From Research to Remediation – 42 Years of AMD Hydrogeochemistry

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USGS
science for a changing world

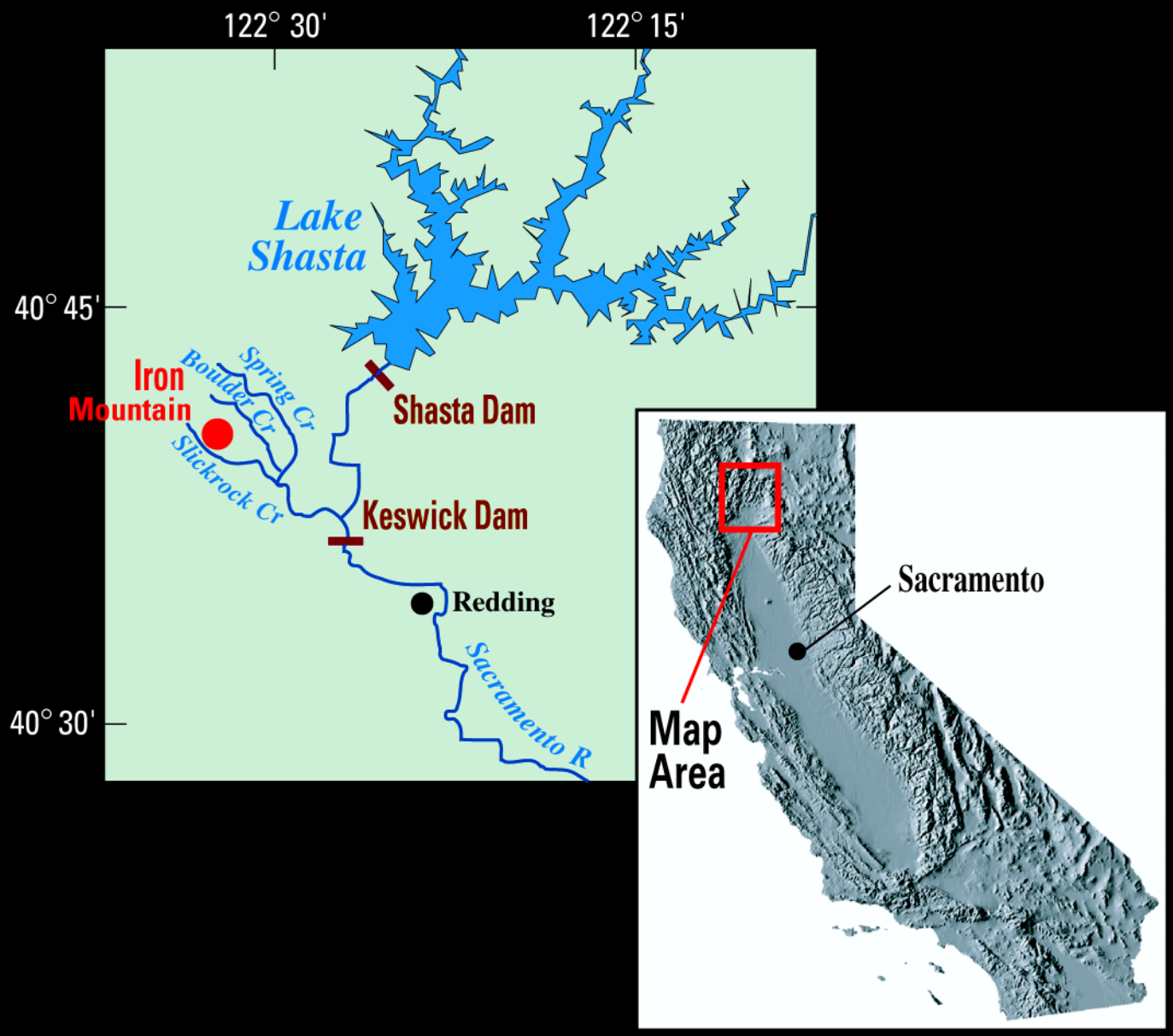
My introduction to AMD: Iron Mountain 1974-76 (with followup)

Iron Mountain – Mining, Waste Discharge, and Superfund site (1983 – present)

- Largest producer of Cu in California
  - Active mining 1880s – 1960s
- Total (pre-weathering) massive sulfide deposit size ~ 34 Mt

- Largest mine waste discharger in California
  - Annual discharge (pre-treatment): 740 kg Cu+Zn / day
  - At current rate, acid discharge would continue for ~ 3,000 yrs
- Numerous (~ 40) fish kills since 1940
  - Up to 100,000 anadromous fish killed in a single event
  - Ranked 3rd worst Superfund site in California

- Oct. 19, 2000: Out-of-court CERCLA settlement reached for a total of $862 million and remediation to be completed by 2030


122° 30'
122° 15'
40° 45'
40° 30'
Lake Shasta
Iron Mountain
Boulder Cr
Spring Cr
Slickrock Cr
Shasta Dam
Keswick Dam
Redding
Sacramento R
Sacramento
Map Area

Mt Shasta
Iron Mountain Mine
Shasta Dam
Keswick Reservoir
CDF
Pump Station 3
Pump Station 2
Pump Station 1
Dredge
Spring Creek Arm of Keswick Reservoir
Spring Creek Debris Dam
Lime Slurry Plant

Photo: Bill Rich
Prior to 1995

Conditions typical circa 1964 to 1995

Mixing point of pH 2.8 AMD with neutral pH lake water

Iron Mountain

Underground in 1990

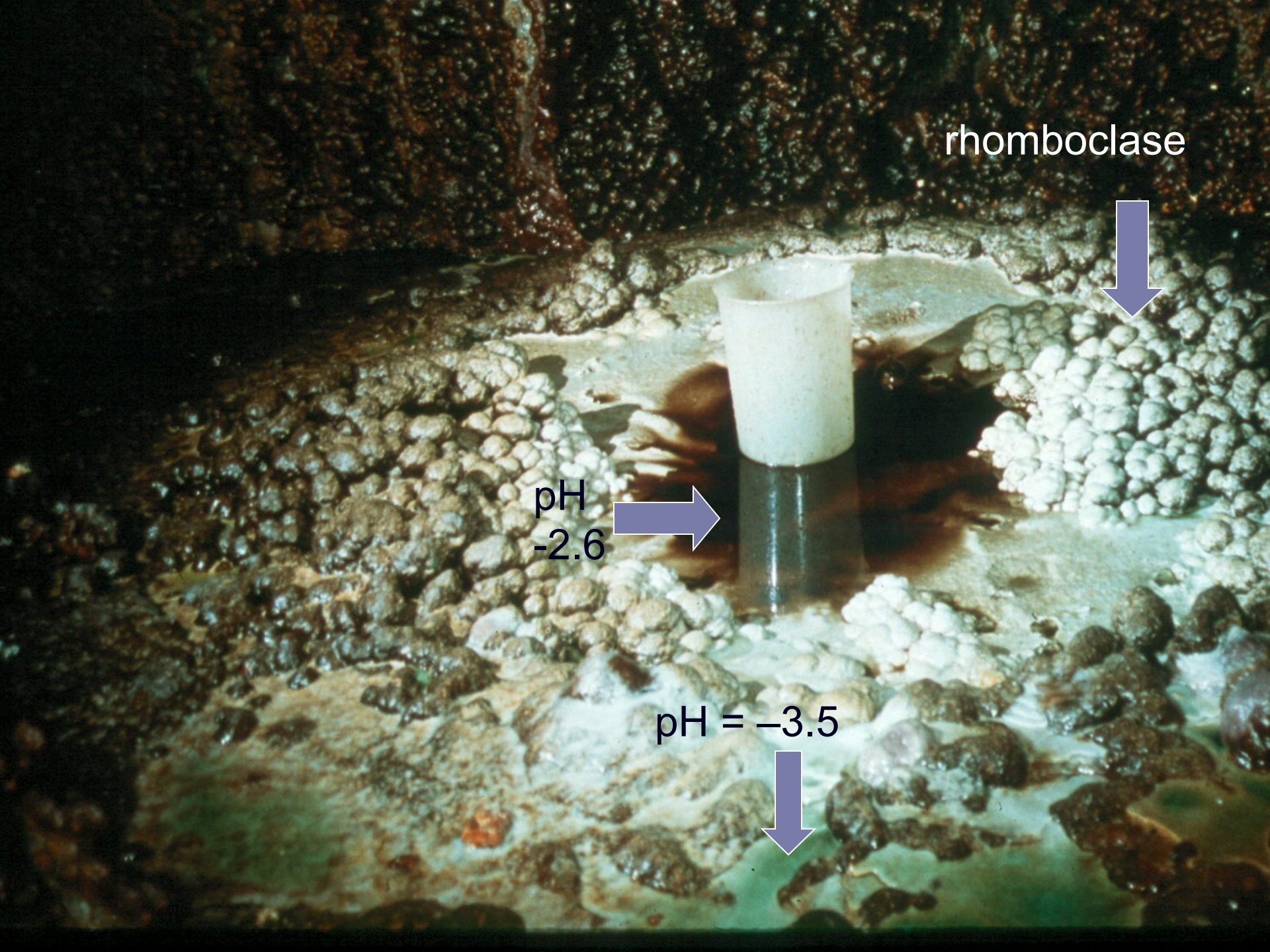
Melanterite

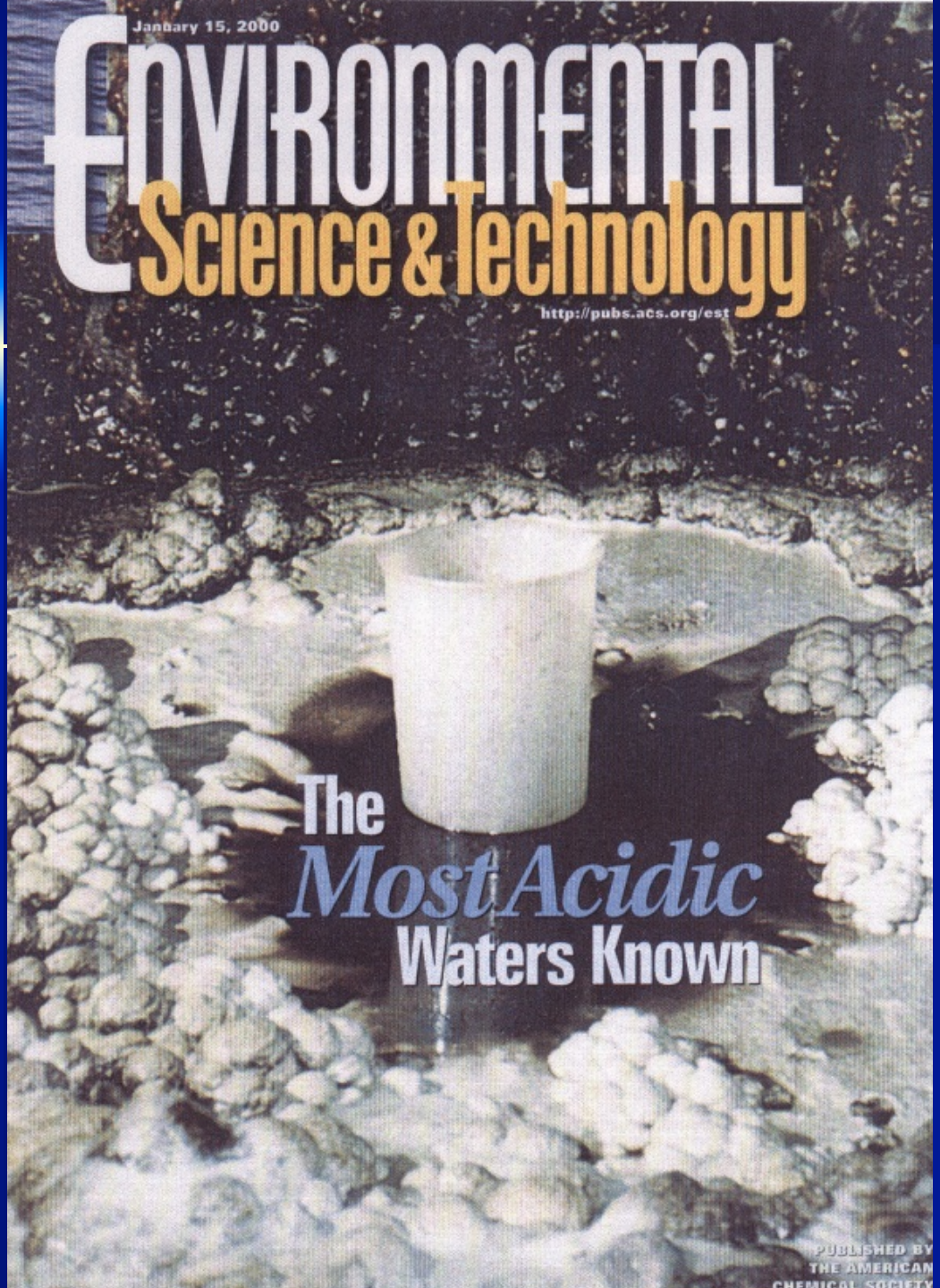
$(Fe^{II}_{.92},Zn_{.04},Cu_{.02},Mg_{.02})$

