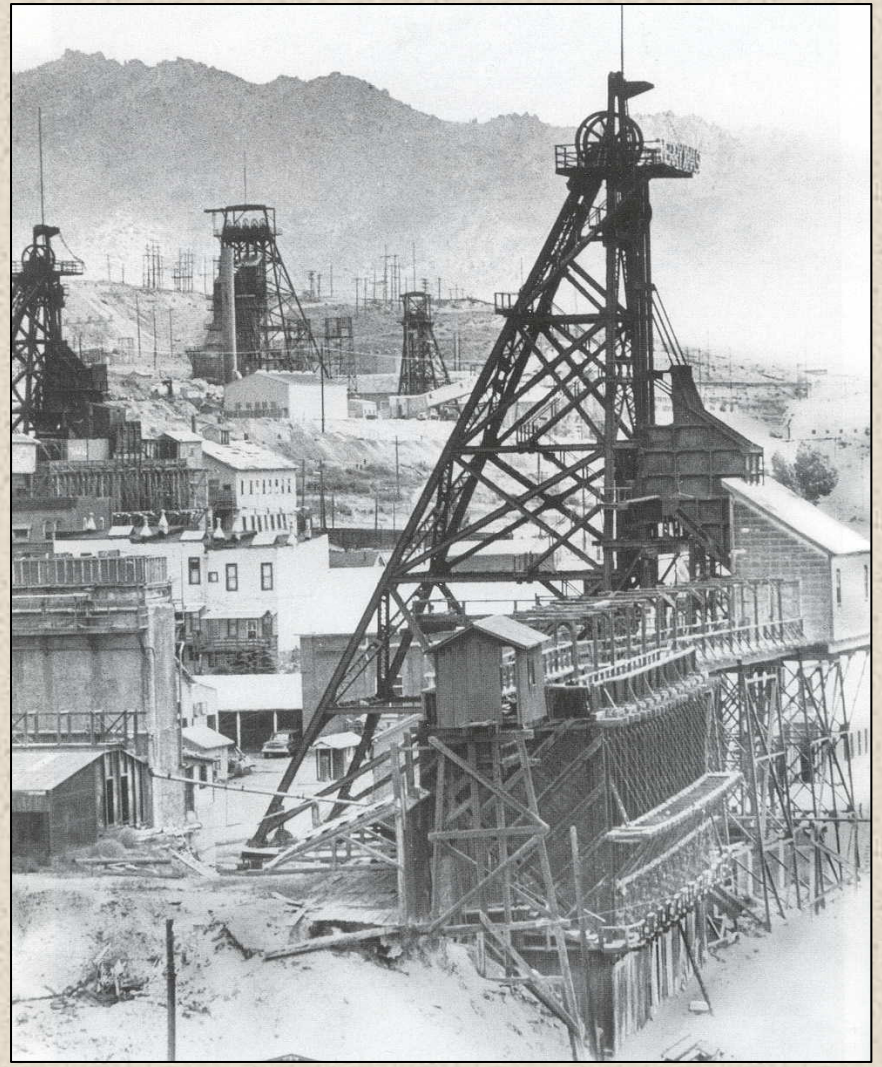

Geochemistry of flooded underground mine waters in Butte, Montana

Chris Gammons, Ph.D.
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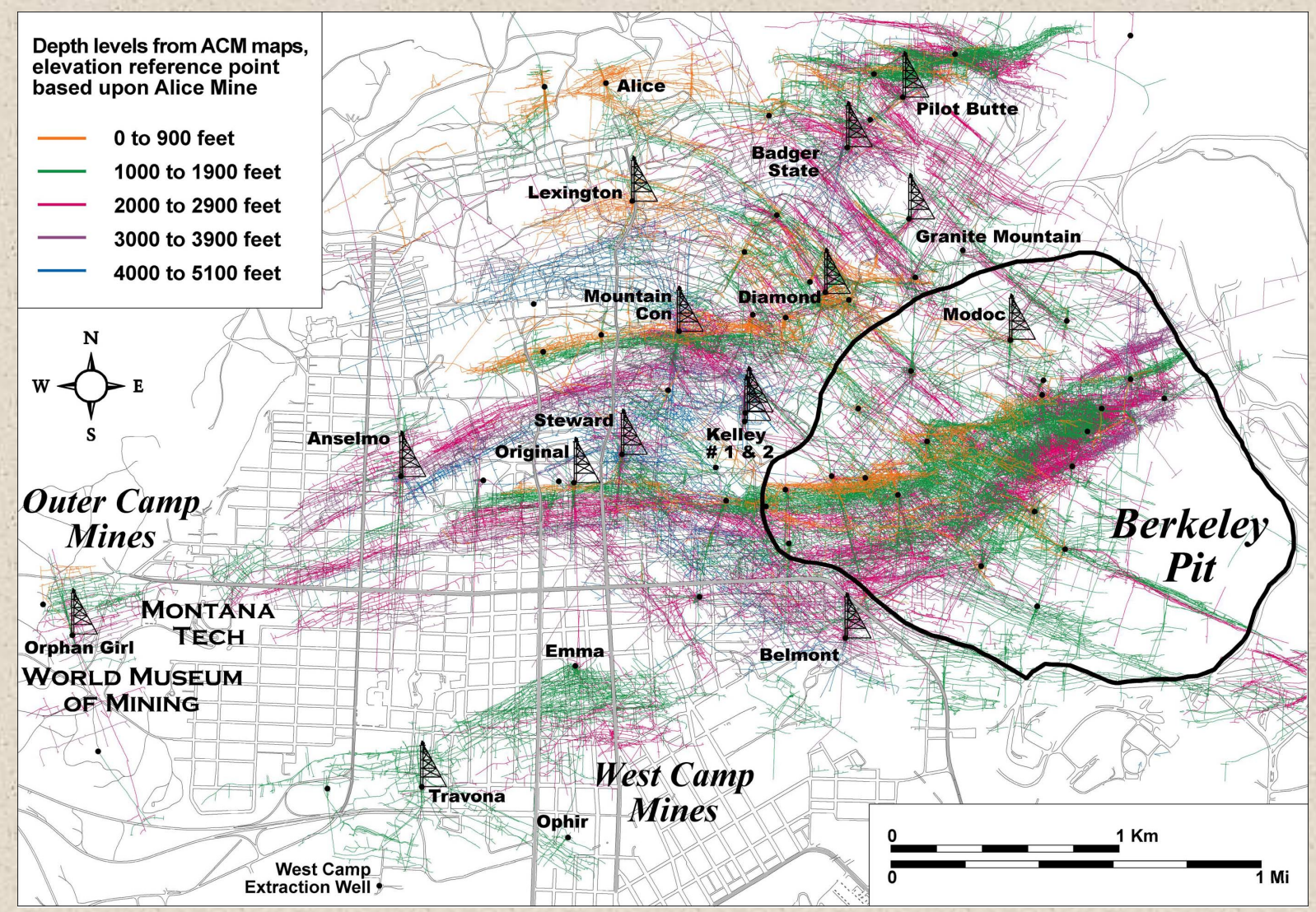
Montana Tech of The University of Montana

Talk overview

- Site orientation
- Horizontal gradients in mine water chemistry
  - Sulfidic zone
  - Transitional zone
  - Acidic zone
- Vertical gradients in mine shaft chemistry

Sampling Kelley shaft

Extent of Butte mine workings (as of 1980)



Over 15,000 km of underground mine workings

Ore mineral zonation

Intermediate Zone
Cu-Fe sulfides
sphalerite, galena,
pyrite,
tennantite,
rhodochrosite

