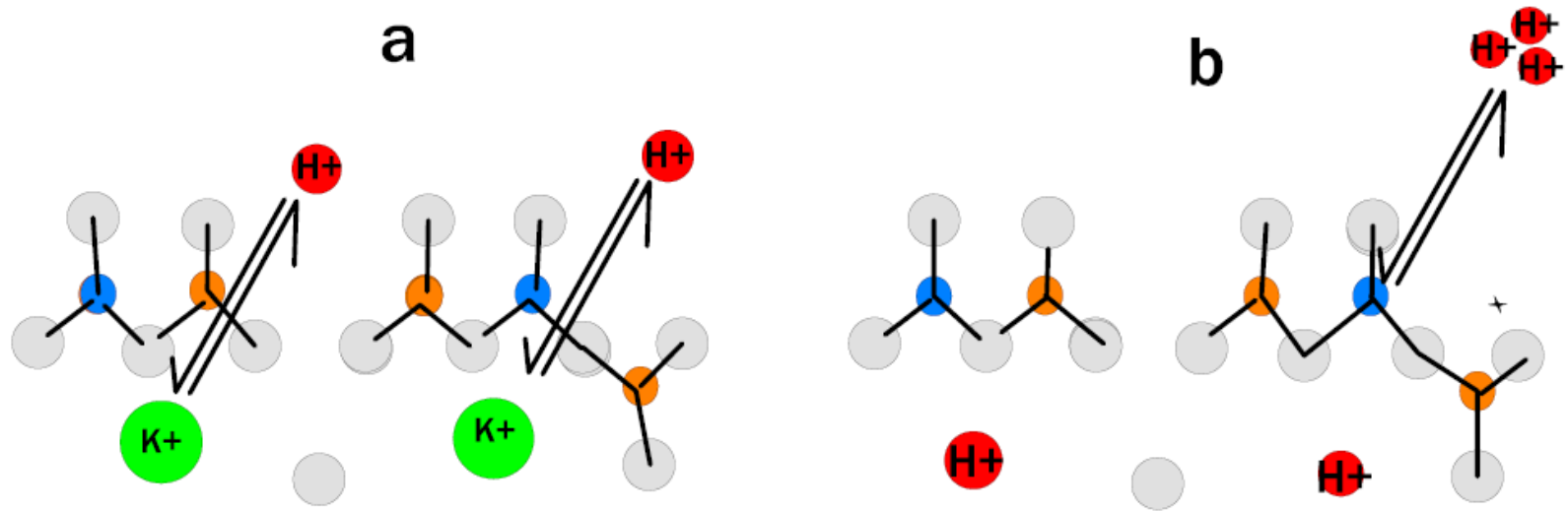Tetrahedra not connected

Olivine

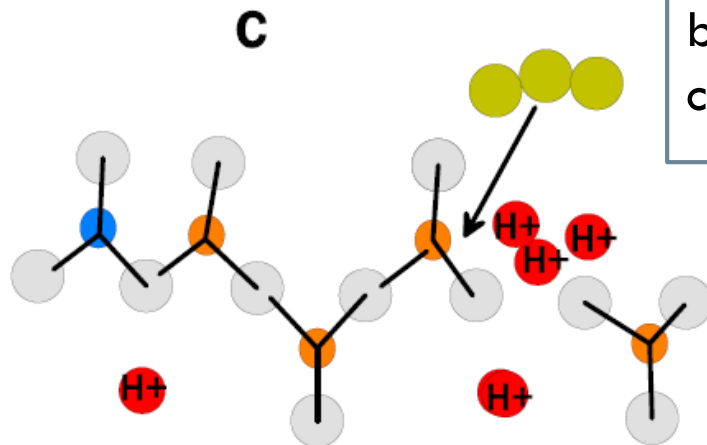Slow dissolution kinetics
Tetrahedra highly connected

Orthoclase

Steps in the Dissolution of Silicate Minerals (Example K-feldspar)

a – Exchange of H+ for K

b - Exchange of 3H+ for Al in Al-O tetrahedra

c - Exchange of 4H+ for Si in Si-O tetrahedra

Oxygen

Silicon

Aluminum

H2O

Mineral dissolution rates depend on mineral composition - plagioclase NaAlSi3O8-CaAl2Si2O8

As the Ca(2+) content of plagioclase increases (and the Na(1+) content decreases), Al(3+) substitutes for Si(4+) in the mineral structure. In the preceding slide we saw that acid solutions break the Al-O bond in aluminosilicate minerals before breaking the Si-O bond. As the proportion of Al relative to Si increases in plagioclase, the rate of mineral dissolution also goes up.
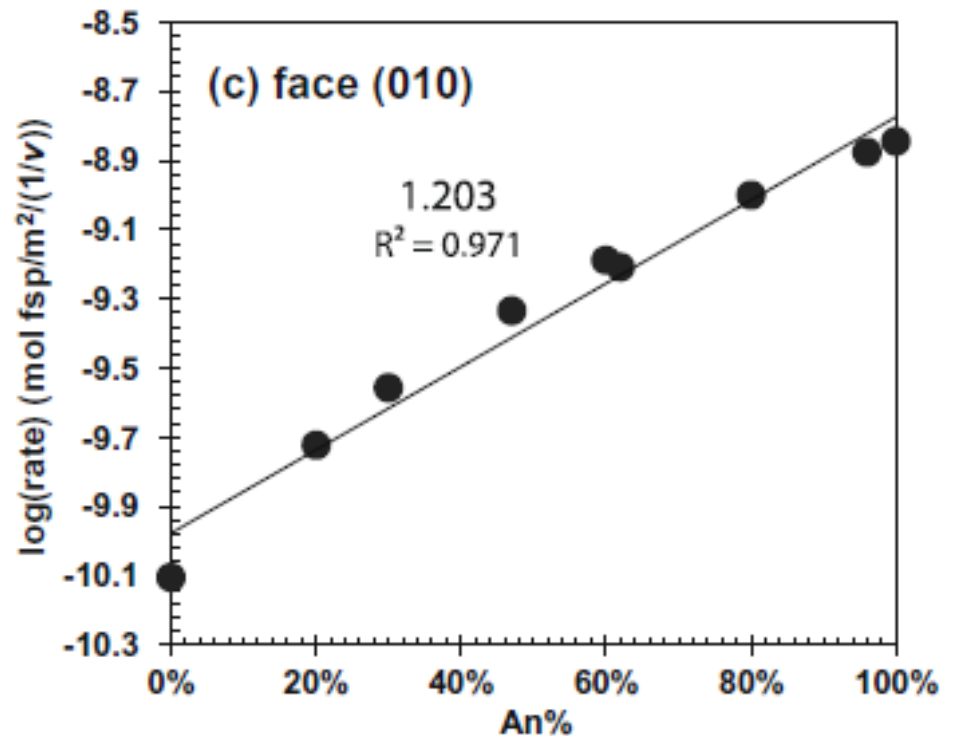

Fig. 5. Dependence of the dissolution rates of plagioclase on anorthite content under the control of Al preferential leaching mechanism (Numbers represent the slopes of linear curves) (a) face (001); (b) face (100); (c) face (010).