$(SO_4)\cdot 7H_2O$

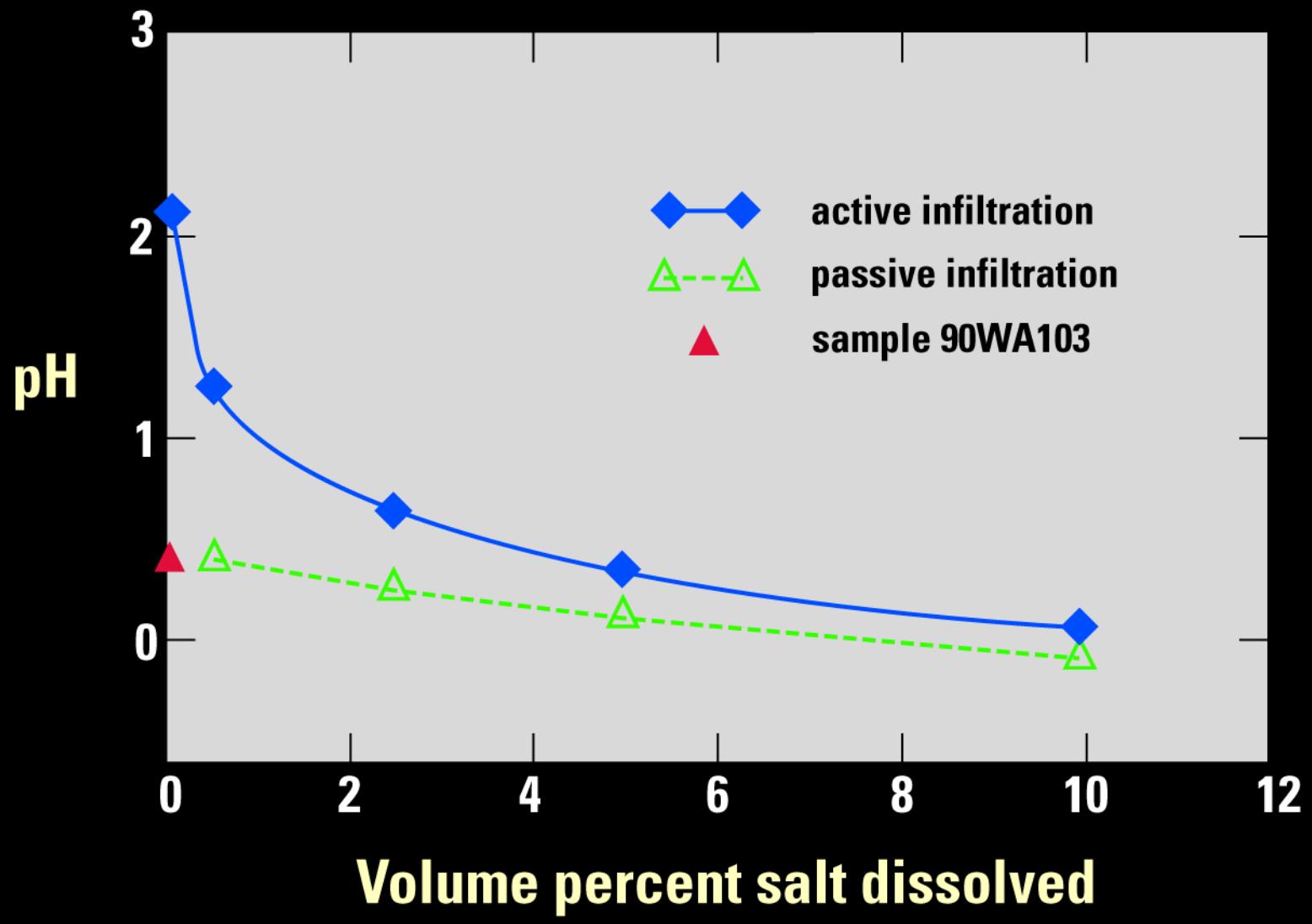
pH = -0.7

T = 35°C


rhomboclase
pH
-2.6
pH = –3.5



Not the most exciting aspect of Iron Mountain research for me: instead, it was presenting the mine plugging scenario to the consultants



Based on salts only, does not take into account negative pH waters

A mine pool of 600,000 cubic meters would be created containing water with pH of 1 or less, sitting on top of the groundwater table, in a rock that contains no neutralizing capacity, and in a few short years it would leak out in numerous unpredictable places because the mountain is an unstable, drilled, excavated, faulted piece of Swiss cheese

Mine plugging is NOT a desirable option

As we rediscovered recently when the Animas river was contaminated.
(This must be the Yellow River…… Are we in China?)

High-density sludge neutralization plant
At Iron Mountain

How long will Iron Mountain need treatment?

- 3,000 years!
- Based on known weathering rates and the mass of pyrite left underground from production and reserves accounts
- So what is the final fix? Great question!

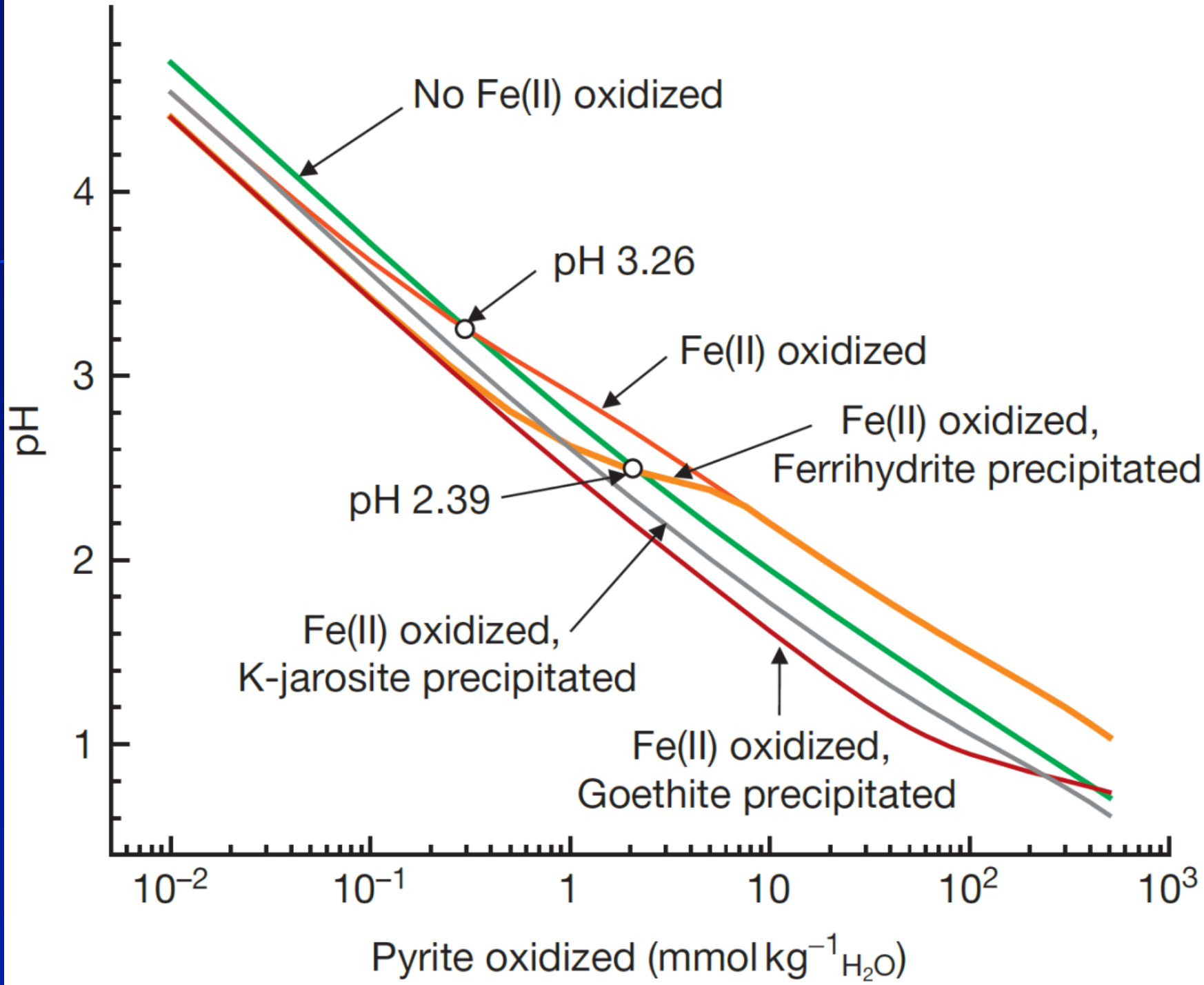
Simulation of pyrite oxidation using PHREEQC