Central Zone
Cu-Fe sulfides
Cu-sulfides
enargite
lots of pyrite

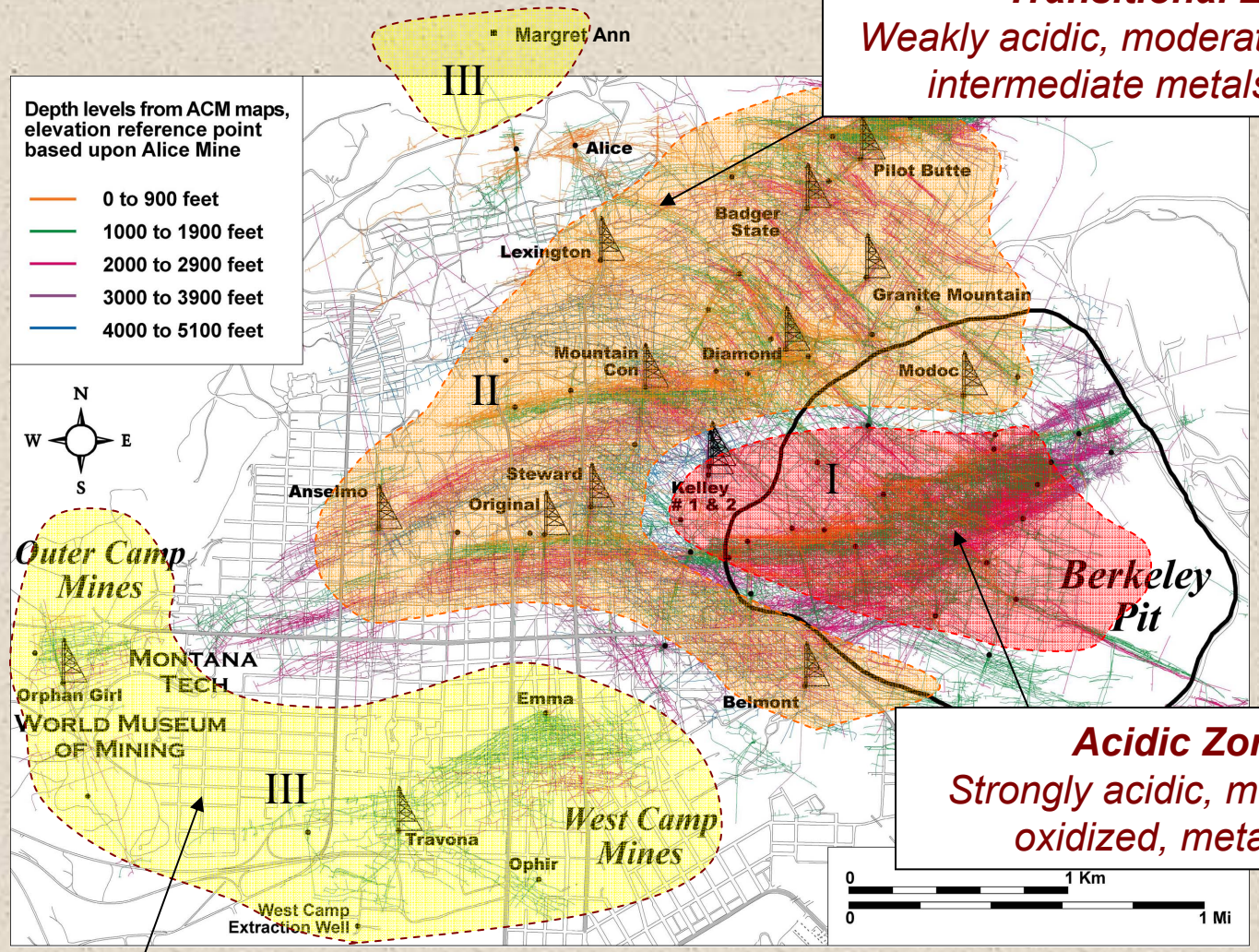
Peripheral Zone
rhodochrosite
sphalerite, galena
tennantite-tetrahedrite

N
W E
S

Pilot Butte
Granite Mountain
Mountain Con
Diamond
Steward
Anselmo
Original
Kelley # 1 & 2
Outer Camp Mines
Berkeley Pit
Orphan Girl
Emma
Belmont
Travona
Ophir
West Camp Mines
0
0