Under equilibrium and near equilibrium conditions as may occur within a rock fragment, mineral dissolution reactions are very slow. Dissolution kinetics increase as solution chemistry shifts away from equilibrium conditions, as may occur within the fines in a heap or on a the surface of a coarse ore particle
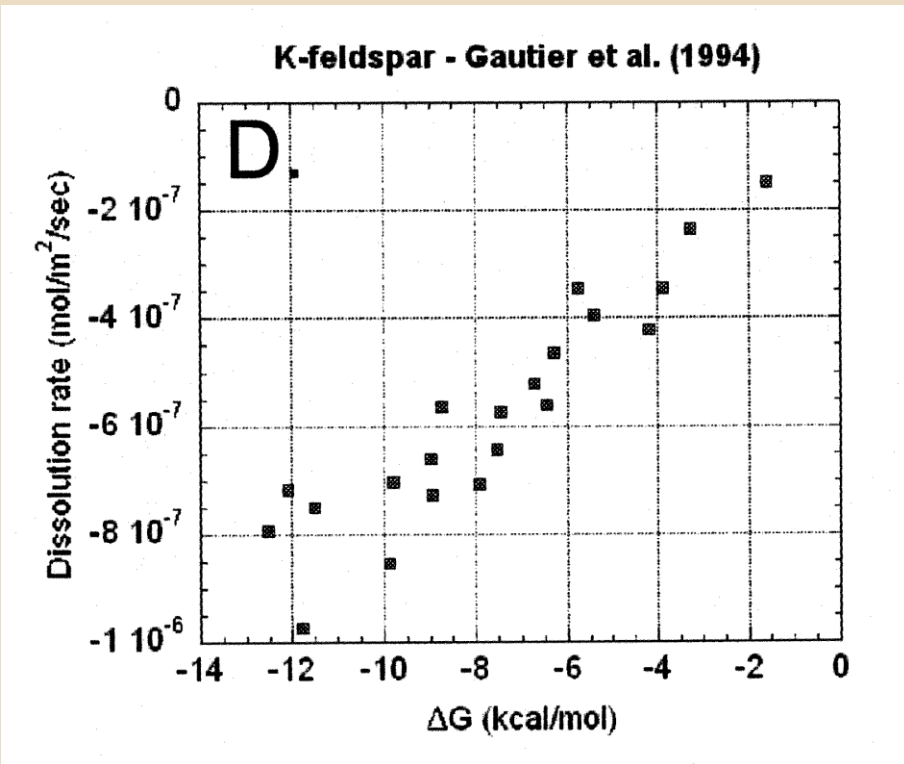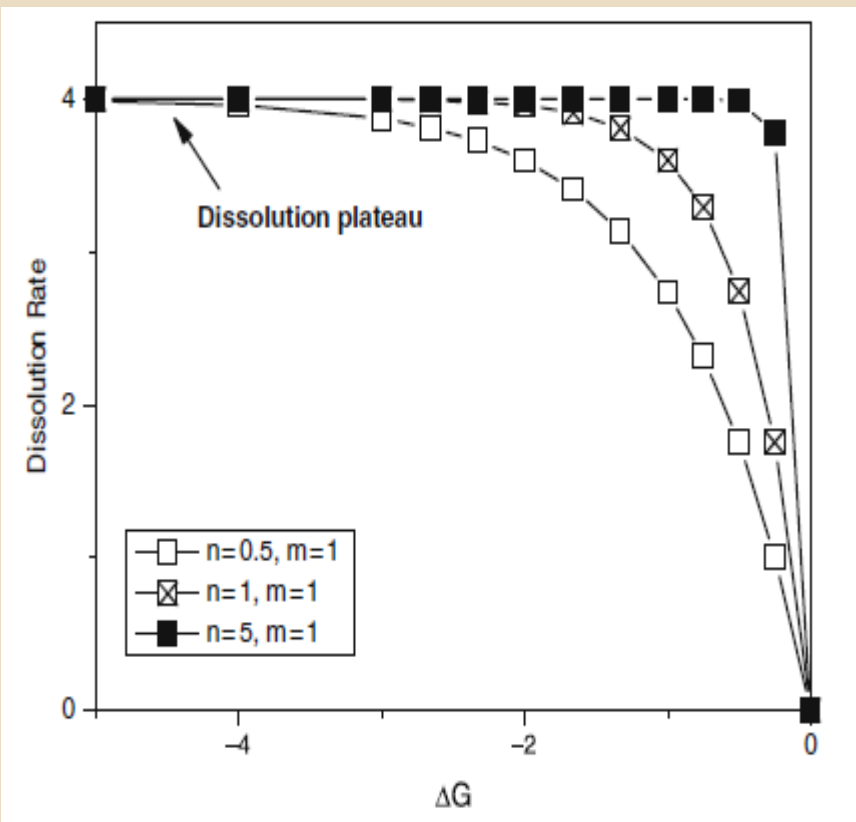

Mineral dissolution rates are measured in moles of mineral per square meter of surface area per second

Most copper minerals dissolve at much higher rates than most gangue minerals

Dissolution kinetics increase as pH is lowered. The lower the pH, the more effective H+ becomes in competing with cations in the mineral for O and other anions.

The chart is based on hundreds of far-from-equilibrium experiments using flow-through reactors to measure the dissolution rates of powered mineral material. The dissolution rates measured are maximum rates.
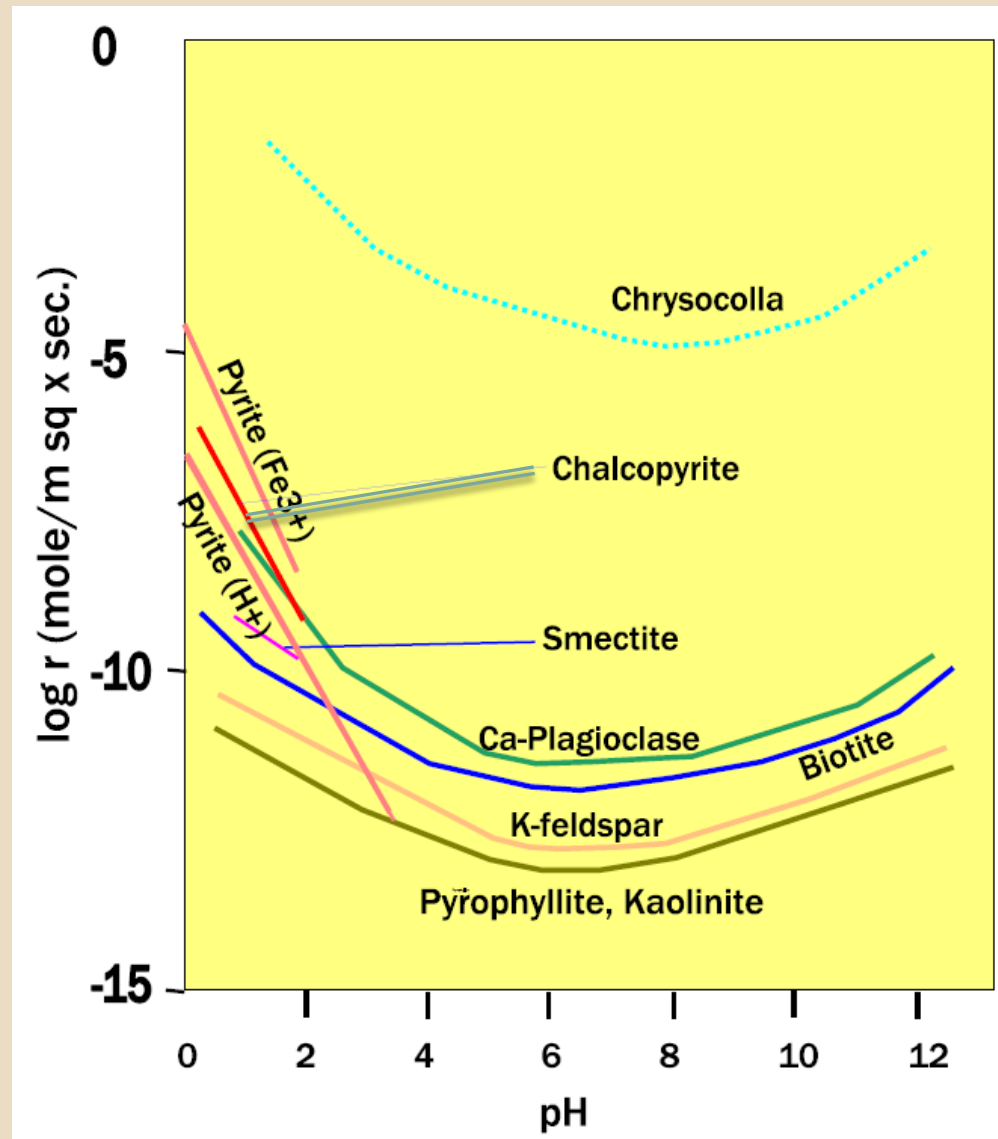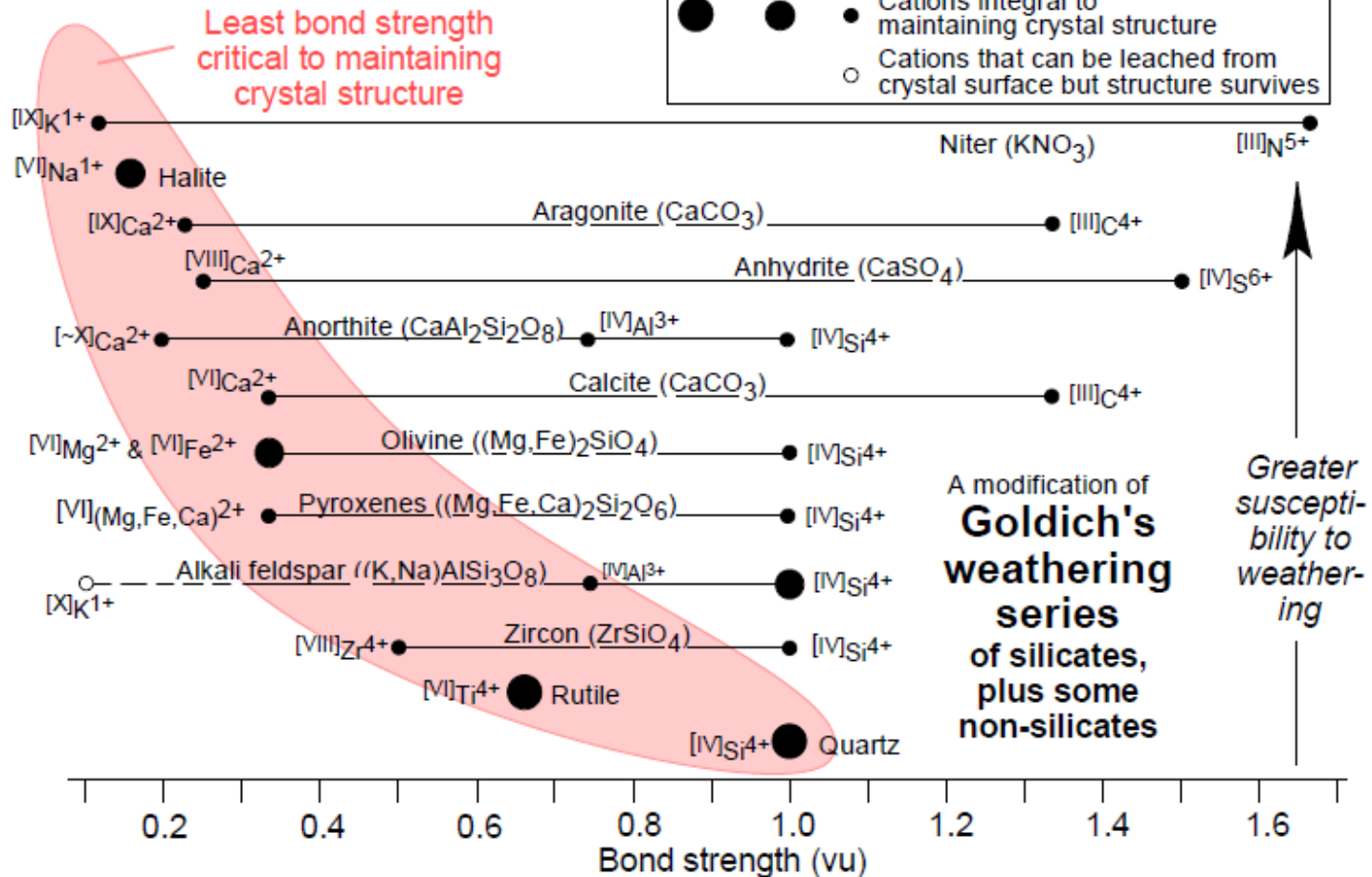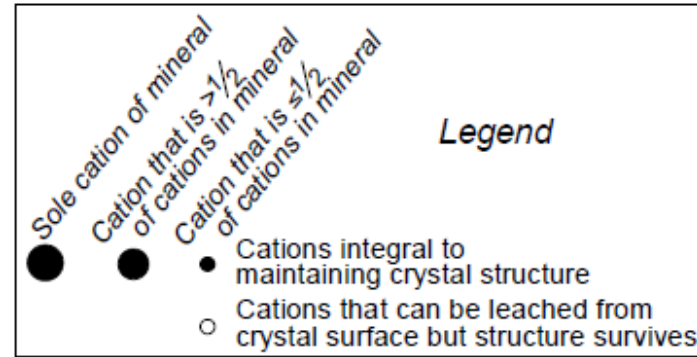