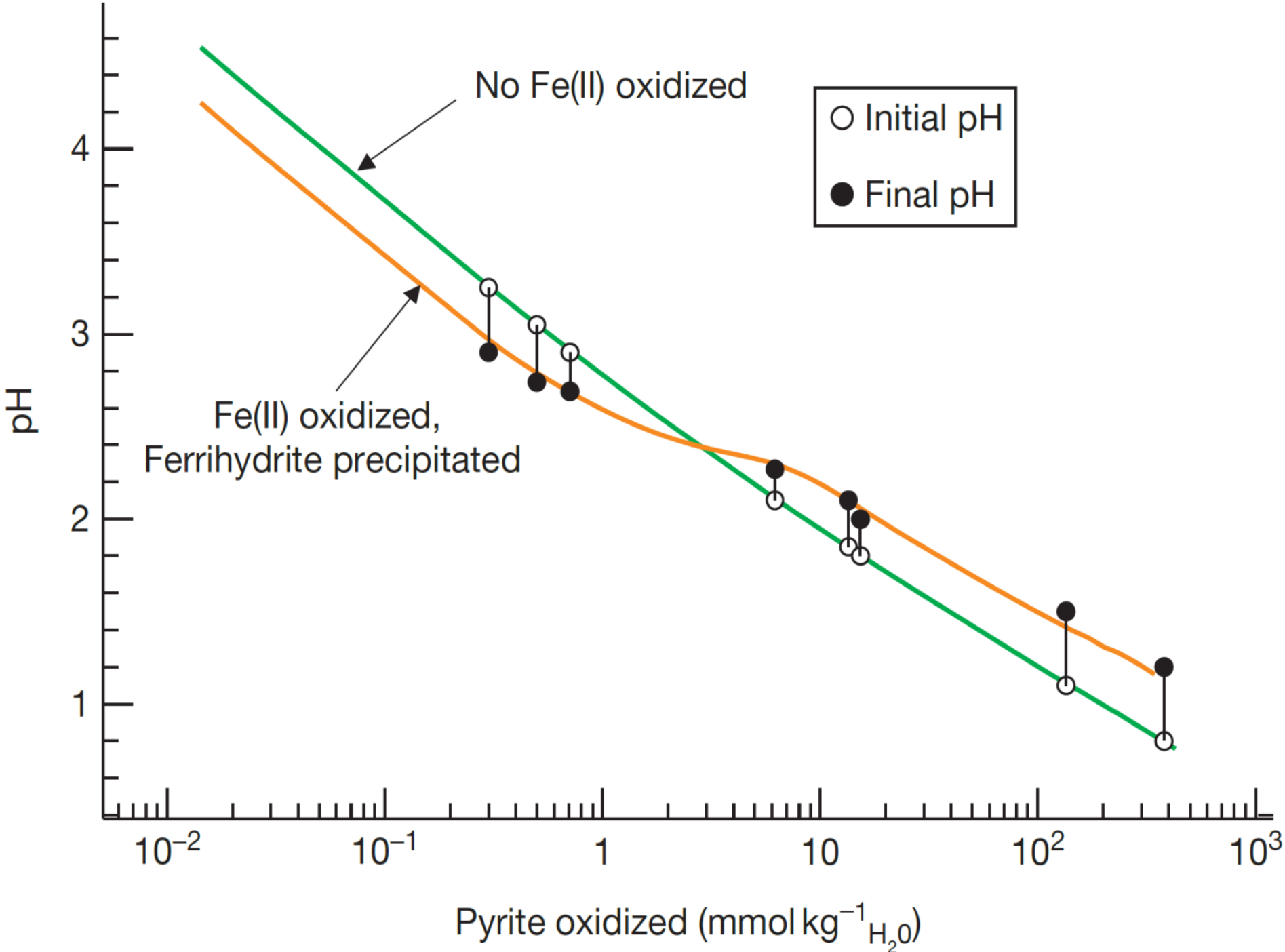
Fundamental reactions:

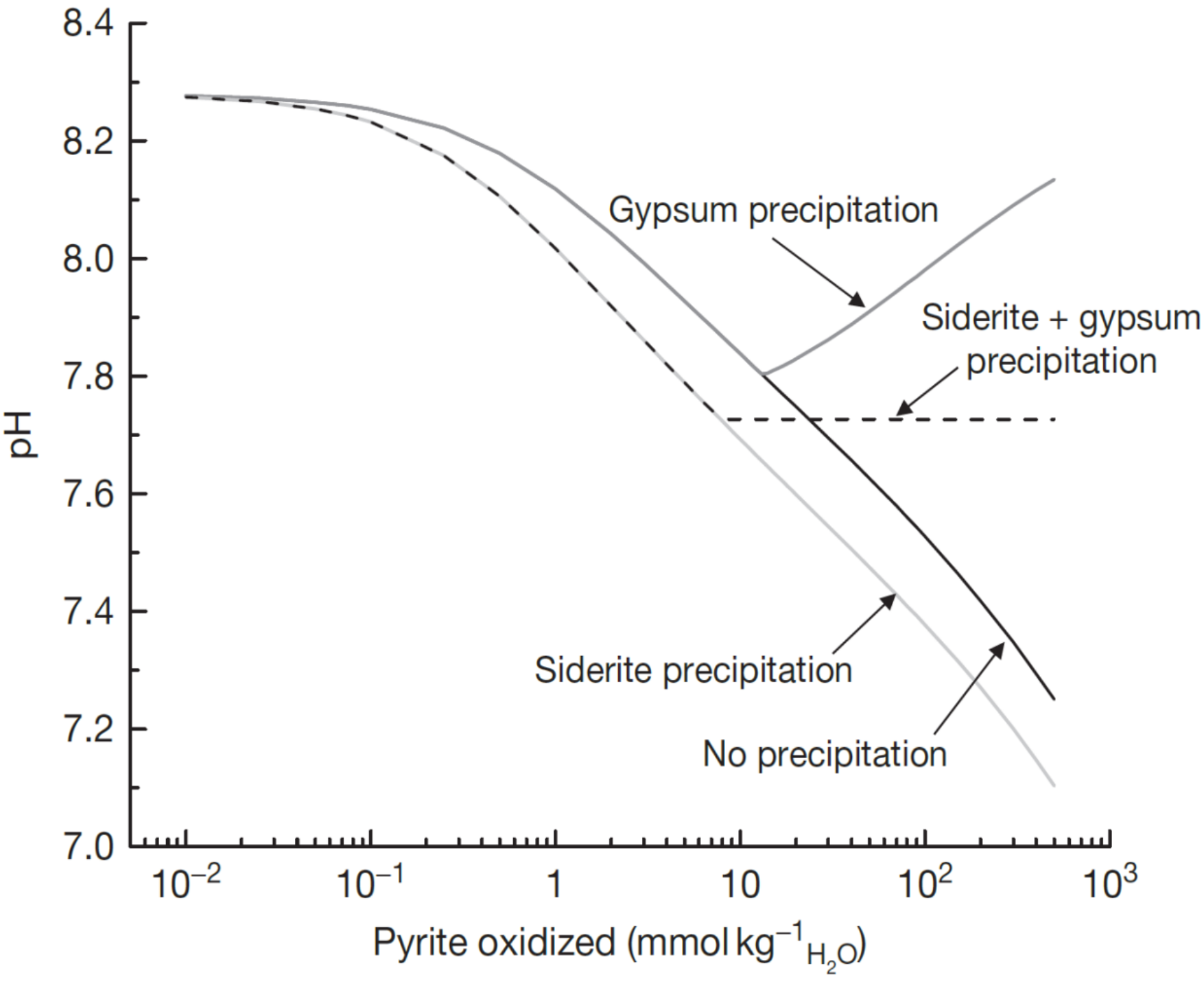
$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$

$Fe^{3+} + \frac{1}{2}H_2O \rightarrow Fe(OH)_3 + 3H^+$


No Fe(II) oxidized
pH 3.26
Fe(II) oxidized
Fe(II) oxidized,
Ferrihydrite precipitated
pH 2.39
Fe(II) oxidized,
K-jarosite precipitated
Fe(II) oxidized,
Goethite precipitated
pH
4
3
2
1
10^{-2}
10^{-1}
1
10
10^{2}
10^{3}
Pyrite oxidized (mmol $kg^{-1}{}_{H_2O}$)

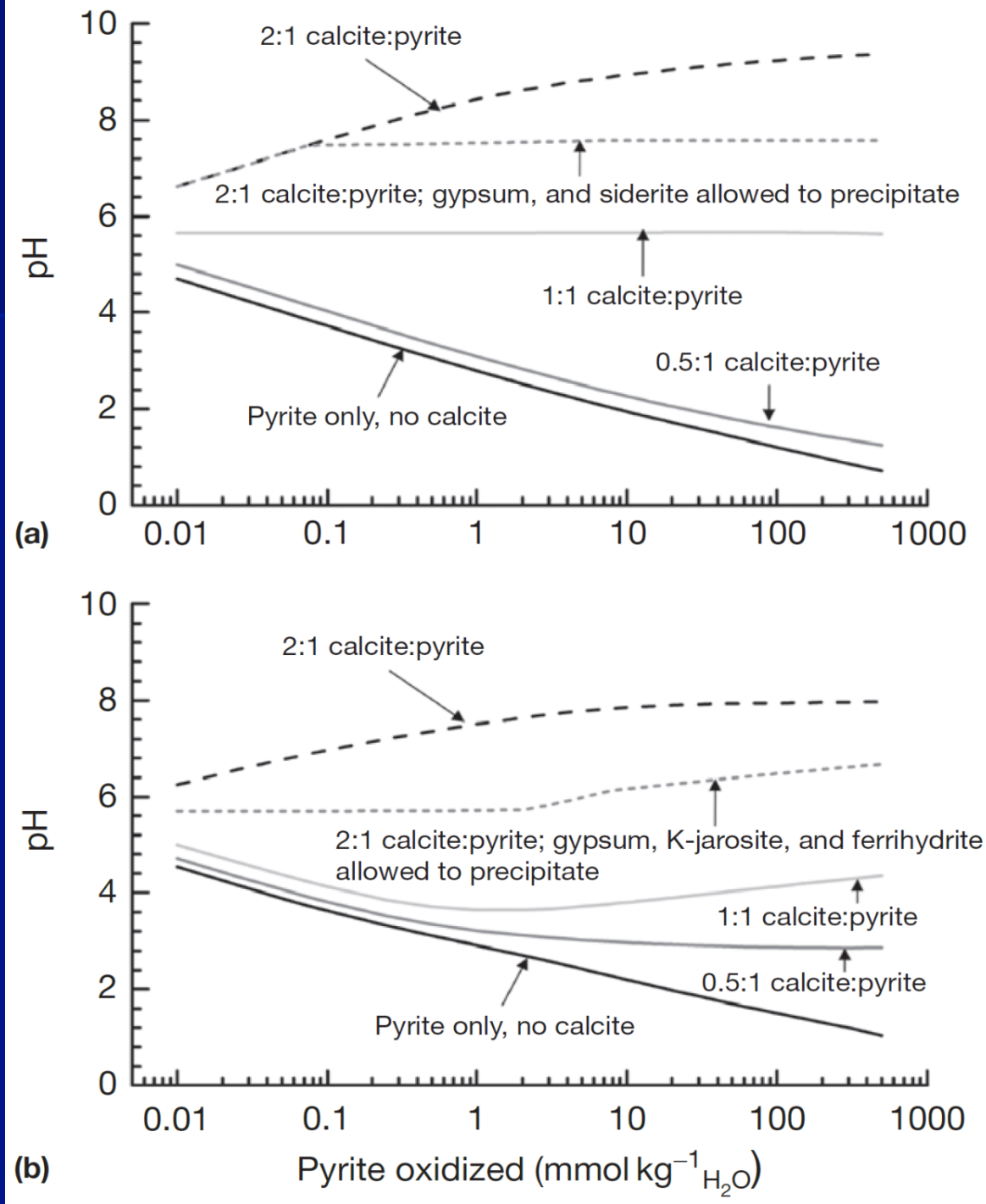

No Fe(II) oxidized
Initial pH
Final pH
Fe(II) oxidized,
Ferrihydrite precipitated
pH
4
3
2
1
10^{-2}
10^{-1}
1
10
10^{2}
10^{3}
Pyrite oxidized (mmol kg^{-1} $_{H_2O}$)