Mine water zonation

Transitional Zone
Weakly acidic, moderately reduced, intermediate metals content



Acidic Zone
Strongly acidic, moderately oxidized, metal-rich

Sulfidic zone
pH neutral, H_2S-rich, metal-poor

Summary of Mine Shaft Chemistry

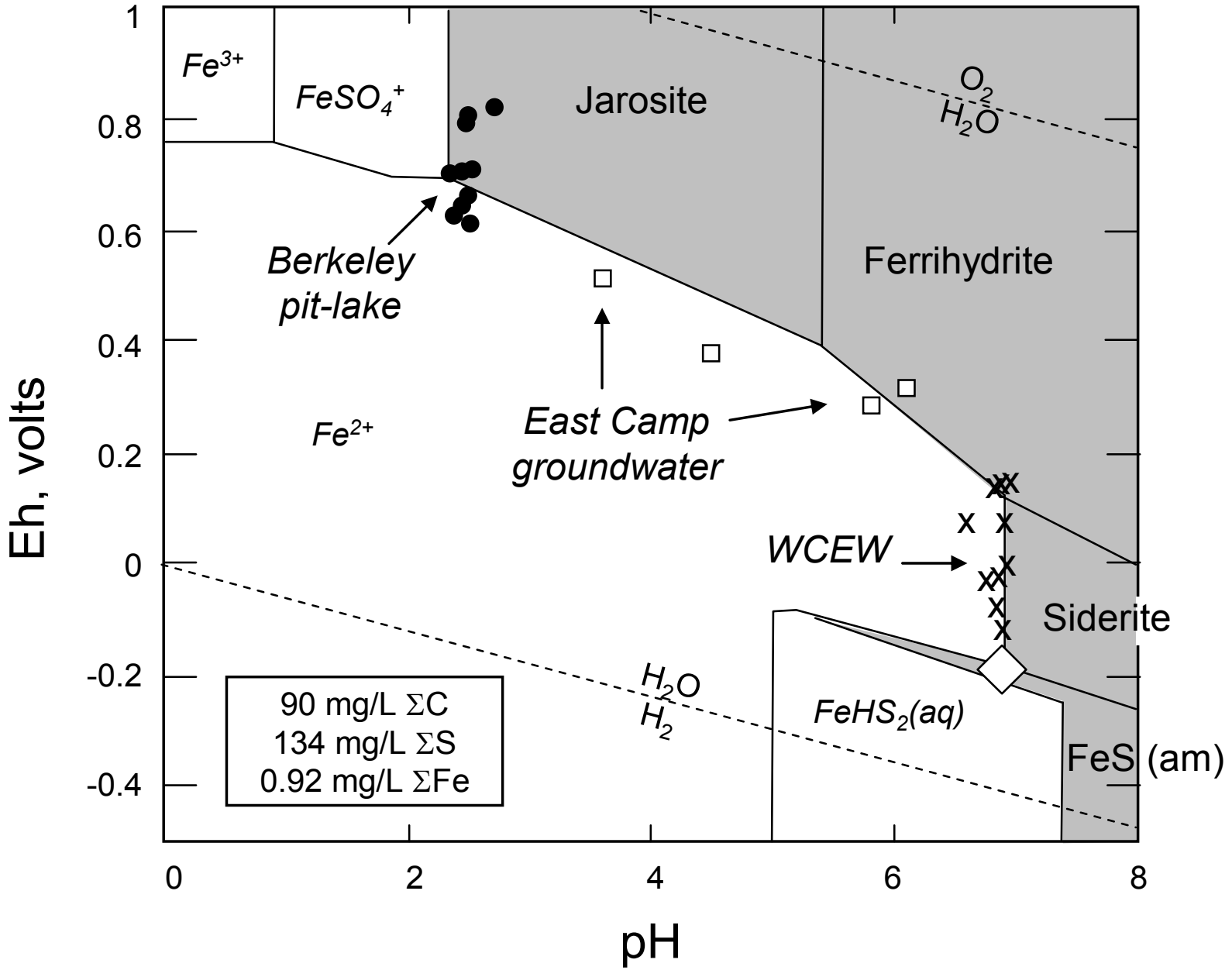
	Temp °C	pH SU	Eh mV, SHE	SC mS/cm	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe mg/l	Mn mg/l
East Camp										
Anselmo	16.0	6.49	+286	2.07	342	92	47	12.8	35.4	17.9
Belmont	13.4	6.85	+196	1.23	182	46	34	7.5	8.30	3.5
Granite Mtn	17.4	5.29	NA	3.19	551	206	33	23.6	72.5	66.3
Kelley	31.3	4.61	+244	6.80	491	395	83	62.9	1770	186
Steward	21.2	5.97	+350	3.14	491	153	44	31.7	249	30.5
Lexington	15.6	5.76	NA	2.58	347	104	49	6.6	22.1	107
Pilot Butte	19.3	5.70	+252	3.73	502	253	40	16.2	69.9	287
West Camp										
Travona	13.1	7.18	+65	1.25	176	47	41	5.7	1.83	5.5
Ophir	10.9	6.79	+345	0.88	112	31	25	4.6	1.54	11.7
Emma	16.3	6.84	+224	1.46	197	58	39	7.5	1.37	20.8
Pumping Well	11.8	7.18	+151	1.22	162	47	42	5.6	1.02	8.4
Outer Camp										
Orphan Boy	25.8	6.7	-49	1.64	227	61	126	10.5	0.1	4.8
Orphan Girl	26.4	6.8	+75	1.63	217	59	117	10.2	0.2	4.4
Marget Ann	10.2	6.9	-3	0.83	134	24	13	4.3	0.2	1.6