r = Rate of Dissolution in Moles/Meters sq. x seconds

Mineral Structure, Composition, and Dissolution Rates

Goldich Chart
The relative rates of gangue mineral dissolution in copper leaching

Slow Gang Dissolution
Low Acid Consumption

→

Rapid Gangue Dissolution
High Acid Consumption

Least
Stable
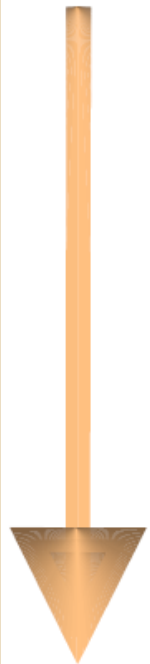
Most
Stable

STABLE IN LEACHING	UNSTABLE During LEACHING	DISSOLVE
Quartz	Pyrite Olivine Ca-Plagioclase Pyroxene Hornblende Biotite Na-feldspar K-feldspar Sericite muscovite	Calcite Dolomite

Summary of Work on Mineral Dissolution Kinetics

□ Mineral dissolution kinetics depend on:

▫ 1. Mineral Structure

▫ 2. Mineral composition

▫ 3. Distance from thermodynamic equilibrium

▫ 4. pH of the leach solution – dissolution kinetics increase as pH decreases. Under far-from-equilibrium conditions the kinetics of mineral dissolution are driven by pH.

Implications

□ Successful leaching requires low pH - high Eh conditions (within the Cu++ field of the preceding Eh-pH diagram) *everywhere* in the heap. This means within all of the micro-environments that may exist in the heap. Leaching does not occur to the extent that low Eh - high pH micro-environments exist in the heap.

□ Given the sensitivity of ore and gangue mineral dissolution rates (and solubilities) to pH and Eh, column &/or crib leach tests must be conducted under the Eh-pH conditions contemplated for the operation, otherwise the test results will give results that are highly misleading.
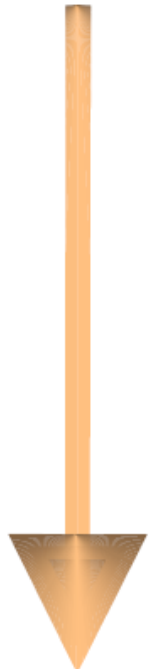
The Importance of Ore Deposit Geology
Acid consumption varies widely among common host rock types due to host rock mineralogy

Quartz-Hematite Breccia
very low acid consumption

Quartz-Sericite and Granite
Low Acid Consumption

Quartz-Sericite Rock

**Granite Porphyry
Quartz-Sericite Alteration**

Granite - quartz-Kfeldspar-biotite
Low Acid Consumption

El Pilar - Andesite-Monzonite- Moderate Acid Consumption

**Monzonite
Moderate Acid Consumption**

Andesite Porphyry
Moderate –Acid Consumption

Basalt
Moderate-High Acid Consumption

Basaltic Andesite "Ocoite"
Mantos de Catemu, Chile

Basaltic Andesite
Frankenstein Deposit, Chile

Basalt
Michilla

The Importance of Ore Deposit Geology
Acid consumption varies widely among common host rock types due to host rock mineralogy

Slow Gang Dissolution
Low Acid Consumption

⟶

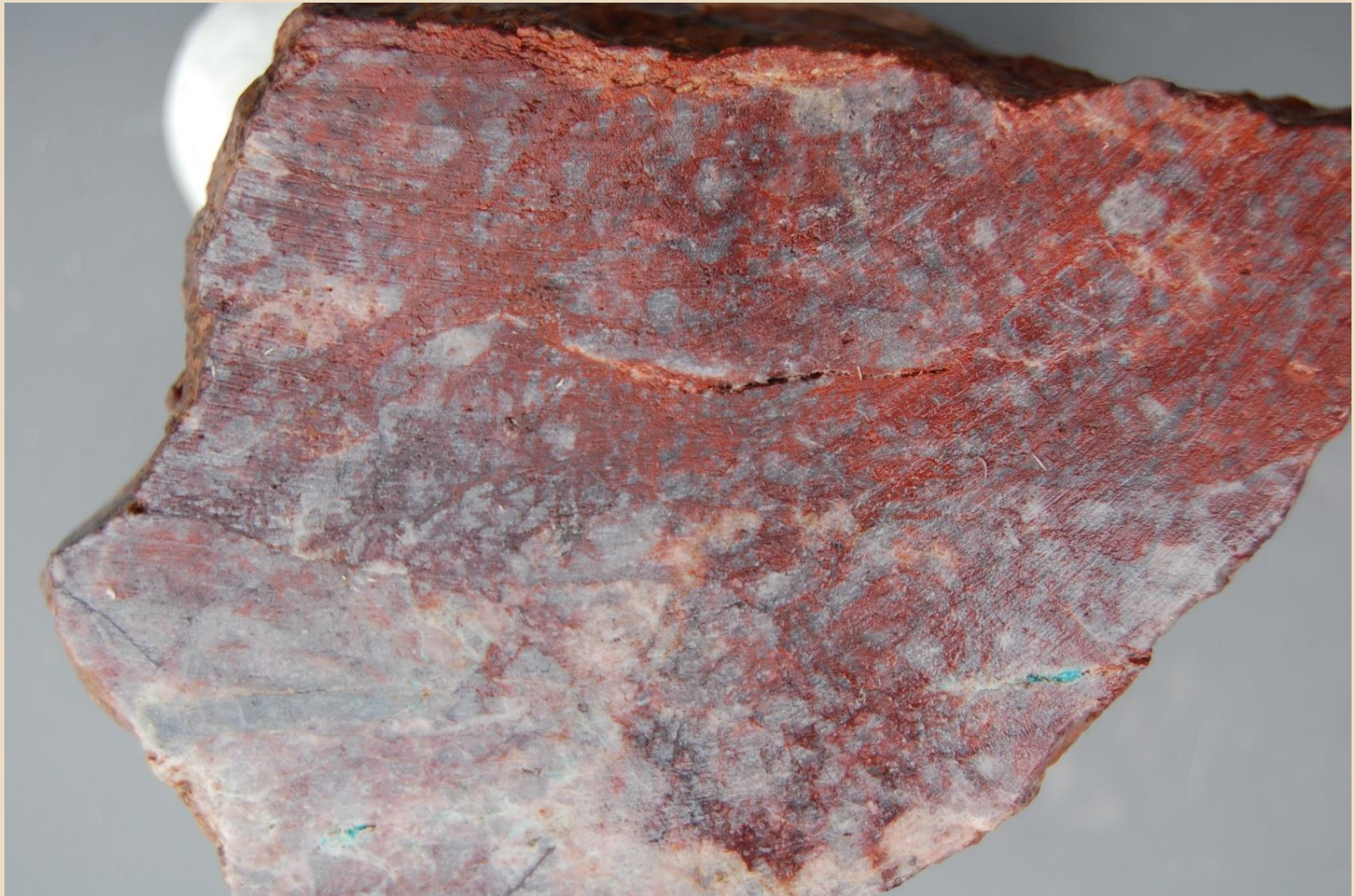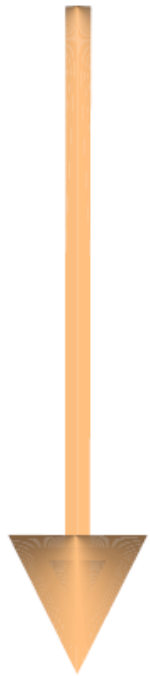**Rapid Gangue Dissolution**
High Acid Consumption