8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
pH
Gypsum precipitation
Siderite + gypsum precipitation
Siderite precipitation
No precipitation
10^{-2}
10^{-1}
1
10
10^{2}
10^{3}
Pyrite oxidized (mmol $kg^{-1}{}_{H_2O}$)

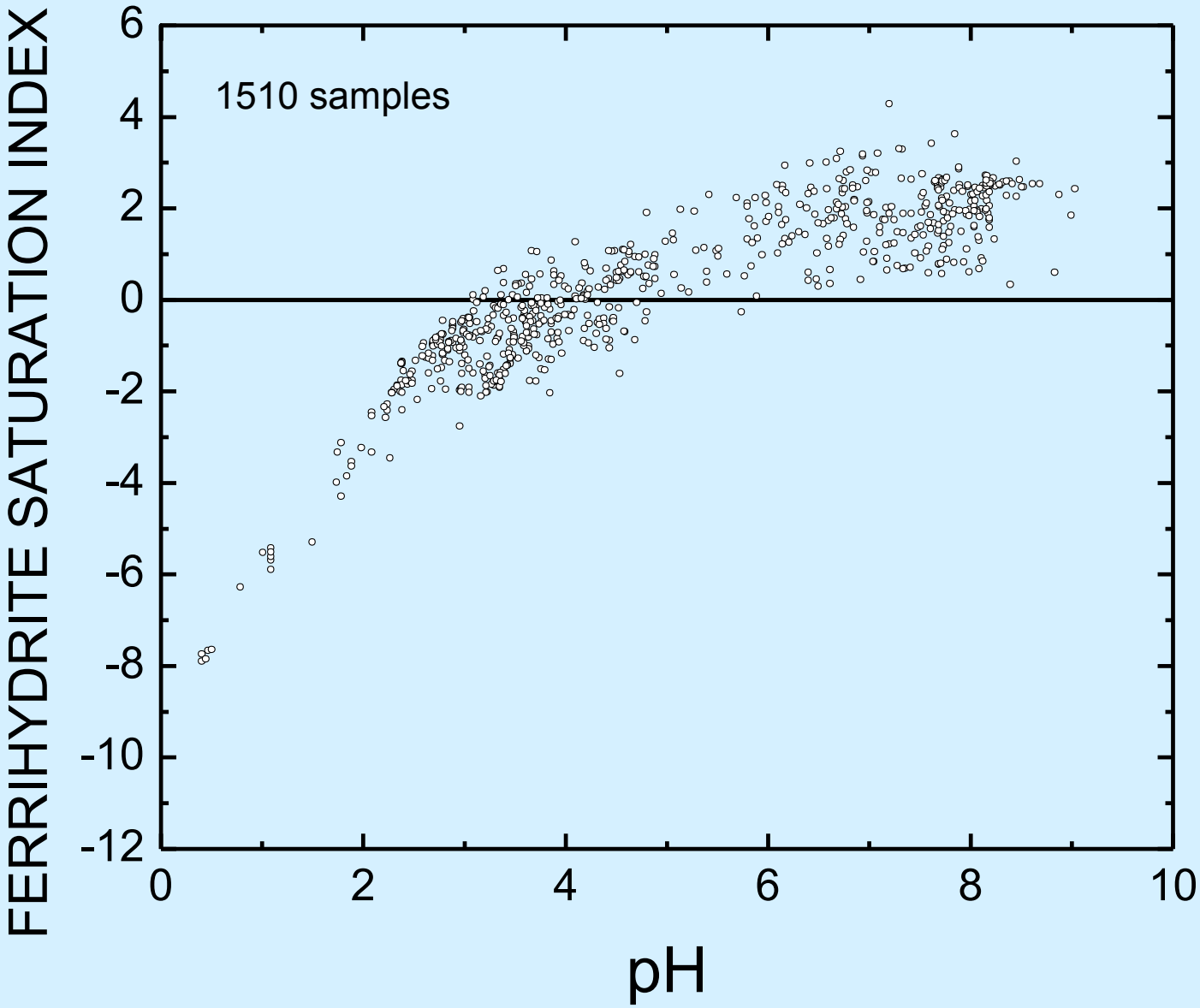
Pyrite oxidation with different proportions of calcite present:

(a) Pyrite oxidizes but ferrous iron does not oxidize – with different proportions of calcite, with and without mineral precipitation

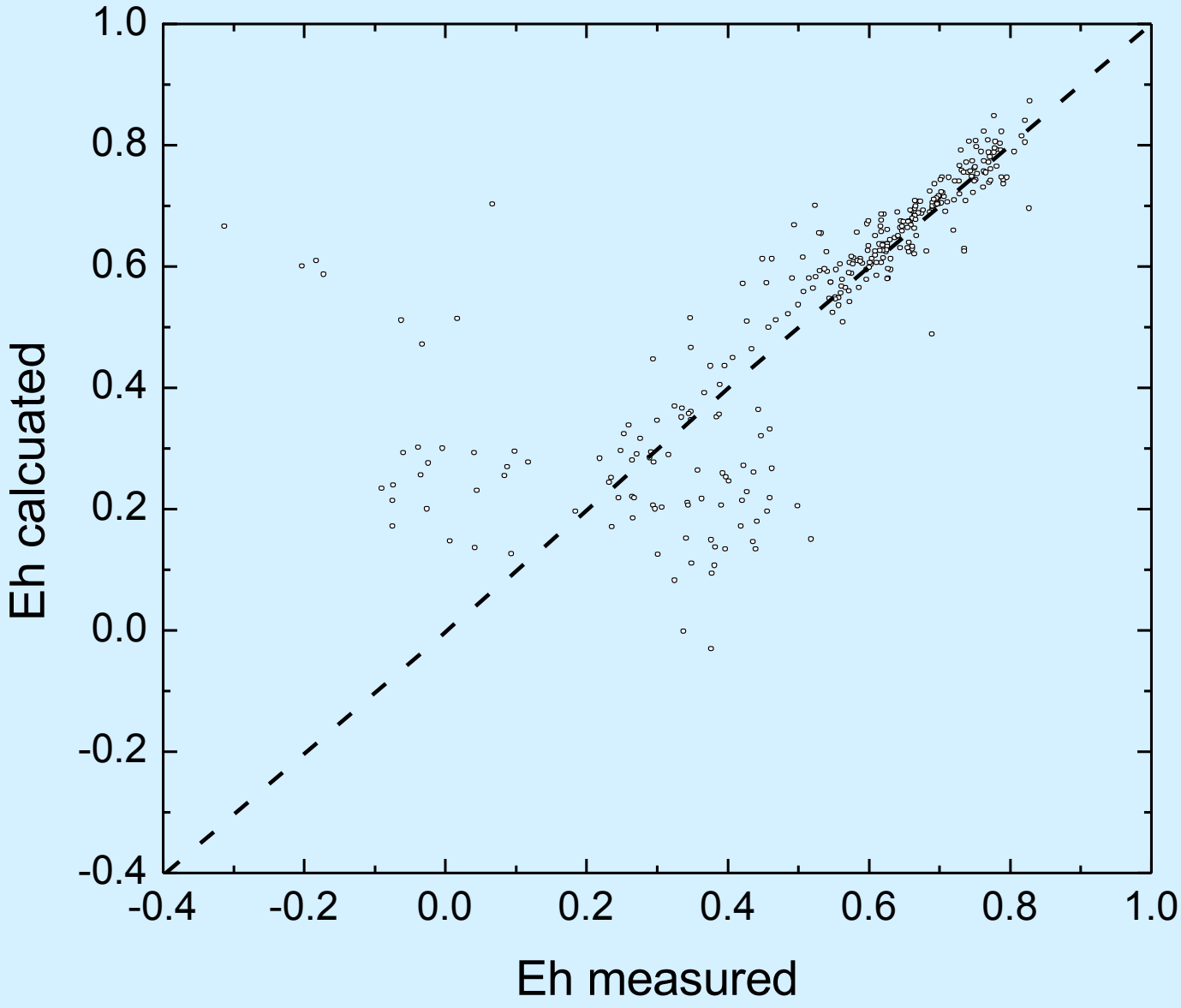
(b) Pyrite oxidizes and ferrous iron also oxidizes – otherwise same scenario



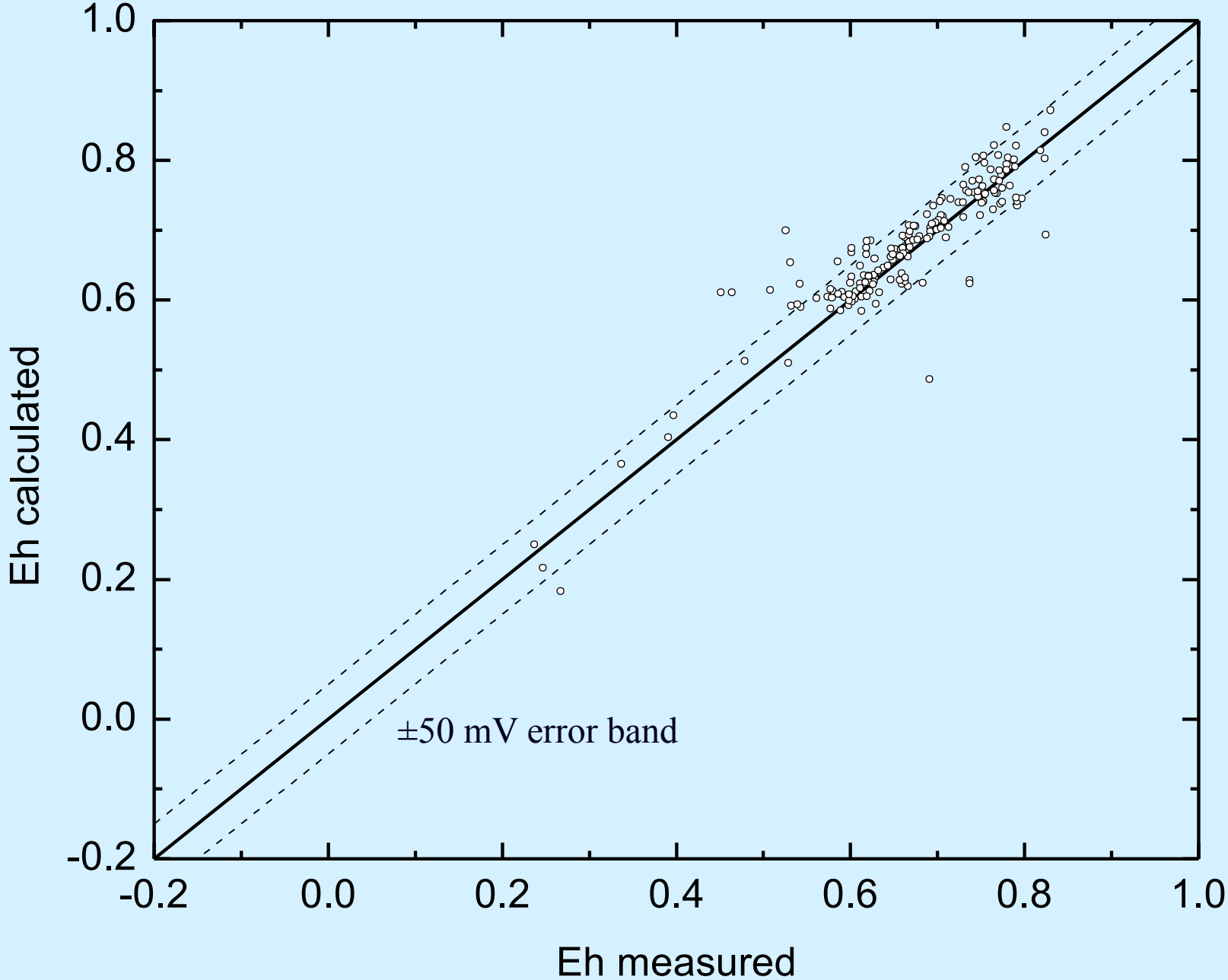
First done in my PhD dissertation in 1976. This is the latest version in 2011 using AMD water analyses from the western US.