Gammons et al., 2006

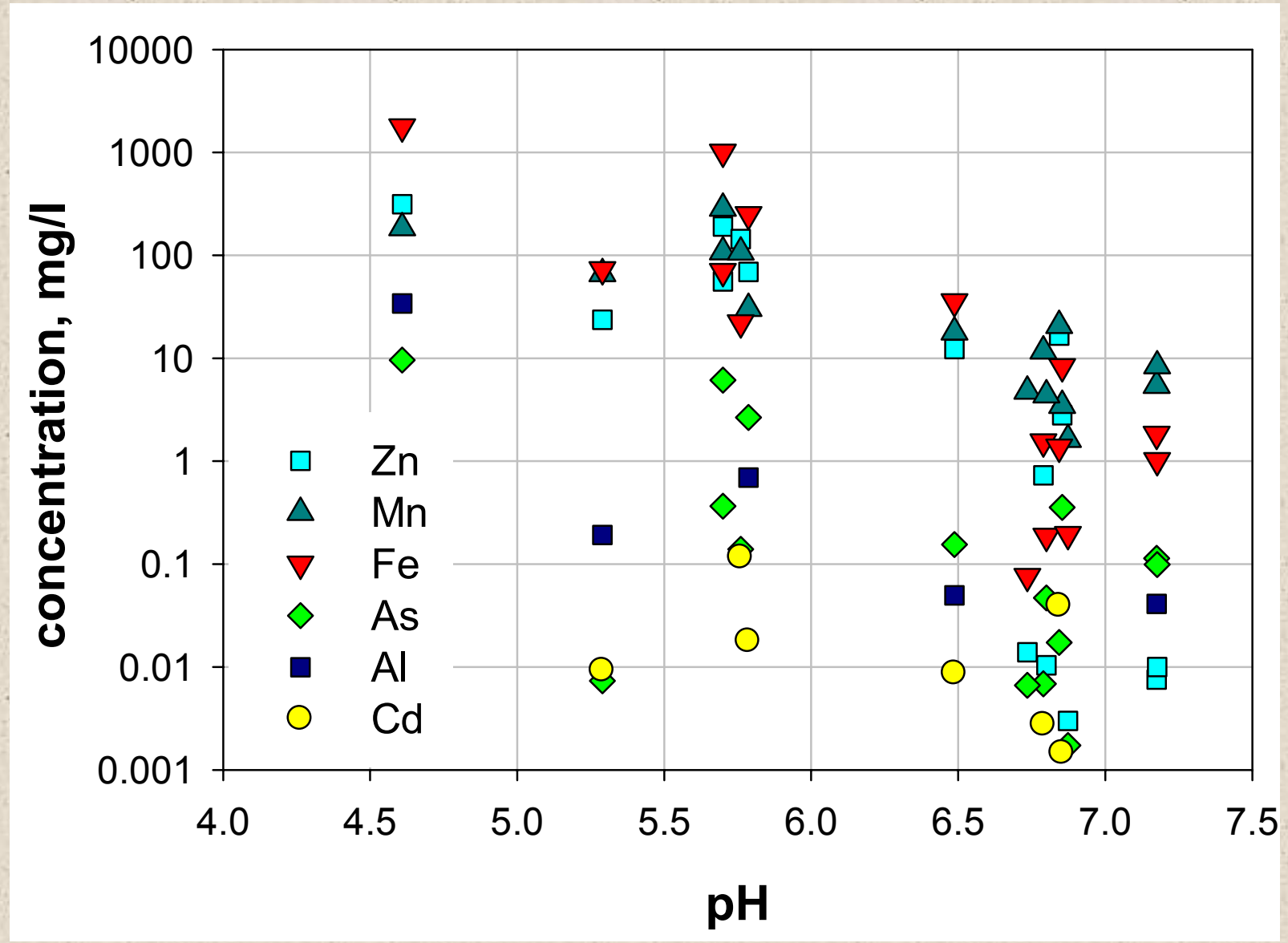
Summary of Mine Shaft Chemistry (Cont.)