Least Stable

Most Stable

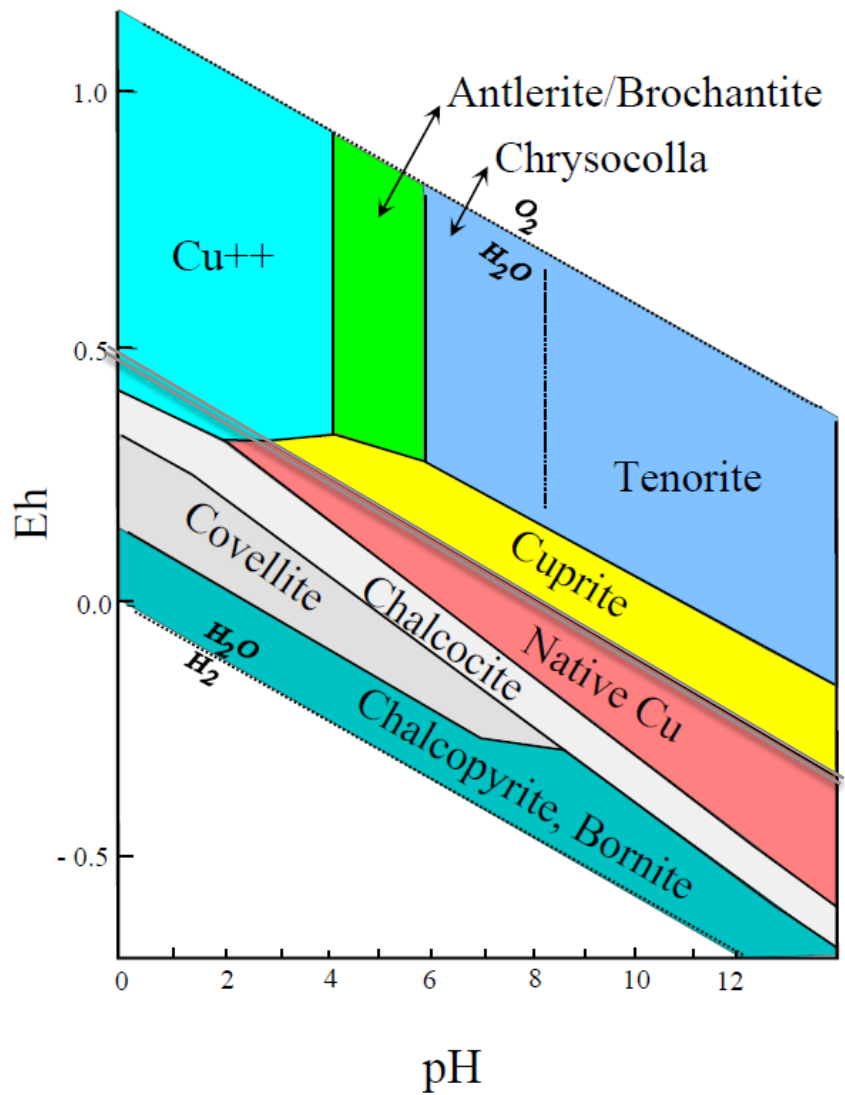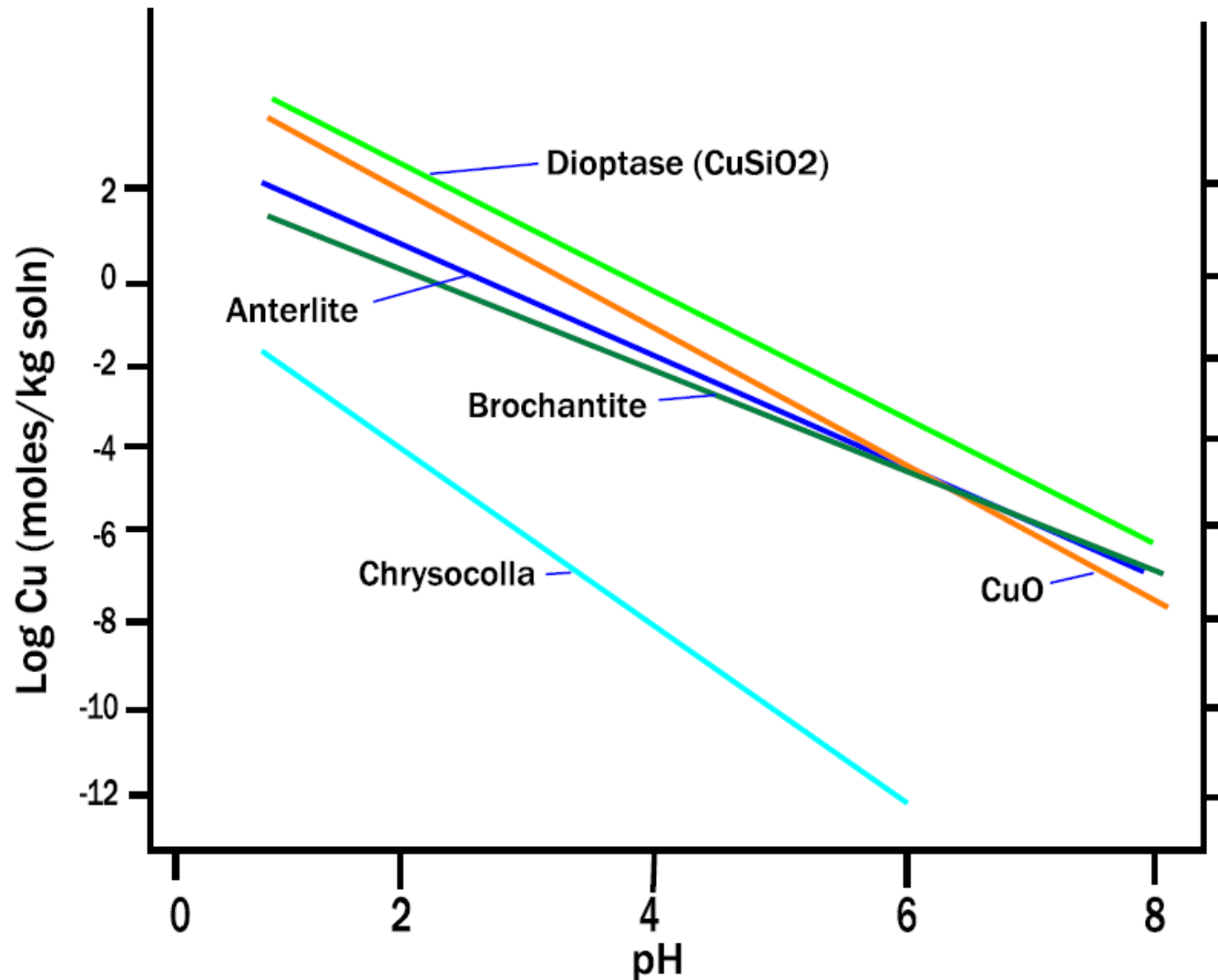| STABLE IN LEACHING	UNSTABLE During LEACHING	DISSOLVE
		Limestone Dolomite Ultramafic Basalt-Gabbro-Diabase Diorite Andesite Granodiorite
Quartzite	**El Pilar** Granite-Rhyolite Sericite Alteration	
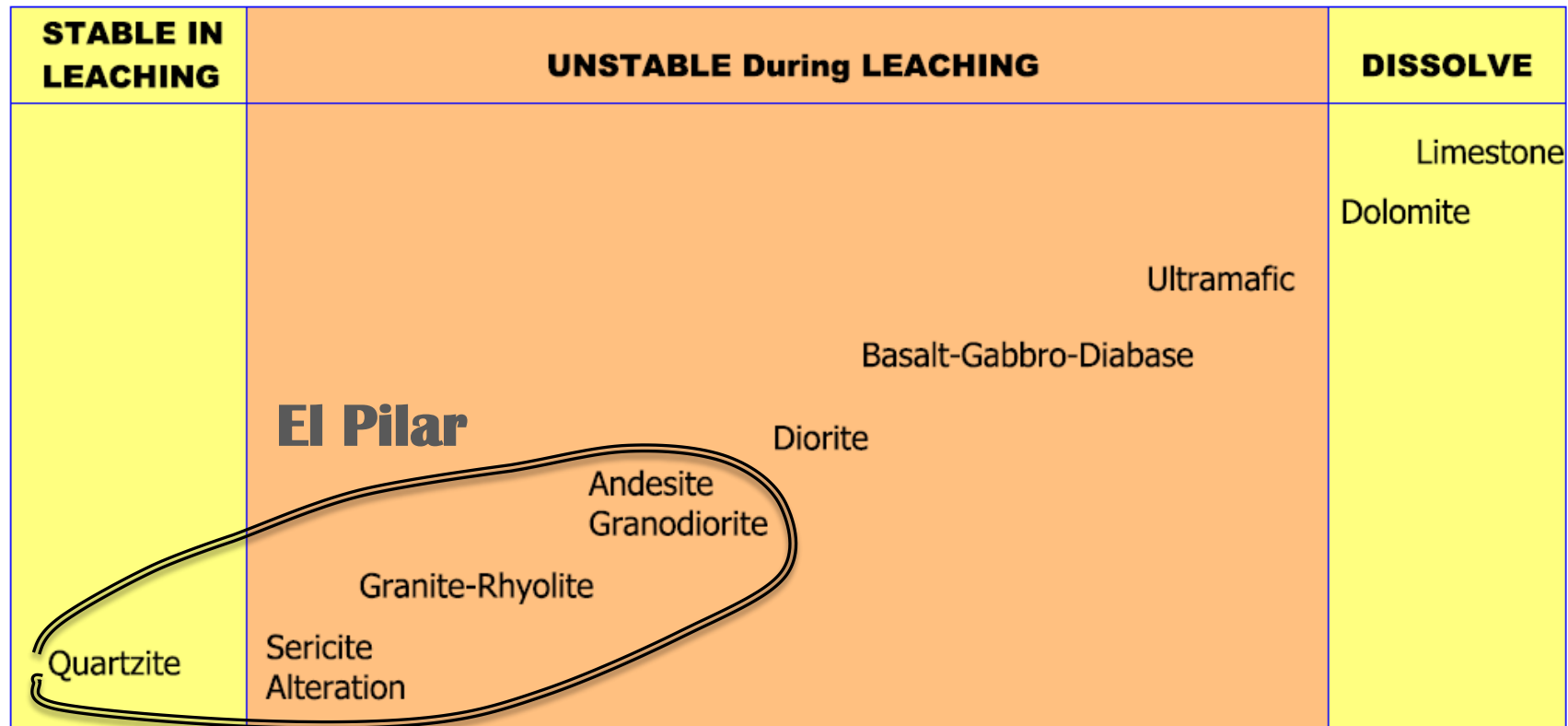
Stability Relationships for Copper Minerals and Dissolved Species