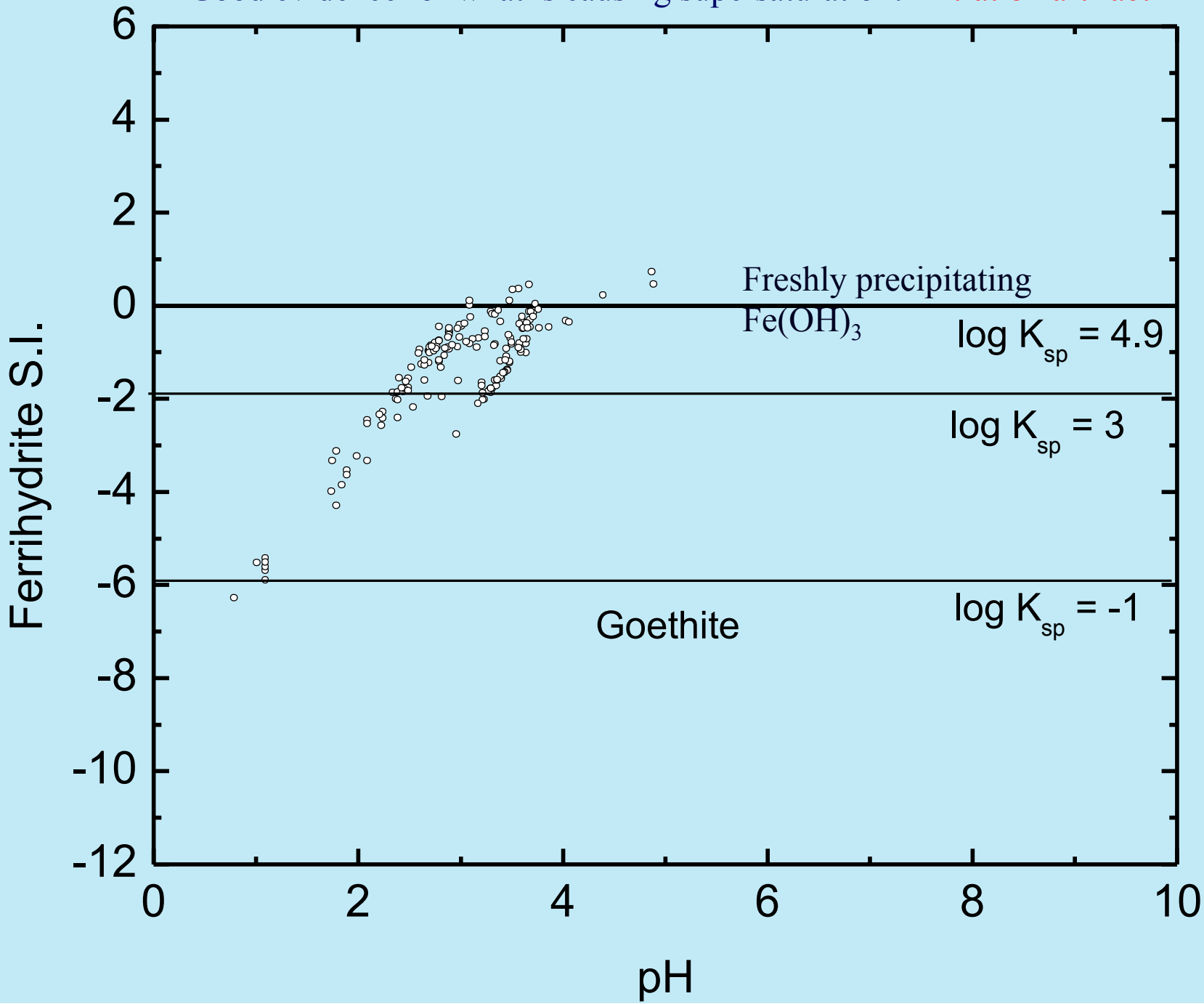
First done in my PhD dissertation using modified WATEQF in 1975. This is the latest version, 2011, using WATEQ4F on same AMD samples

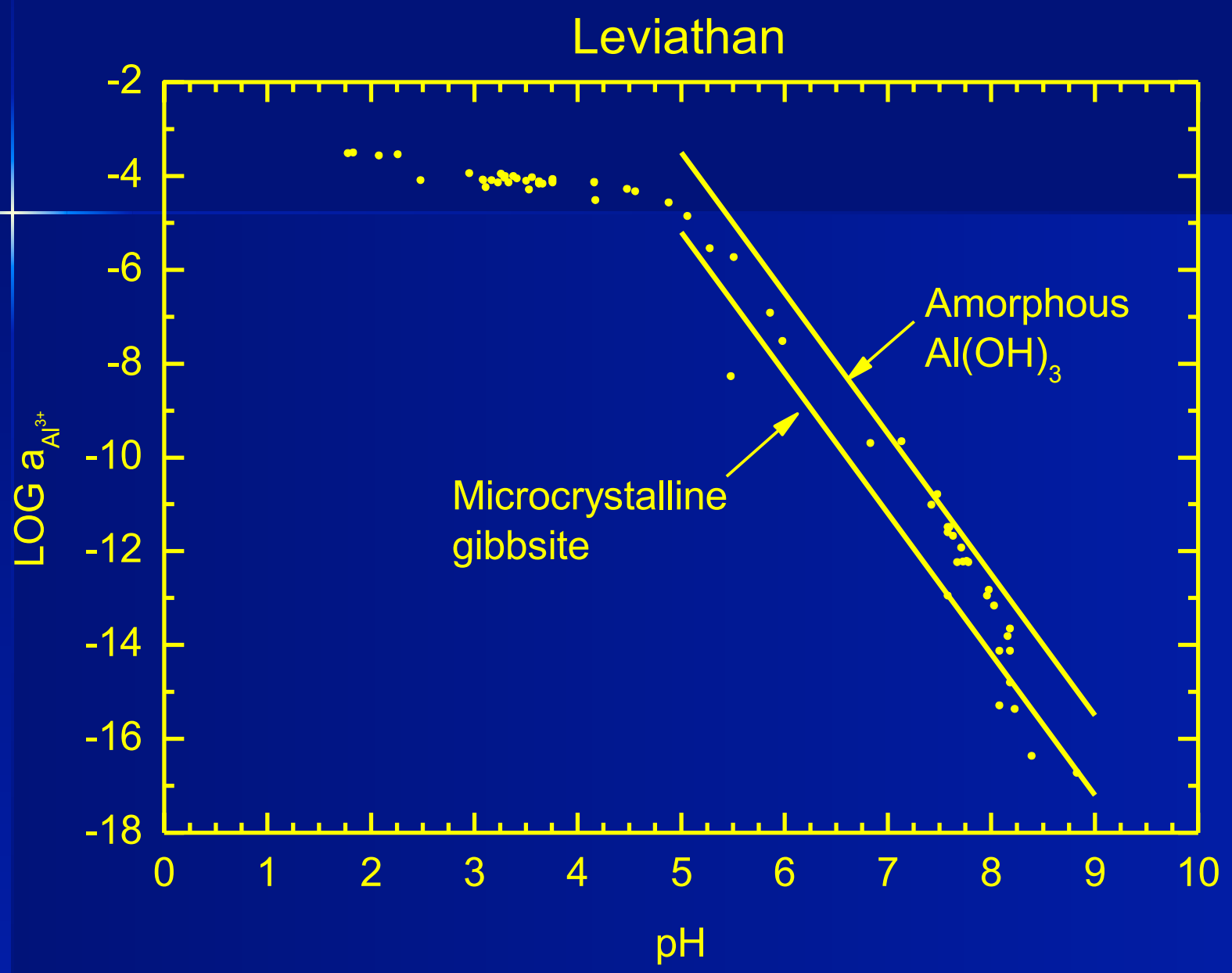


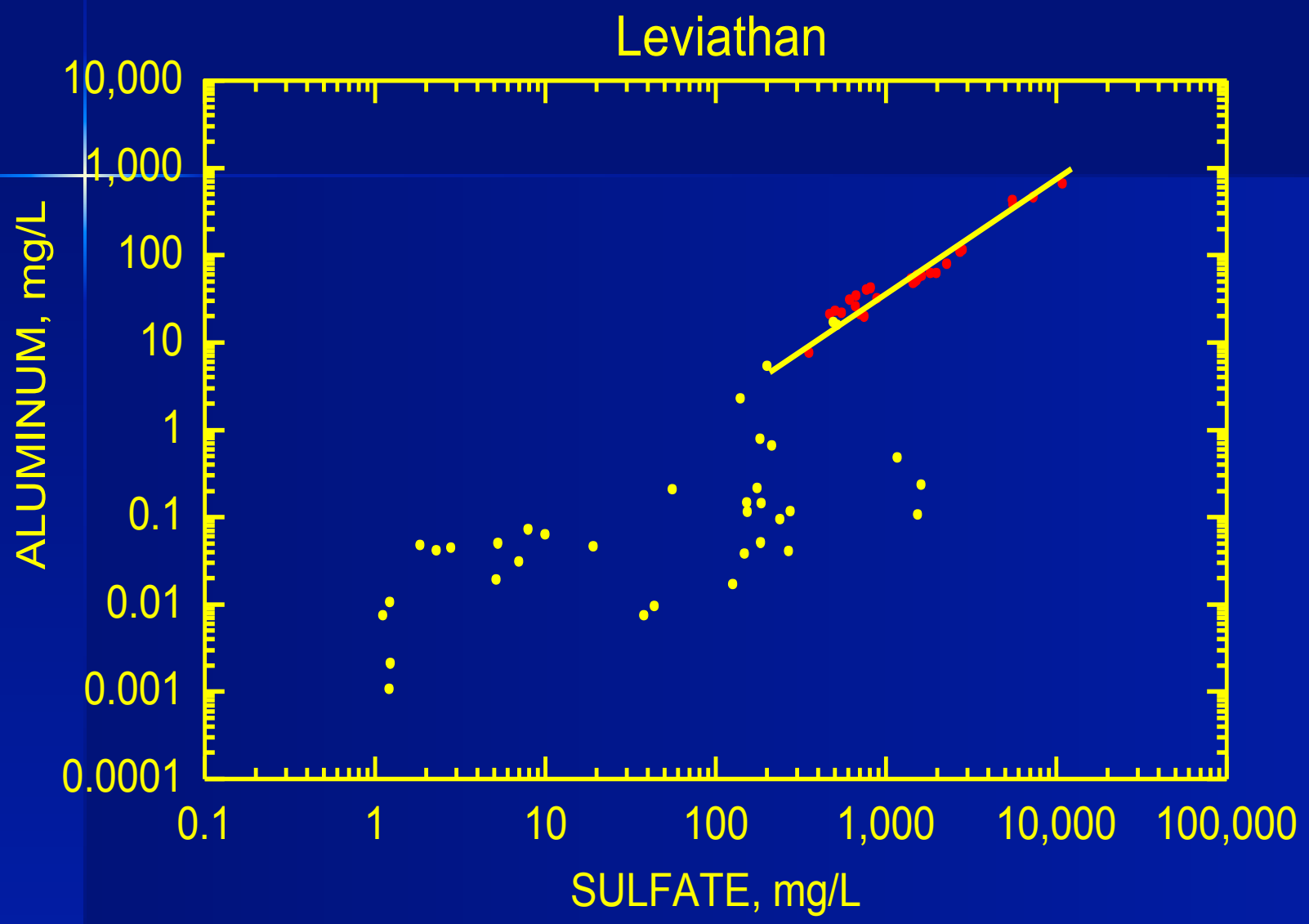
After removing data points with non-detects for Fe(III) and measured Eh.