	SiO_2 mg/l	HCO_3 mg/l	SO_4 mg/l	Cl mg/l	Al µg/l	As µg/l	Cd µg/l	Cu µg/l	U µg/l	Zn µg/l
East Camp										
Anselmo	22	315	1124	34	50	155	9	8	23	12300
Belmont	21	142	590	18	< 23	354	1	4	4	2790
Granite Mtn	26	NA	2390	12	192	7	9	189	NA	23600
Kelley	78	NA	7740	25	34100	9610	36	47	8	313000
Steward	42	156	2320	38	691	2650	18	68	6	68900
Lexington	20	243	1570	40	< 37	140	116	8	NA	144000
Pilot Butte	35	35	3030	13	442	365	< 2	55	8	55900
West Camp										
Travona	18	342	401	37	41	114	< 2	< 3	16	8
Ophir	18	242	235	35	< 25	7	3	3	17	729
Emma	19	417	512	41	< 26	17	39	14	23	16600
Pumping Well	17	328	396	40	< 28	99	< 2	2	25	10
Outer Camp										
Orphan Boy	29	954	282	15	<25	7	<2	<3	62	14
Orphan Girl	25	780	303	17	<30	47	<1	<5	34	10
Marget Ann	7.7	204	281	18	<25	2	< 1	<3	13	3

Gammons et al., 2006


Eh, volts
pH
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
0
2
4
6
8
Fe^{3+}
$FeSO_4^+$
Jarosite
O_2
H_2O
Ferrihydrite
Berkeley
pit-lake
Fe^{2+}
East Camp
groundwater
WCEW
Siderite
H_2O
H_2
$FeHS_2(aq)$
FeS (am)
90 mg/L ΣC
134 mg/L ΣS
0.92 mg/L ΣFe

Dissolved metal concentrations vs. pH



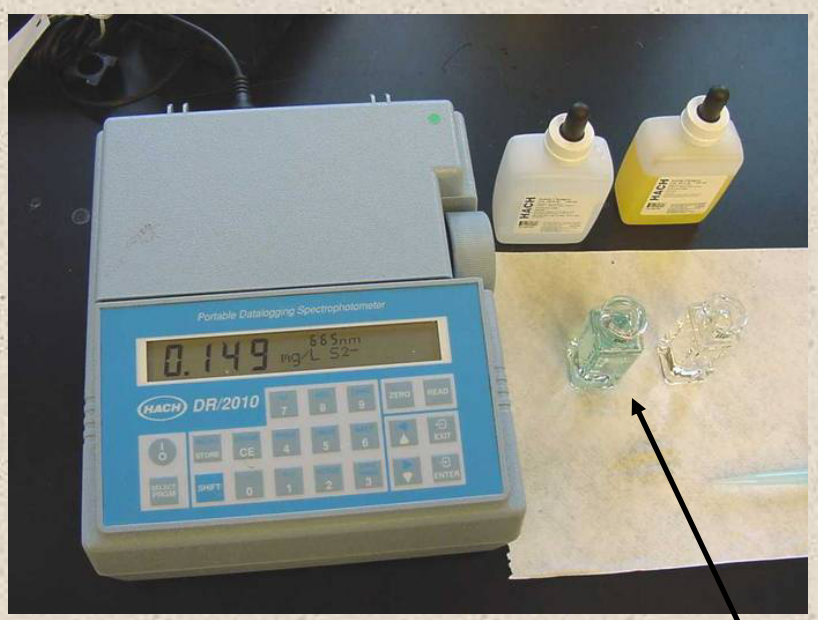
Gammons et al., 2006

Butte veins were rich in copper

So.. why is their so little Cu in the shaft water?