The solubilities of Copper Oxide Minerals are a function of pH
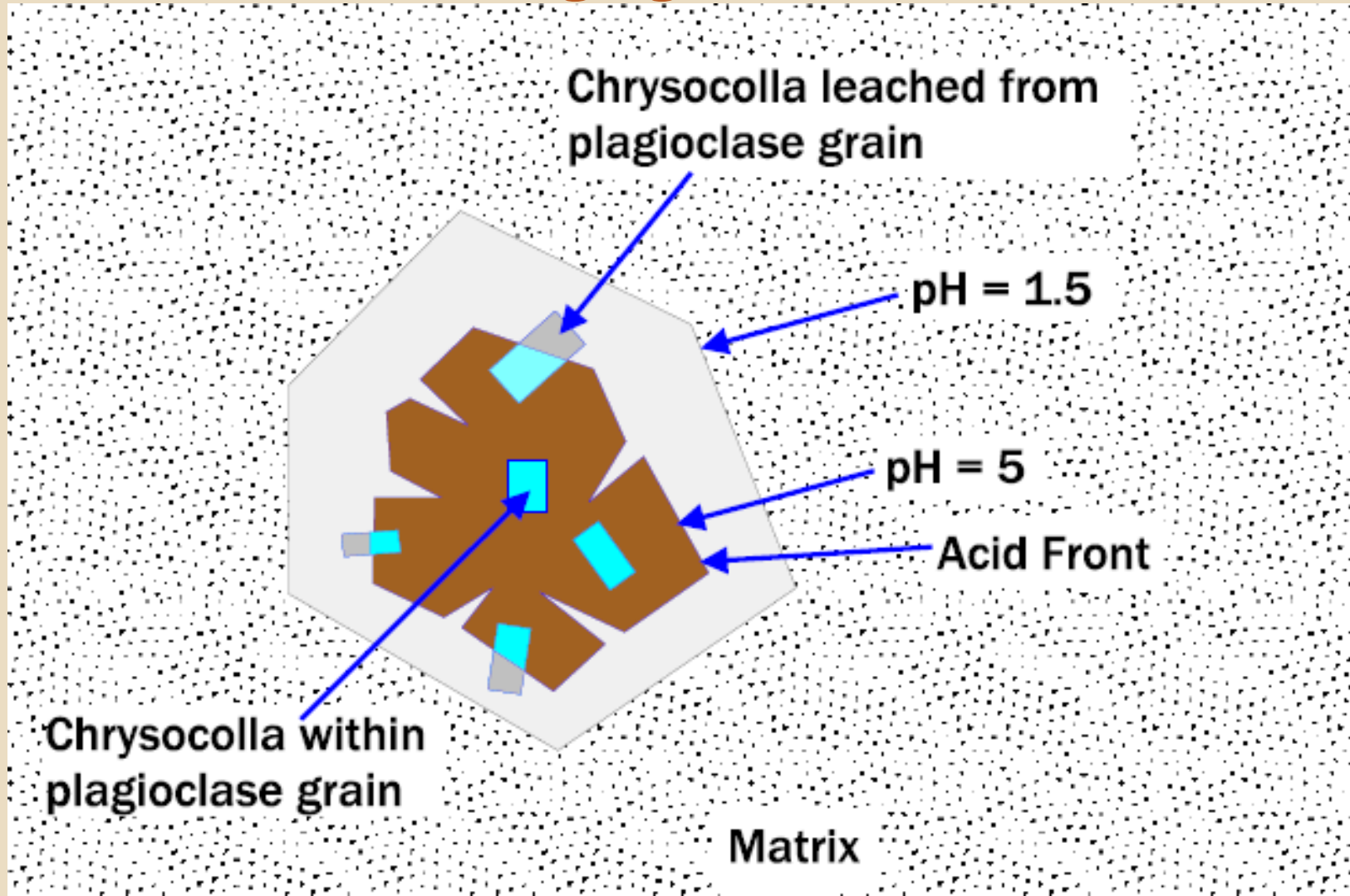
Monzonite After 240 Days of Leaching

5 cm

Rock Type and Copper Leach Kinetics
As the leach solution penetrates reactive rocks, pH increases and copper solubility and dissolution kinetics decrease –as do those for the gangue minerals

Chrysocolla leached from plagioclase grain

pH = 1.5

pH = 5

Acid Front

Chrysocolla within plagioclase grain

Matrix

The Dissolution of Ore and Gangue Minerals Consumes acid and Liberates Cations and Anions

K-feldspar

☐ $KAlSi_3O_8 + 4H^+ = K^+ + Al^{3+} + 3SiO_{2(quartz)} + 2H_2O$

Ca-plagioclase

☐ $CaAl_2Si_2O8 + 8H+ = Ca^{2+} + 2Al^{3+} + 2SiO_2 + 4H_2O$

Na-plagioclase (albite)