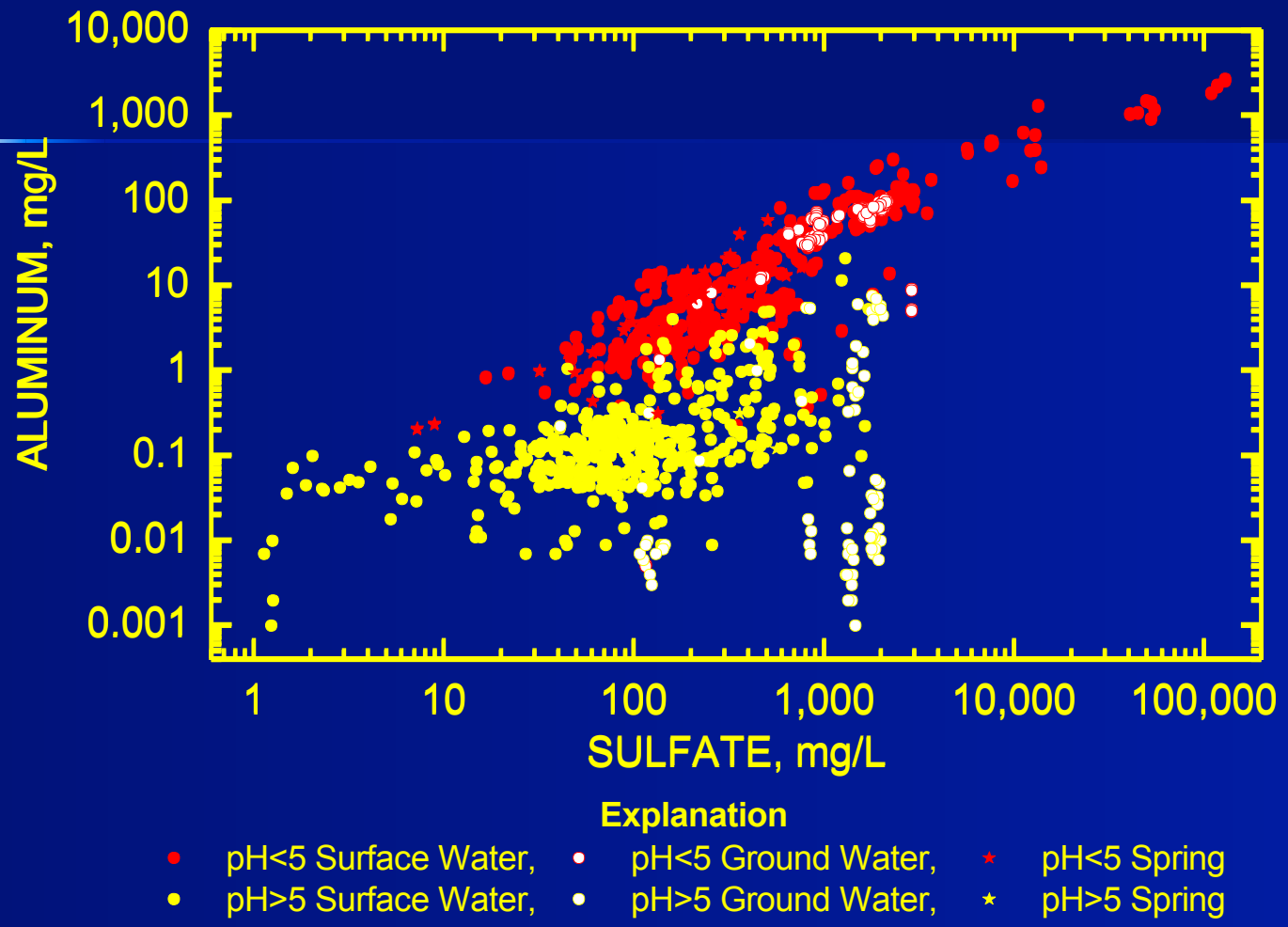
Good evidence for what is causing supersaturation! Filtration artifact



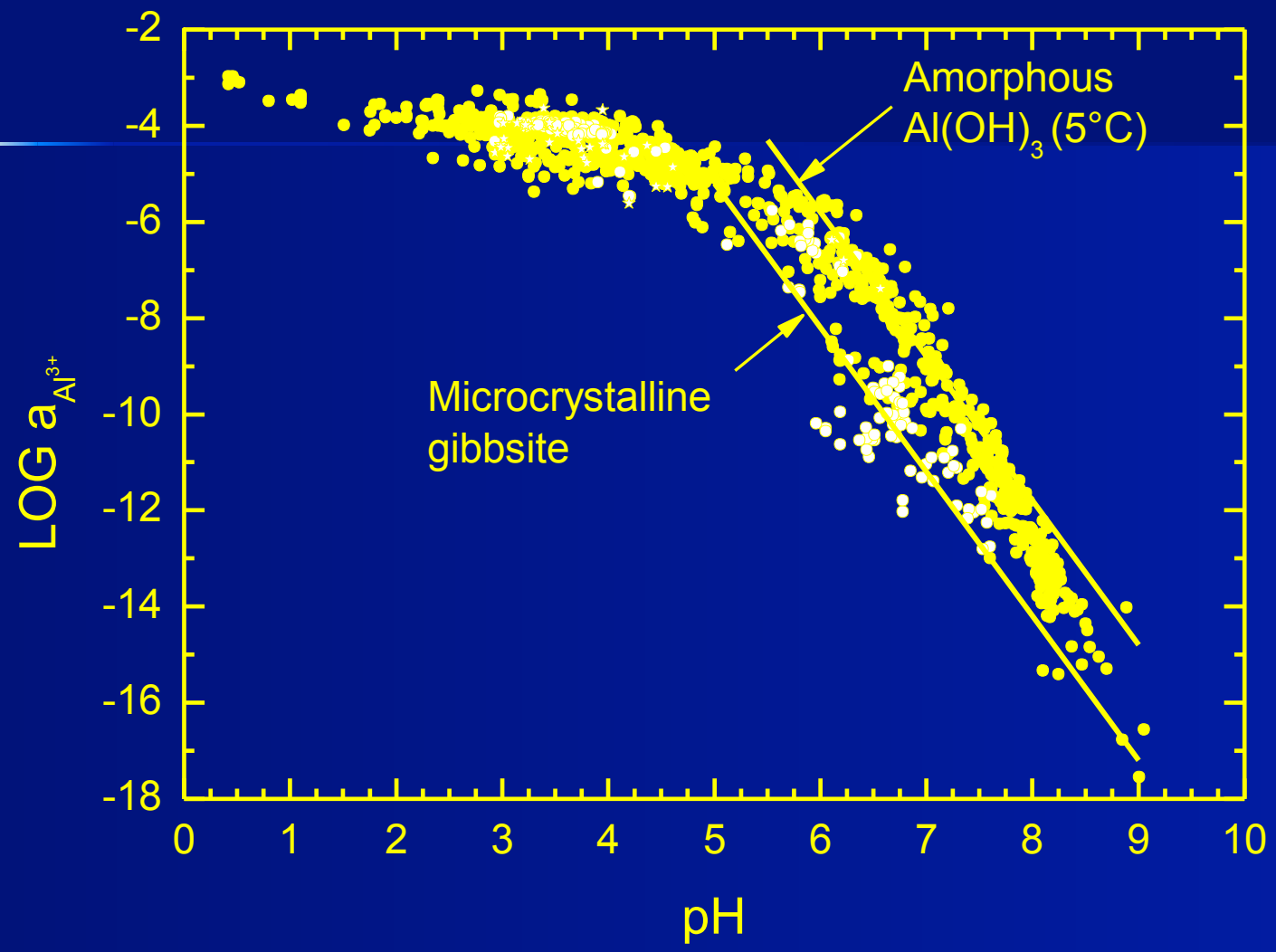

Leviathan
-2
-4
-6
-8
-10
-12
-14
-16
-18
LOG $a_{Al^{3+}}$
0
1
2
3
4
5
6
7
8
9
10
pH
Amorphous
$Al(OH)_3$
Microcrystalline
gibbsite


Leviathan
10,000
1,000
100
10
1
0.1
0.01
0.001
0.0001
ALUMINUM, mg/L
0.1
1
10
100
1,000
10,000
100,000
SULFATE, mg/L