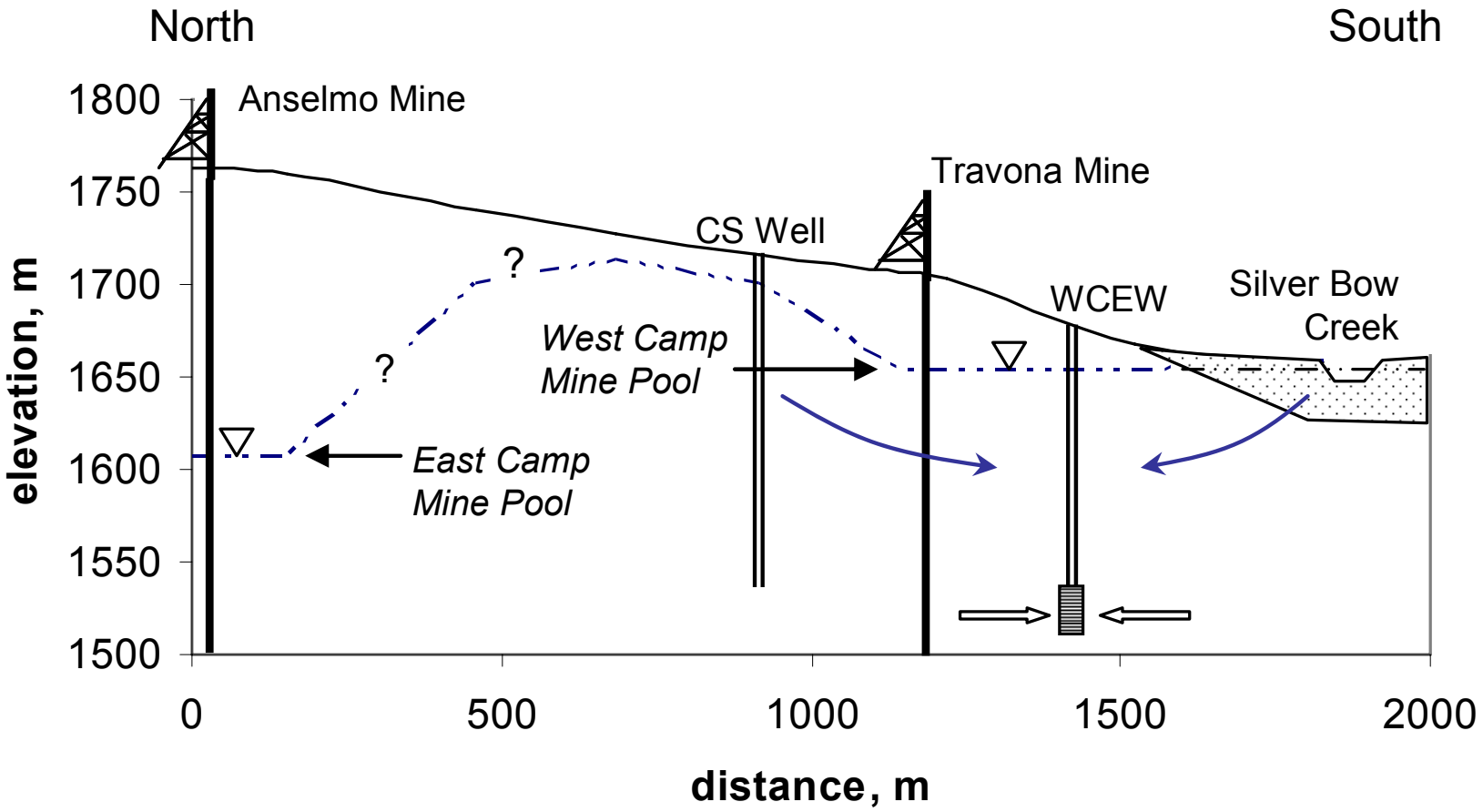
Cu-cemented steel? (railways, cables, bolts & dooey-dags, etc…)

Amber Roesler sampling the West Camp extraction well



0.15 mg/L S^{2-} in West Camp extraction well

West Camp mine pool is isolated from East Camp
Possible recharge from Silver Bow Creek?