☐ $NaALSi_3O_8 + 4H^+ = Na^+ + Al^{3+} + 3SiO_2 + 2H_2O$

Biotite

☐ $K(Mg)_3(AlSi_3O_{10})(OH) +10H^+ = K^+ + 3Mg^{2+} +Al^{3+} + 3SiO_2 +5H_2O$

Chrysocolla

☐ $CuSiO_3.H_2O + 2H^+ = Cu^{2+} + SiO_2 + 2H_2O$
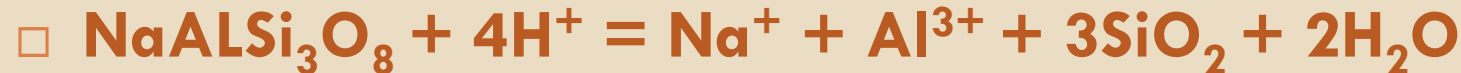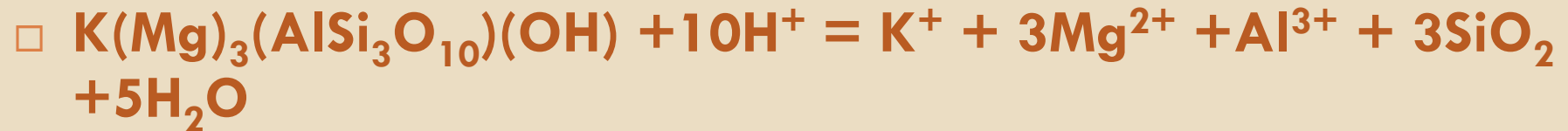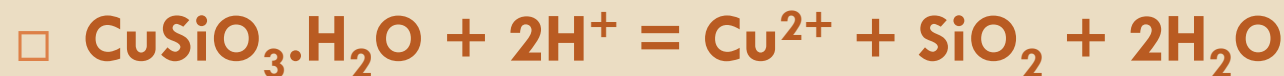
Dissolved Al vs. Weeks of Leaching
The Al Concentration Stabilized – Why?

Jarosite
Saturation vs. Weeks Leaching

Saturation Index (y-axis)

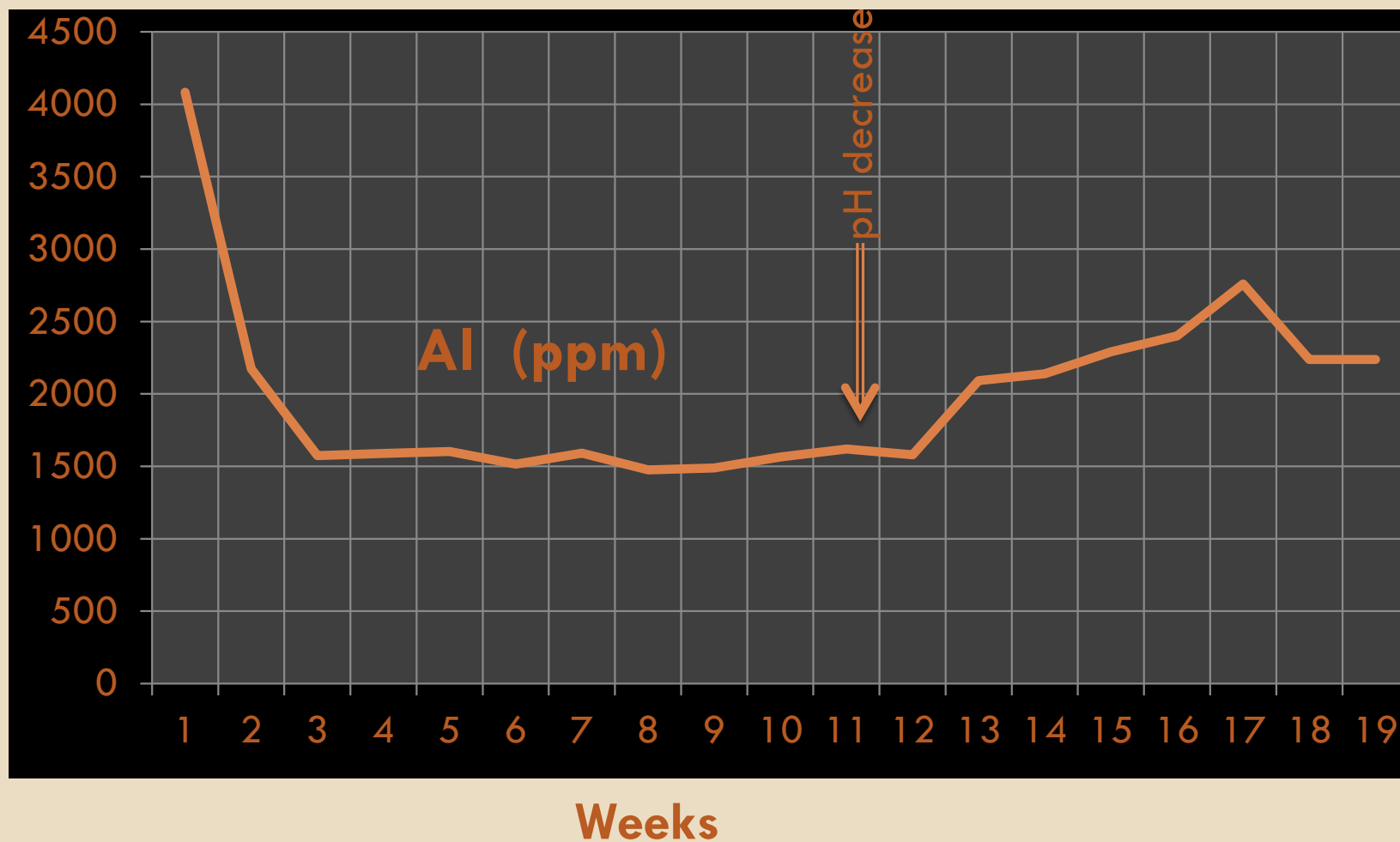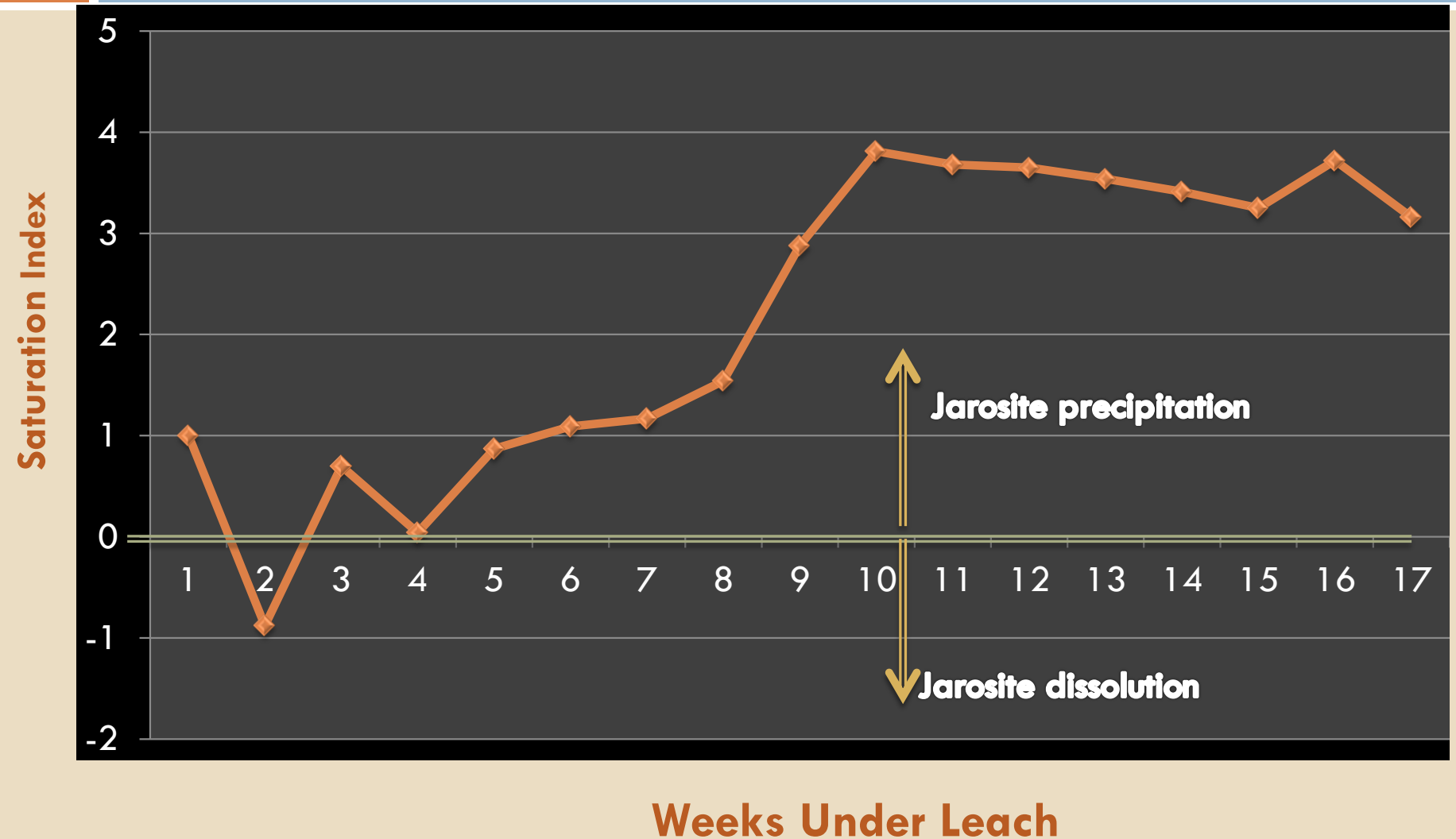**Weeks Under Leach** (x-axis)