With total database

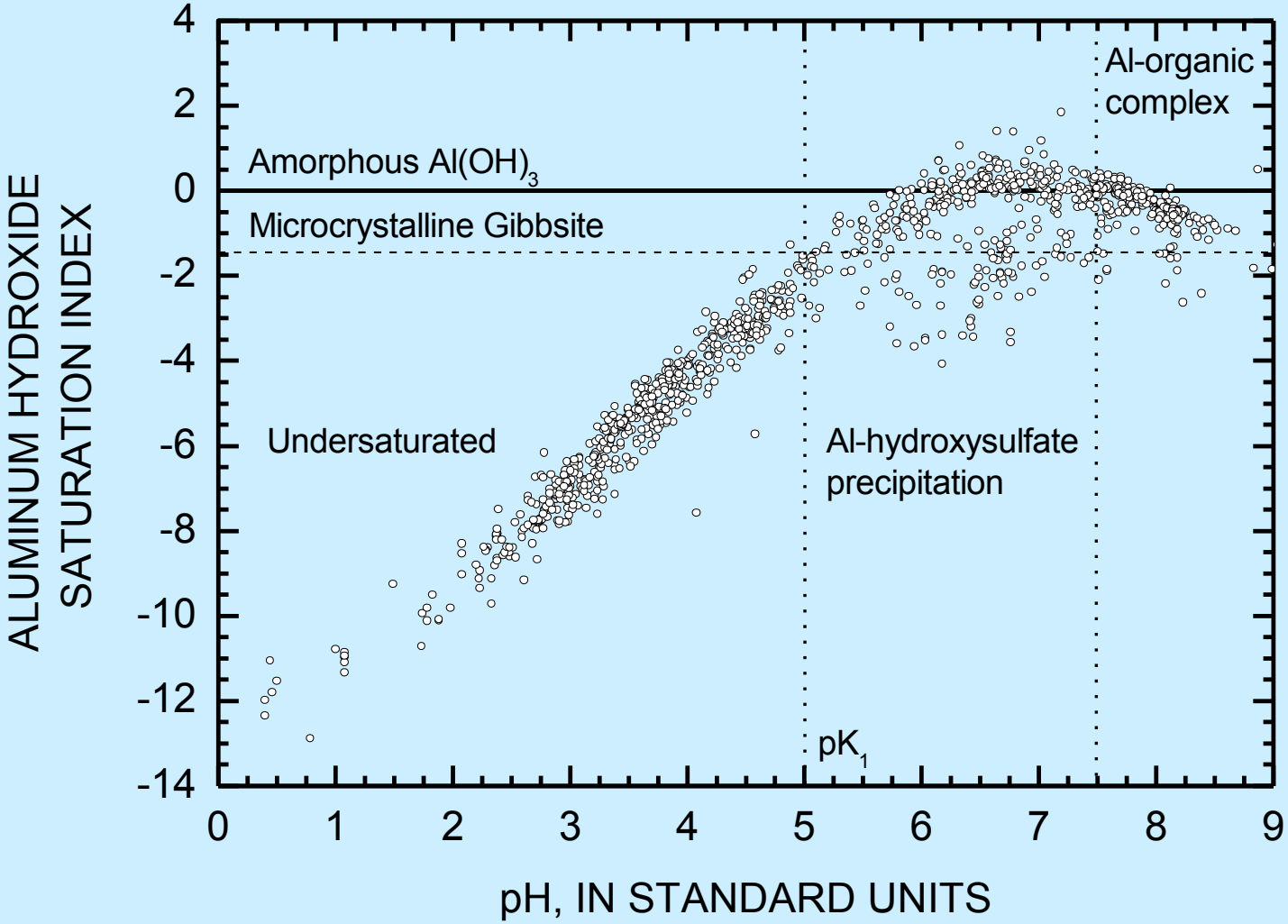


With total database



Explanation

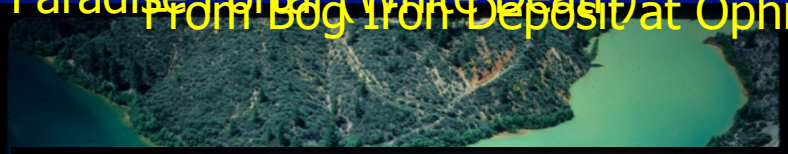
• Surface Water, • Ground Water, ⋆ Spring

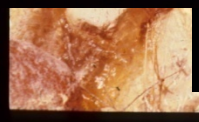

ALUMINUM HYDROXIDE SATURATION INDEX
pH, IN STANDARD UNITS
Amorphous Al(OH)3
Microcrystalline Gibbsite
Undersaturated
Al-hydroxysulfate precipitation
Al-organic complex
pK1
4
2
0
-2
-4
-6
-8
-10
-12
-14
0
1
2
3
4
5
6
7
8
9

From Iron Mountain

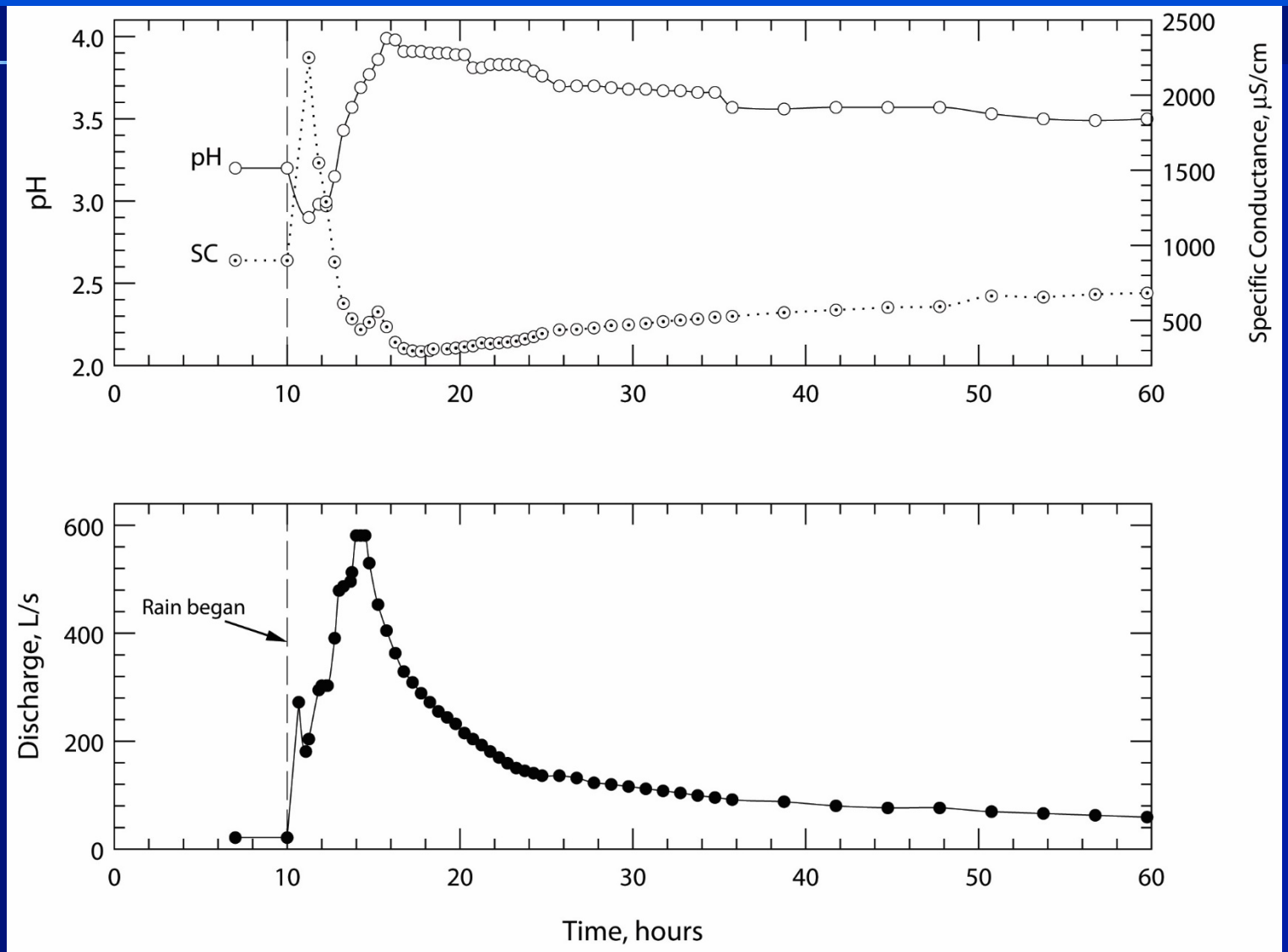
From Paradise Portal (White Death)

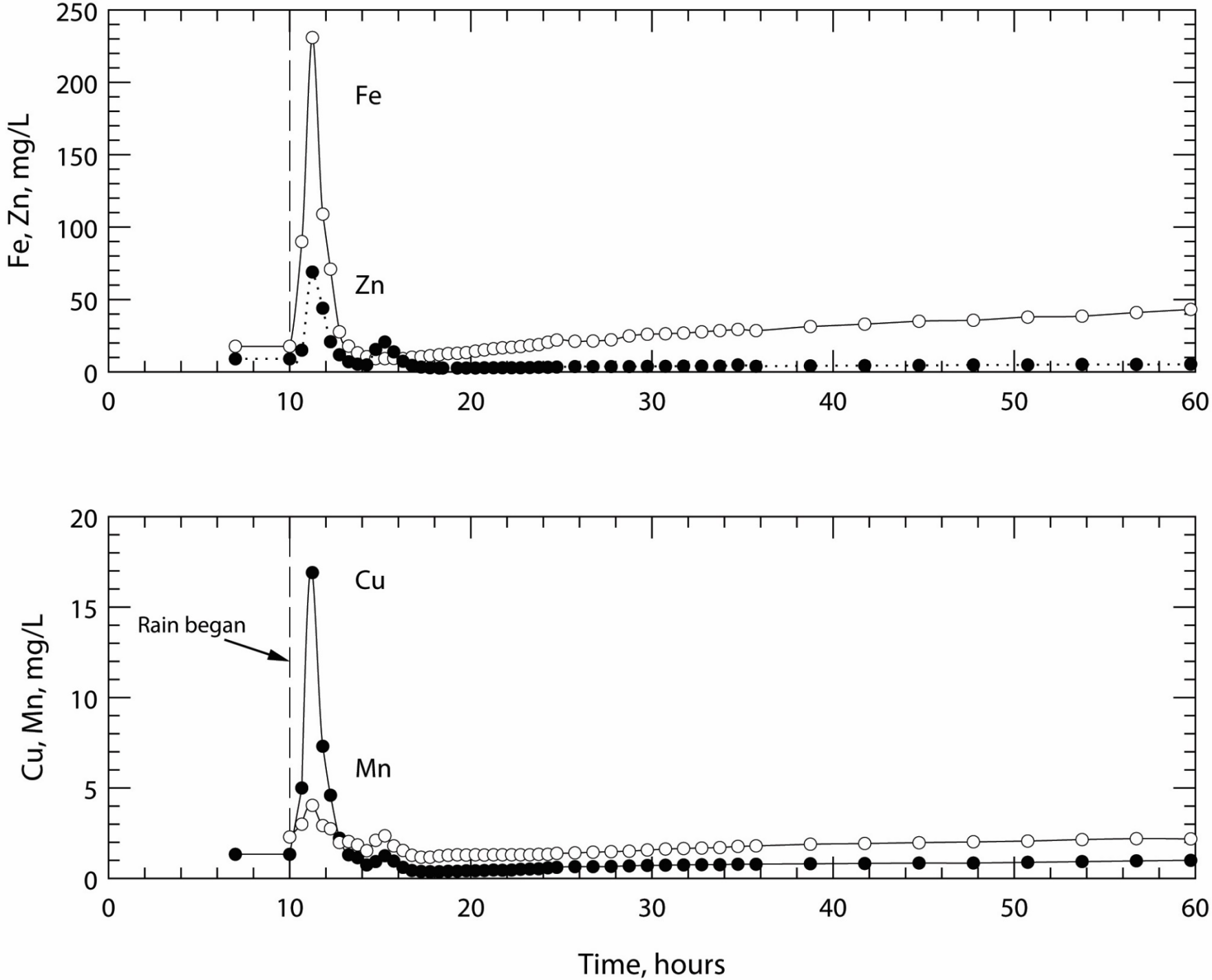
From Bog Iron Deposit at Ophir, CO



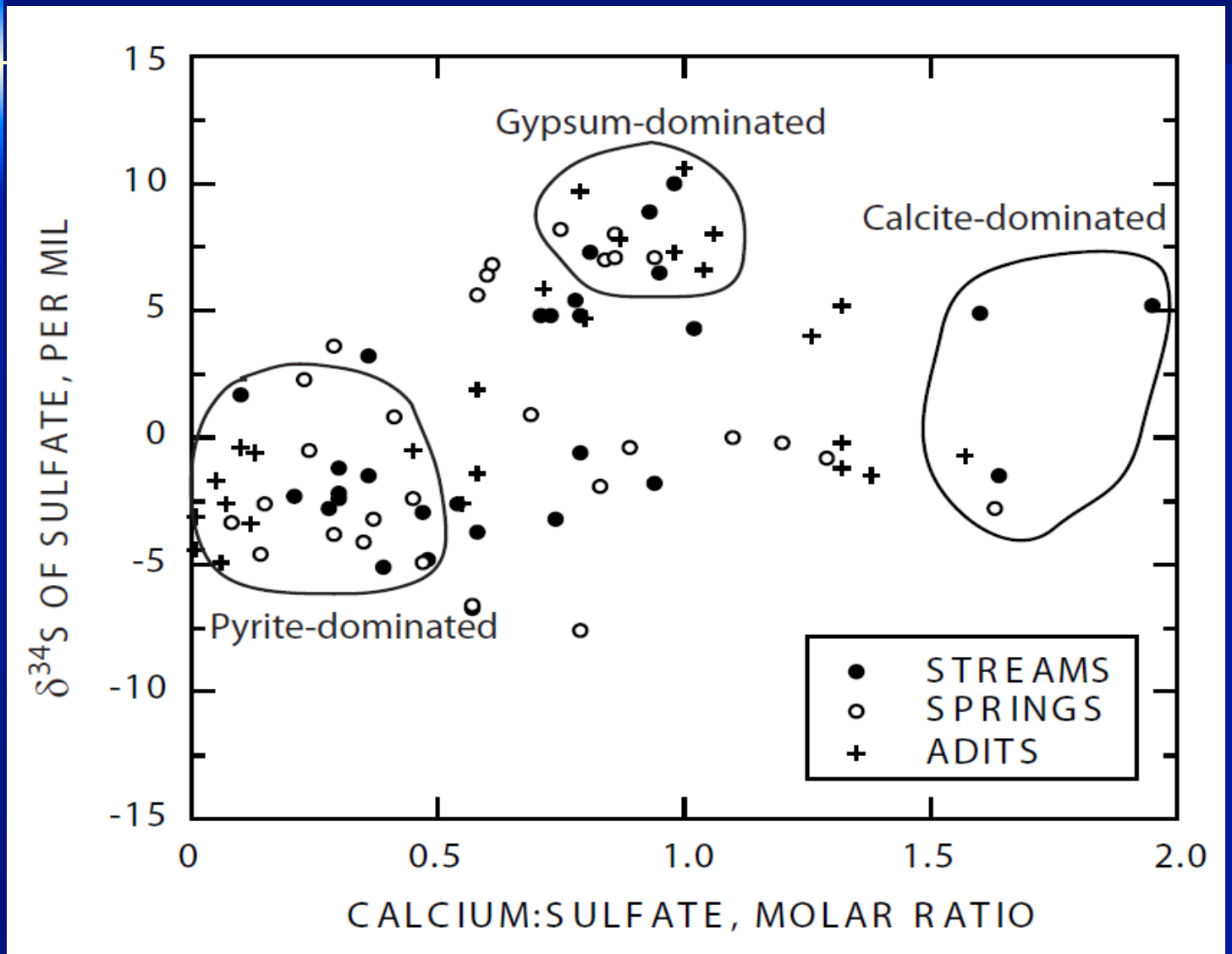


Effect of rainstorm on abandoned mine tailings piles located on Contrary Creek, Virginia (MS Thesis, 1980, Thomas Dagenhart, Jr)




Fe, Zn, mg/L
250
200
150
100
50
0
Fe
Zn
0
10
20
30
40
50
60
Cu, Mn, mg/L
20
15
10
5
0
Rain began
Cu
Mn
Time, hours

Two simple parameters, $\delta^{34}S$ and Ca/SO_4 ratio, could show graphically the main processes controlling the water chemistry for mine drainage in the San Juan Mountains



Potential alternate remedies

- Lime/limestone neutralization (quick fix only)
  - Must continue for 100s to 1000s of years
  - Not economically feasible in the long-term
- Mine plugging
  - Numerous examples of failures; water will eventually out
- Groundwater interception
  - Never tested; how much water captured is unknown
- Permeable reactive barriers (also short term only)
  - Has been tested in some places; shows promise for groundwater contamination but must be replenished

The Gold King Mine blowout

August 5, 2015

Figure 53.—Photograph showing the blowout at 10:56 a.m. on August 5, 2015 (photograph from EPA project files).

Figure 54.—Photograph showing the peak outflow from the blowout. The waste-rock dump is eroding on the right side of the photograph (still frame extracted from a video taken on August 5, 2015, at approximately 10:57 a.m.).

- Prevent water access
  - Capping (impermeable barriers)
    - difficult to implement in most places; often cannot prevent all water infiltration; efficiency not always known
  - Surface water diversions
    - easy to implement and successful but only decreases the problem in minor ways
- Flood mine workings with nitrogen or install air seals
    - nearly 100% of air must be eliminated and that is too difficult to achieve
- Destroy iron-oxidizing microbes (bacteriacide)
  - bacteriacides contaminate the environment and must be continually reapplied; not feasible except for small, short term fixes

Potential alternate remedies

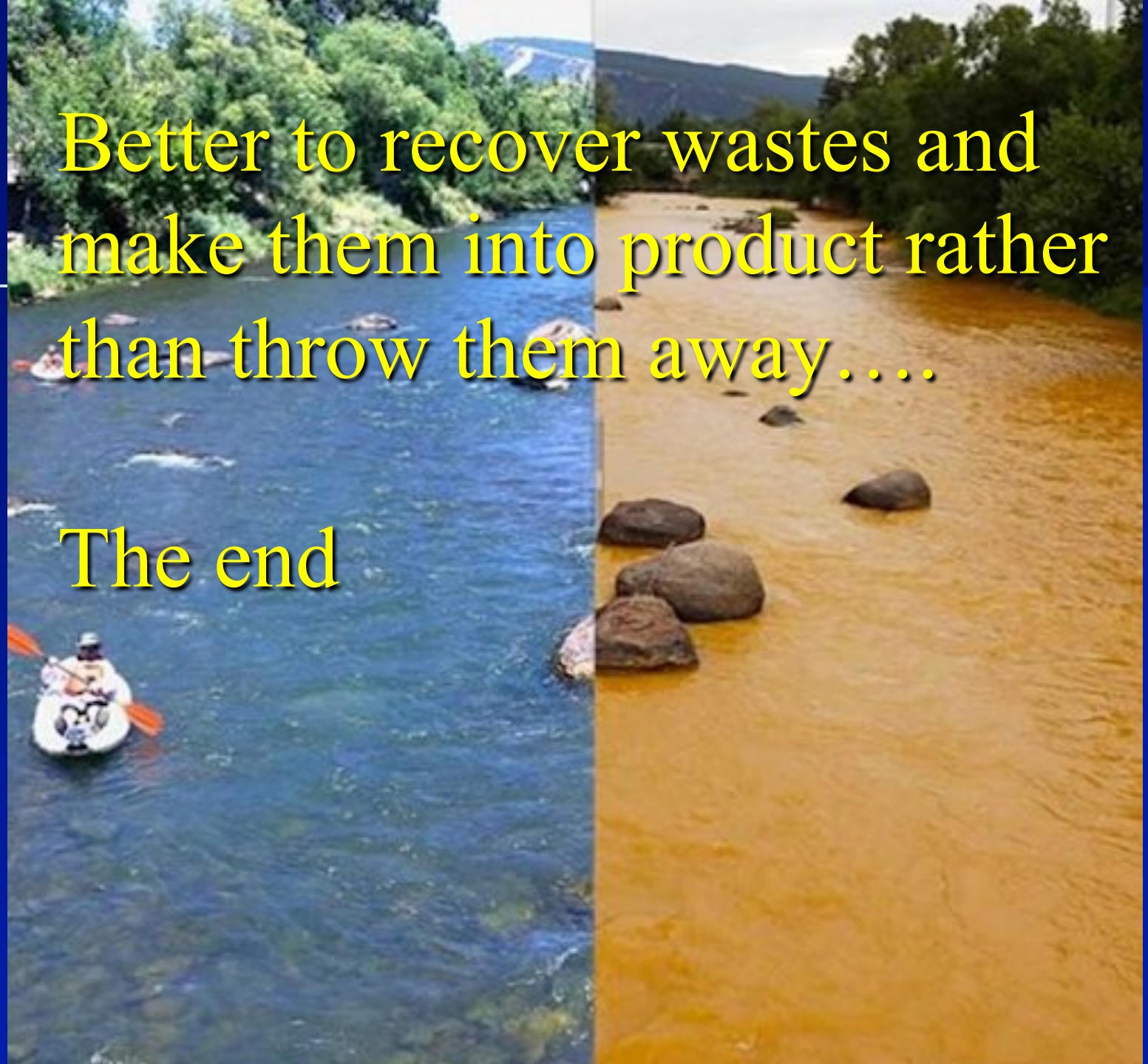
- Other water treatment procedures
  - Reverse osmosis
  - Anoxic limestone drains
  - Bioremediation
- Product extraction for recycle
  - Sulfide precipitation
  - Mineral precipitation (Gypsum, jarosite, goethite)
  - Electrochemical metal & hydrogen extraction
  - Solvent extraction
  - Ion exchange

Best options?

- Design for environmental consequences during the mine planning stages, not after mining has begun
- If mining has started or finished; do careful characterization and assessment of the waste materials, the geology, the hydrology, the geochemistry and seriously consider turning wastes into resources

Potential metal values at IMM

	average	Annual Load		Recent		Annual value	
	concentration	Low	High	metal		Low	High
	(mg/L)	lb/yr	lb/yr	price	Units		
	(Richmond 5-way)						
Cu	200	100,000	500,000	$3.63	per lb.	$363,000	$1,815,000
Zn	1200	600,000	3,000,000	$0.92	per lb.	$552,000	$2,760,000
Au	0.00003	0.015	0.075	$1,689	per troy oz.	$369	$1,847
Ag	< 0.0003	< 0.15	< 0.75	$31.96	per troy oz.	< $ 70	< $ 350
Pb	5	2,500	12,500	$1.04	per lb.	$2,600	$13,000
Ni	5	2,500	12,500	$7.87	per lb.	$19,675	$98,375
Cd	10	5,000	25,000	$12.00	per lb.	$60,000	$300,000
Co	1	500	2,500	$35.00	per lb.	$17,500	$87,500
Fe	16000	8,000,000	40,000,000	$0.10	per lb (ferric sulfate)	$800,000	$4,000,000
Fe	16000	8,000,000	40,000,000	$0.05	per lb (ferrous sulfate)	$400,000	$2,000,000
Fe	16000	8,000,000	40,000,000	$0.13	per lb (ferric chloride)	$1,000,000	$5,000,000
Al	700	350,000	1,750,000	$0.10	per lb (aluminum sulfate)	$35,000	$175,000
					TOTAL	$1,850,144	



Better to recover wastes and make them into product rather than throw them away….

The end