Jarosite precipitation

Jarosite dissolution

The precipitation of new minerals in the heap consumes cations and anions and <u>produces</u> acid

Gypsum

- $Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4.2H_2O$: log Ksp = -4.6

Jarosite

- $K^+ + (Al^{3+} Fe^{3+}) + 2SO_4^{2-} + 6H_2O = K(AlFe)(SO_4)_2(OH)_6 +$ **$6H^+$**

Goethite

- $Fe^{3+} + 2H_2O = FeO(OH) +$ **$3H^+$**

Hematite

- $2Fe^{3+} + 3H_2O = Fe_2O_3 +$ **$6H^+$**
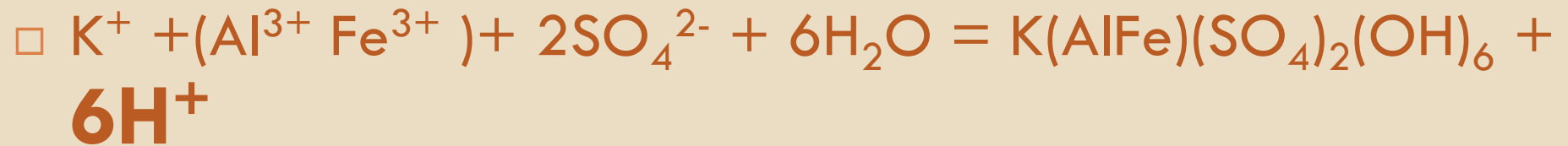
Jarosite Precipitation

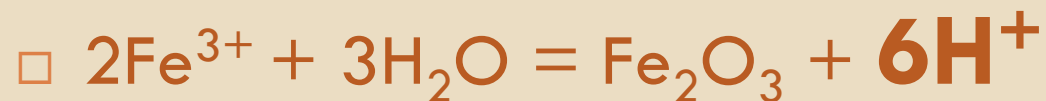- $K^+ + Fe^{3+} + 2SO_4^{2-} + 6H_2O = KFe(SO_4)_2(OH)_6 + 6H^+$

- A 1 tonne ore block in a heap saturated to 15% moisture containing 5 g/l Fe is capable of generating 3.94 kg of acid on the precipitation of jarosite.

- The precipitation of 5 g/l Al as aluminojarosite produces 8.5 kg of acid.

- Bottom line –

  - (1) Chances are, your leach solution has a lot more acid in it than you think

  - (2) Do not use free acid determinations to measure acid consumption they may over estimate acid consumption by 10kg/t or more!

  - The closure of a heap will take much more time and water than you might otherwise anticipate

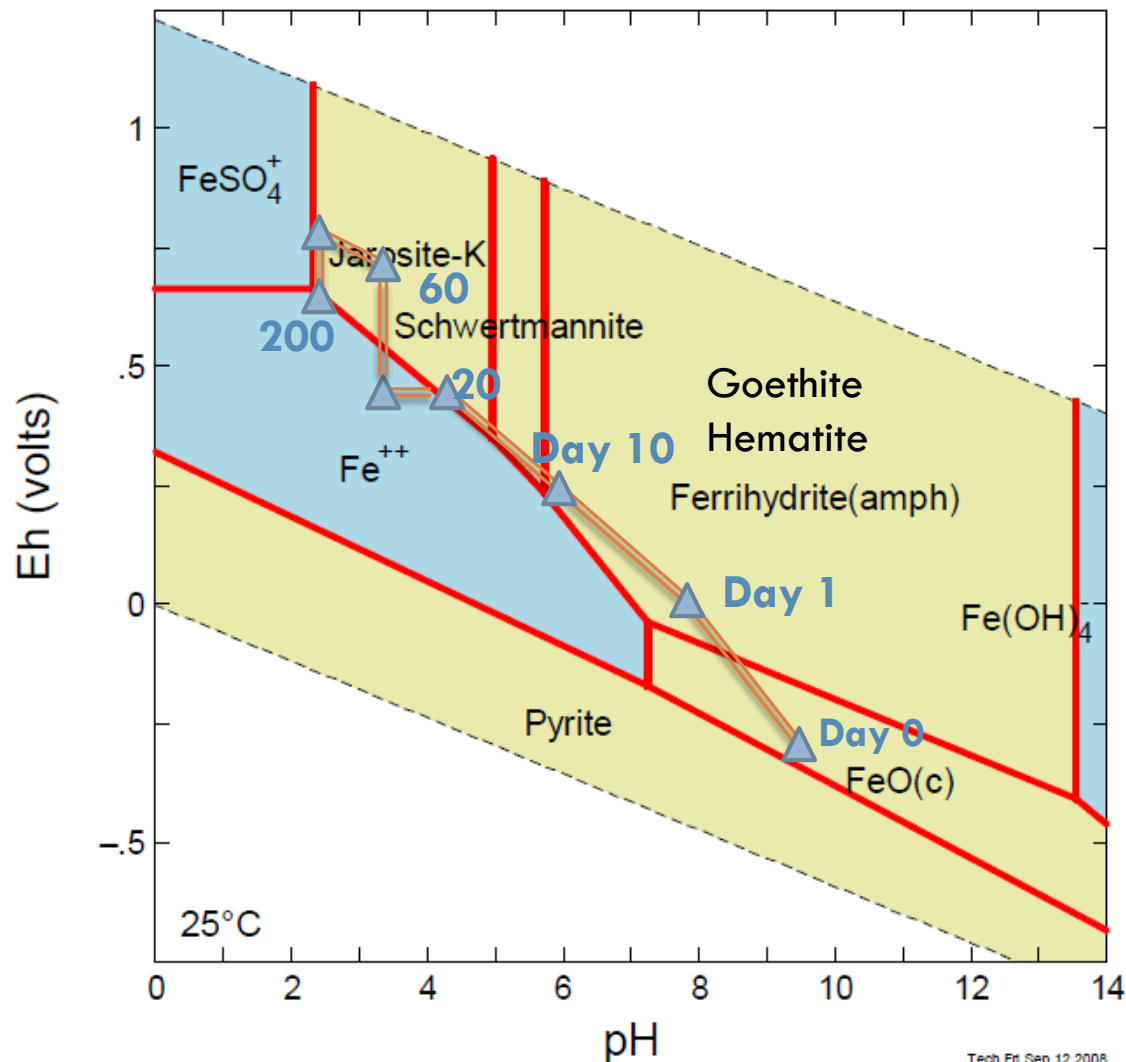# Eh-pH Controlled by Precipitation and Dissolution of Jarosite

$$K^+ + Fe^{3+} + 2SO_4^{2-} + 6H_2O = KFe(SO_4)_2(OH)_6 + 6H^+$$

Eh-pH path of a leach solution during a 200 day column leach test. Solution chemistry tends to stabilize at or near the jarosite-Fe3+ or Fe2+ boundaries
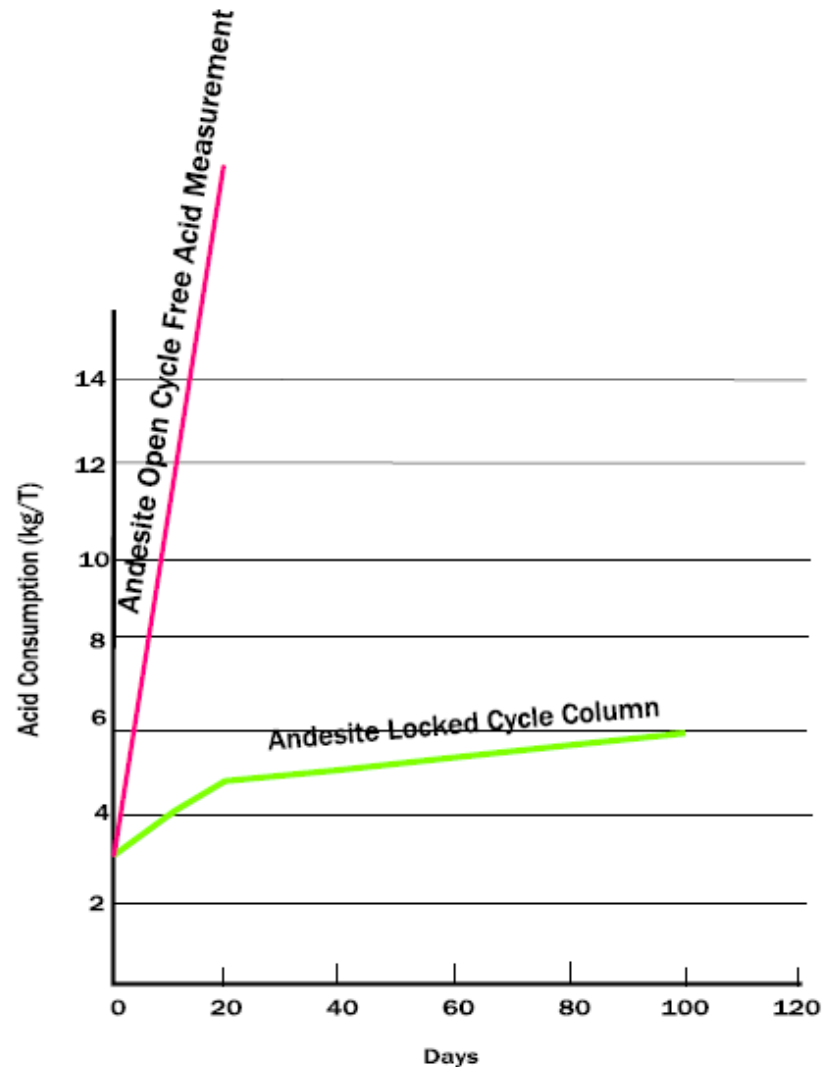
Incongruent Dissolution of Silicate Minerals

El Pilar C-1 clay formed in plagioclase sites after 120 days of leaching

The Incongruent Dissolution of Ca-Plagioclase and Montmorillonite

Anorthite + $2H_4SiO_4$ ⇒ $1/2$Ca-Montmorillonite + H_2O

Montmorillonite + $4H^+$ + $4H_2O$ ⇒ Kaolinite + $2Ca^{2+}$ + $4H_4SiO_4$
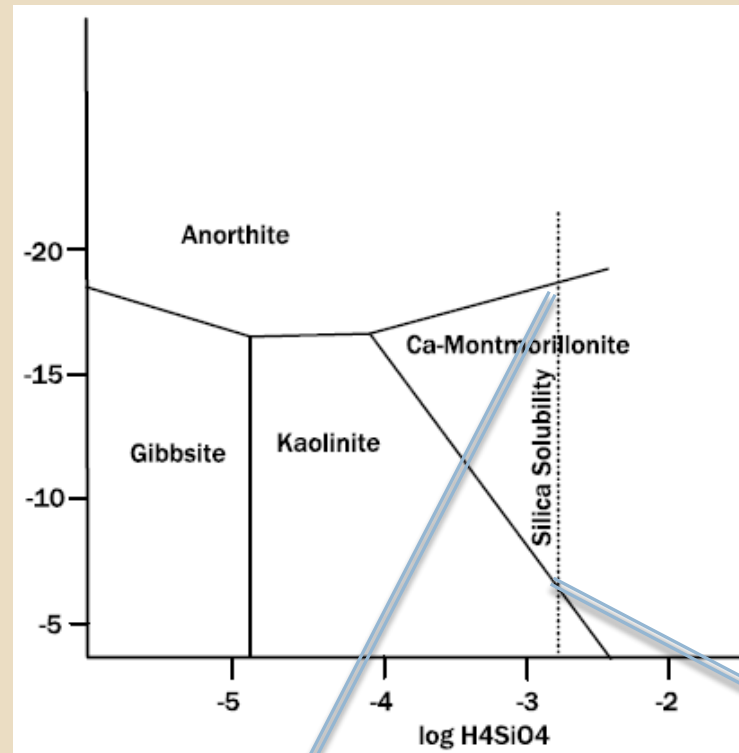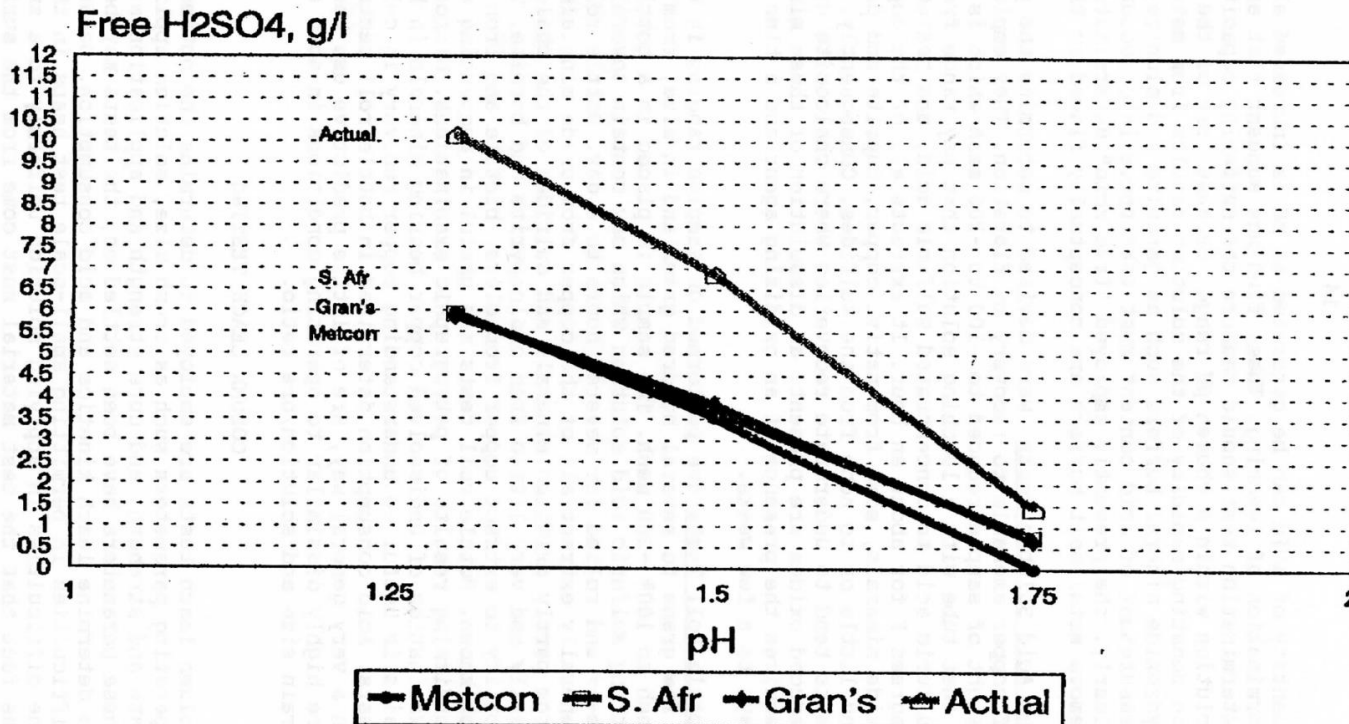
Acid Consumption
Open Cycle vs. Locked Cycle

Free Acid Measurement in Synthetic Solutions

Free Acid Concentration vs. pH
10 g/l Synthetic Leaching Solution

Free H2SO4, g/l

Fig. 16. Comparison of "free acid" measured by 3 methods and the actual amound added to the sample.

The use of free acid measurements to determine acid consumption is highly problematic

Summary

- Mineral dissolution kinetics and solubilities are dependent on pH and Eh.

- *Thus, column and crib leach tests must be run under the conditions of Eh and pH anticipated for the operation or the results will be meaningless and highly misleading.*

- Copper leaching includes mineral dissolution and mineral precipitation reactions.

- Leach kinetics and acid consumption depend on ore and gangue mineralogy

Summary

- The incongruent dissolution of silicate gangue minerals consumes acid and liberates cations & anions.

- The precipitation of new minerals consumes cations & anions and produces acid.

- Due to the acid consumption-creation duality of copper heap leaching, the determination of acid consumption and the overall chemistry of the leaching process must be quantified by means of locked-cycle column and crib tests. This is also important in evaluating potential environmental impacts.

- Free acid determinations give highly misleading results as they destroy the acid producing half of the duality.

Tibet
Chrysocolla coating a stream bed 10 km downstream from a porphyry copper deposit