Sources of H_2S in flooded mine waters

INORGANIC PATHWAY

$ZnS + 2H^+ \leftrightarrow H_2S + Zn^{2+}$

little or no isotopic fractionation of S

BACTERIAL PATHWAY

Step 1: pyrite oxidation (before mine flooding)

$FeS_2 + 7/2H_2O + 15/4O_2 \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$

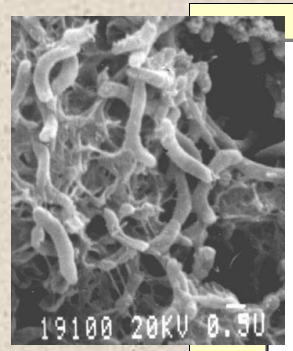
little or no isotopic fractionation of S

Step 2: bacterial sulfate reduction (after flooding)

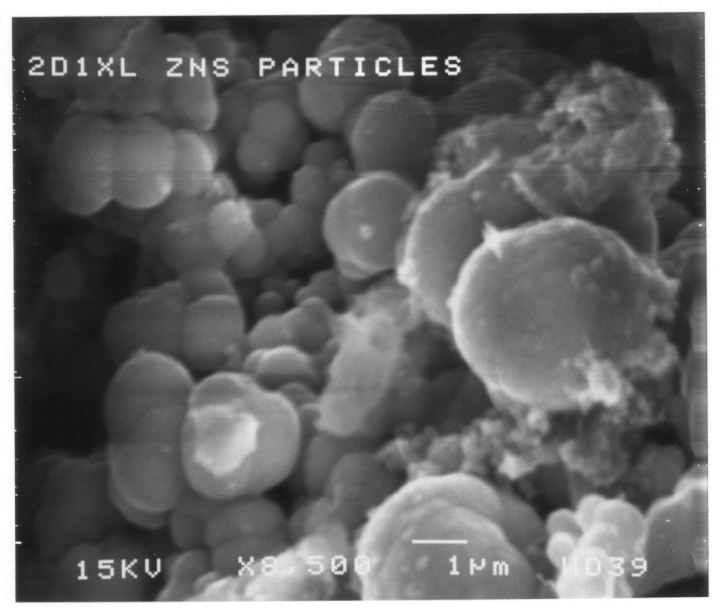
$SO_4^{2-} + 2CH_2O$ (org. C) $\rightarrow H_2S + 2HCO_3^-$

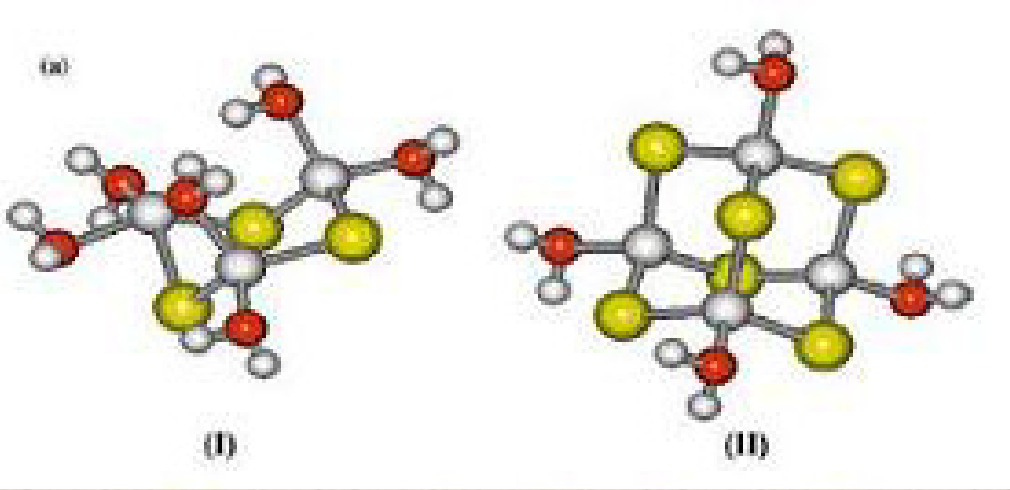
strong isotopic fractionation of S

S isotopes of Butte rock and water



Roesler et al., in review





H_2S generated by SRBs forms insoluble metal sulfides (ZnS, top left), and also dissolved metal sulfide “cluster” compounds (bottom left).

These are poorly known, but our recent work has shown they are abundant in the West Camp mine water.

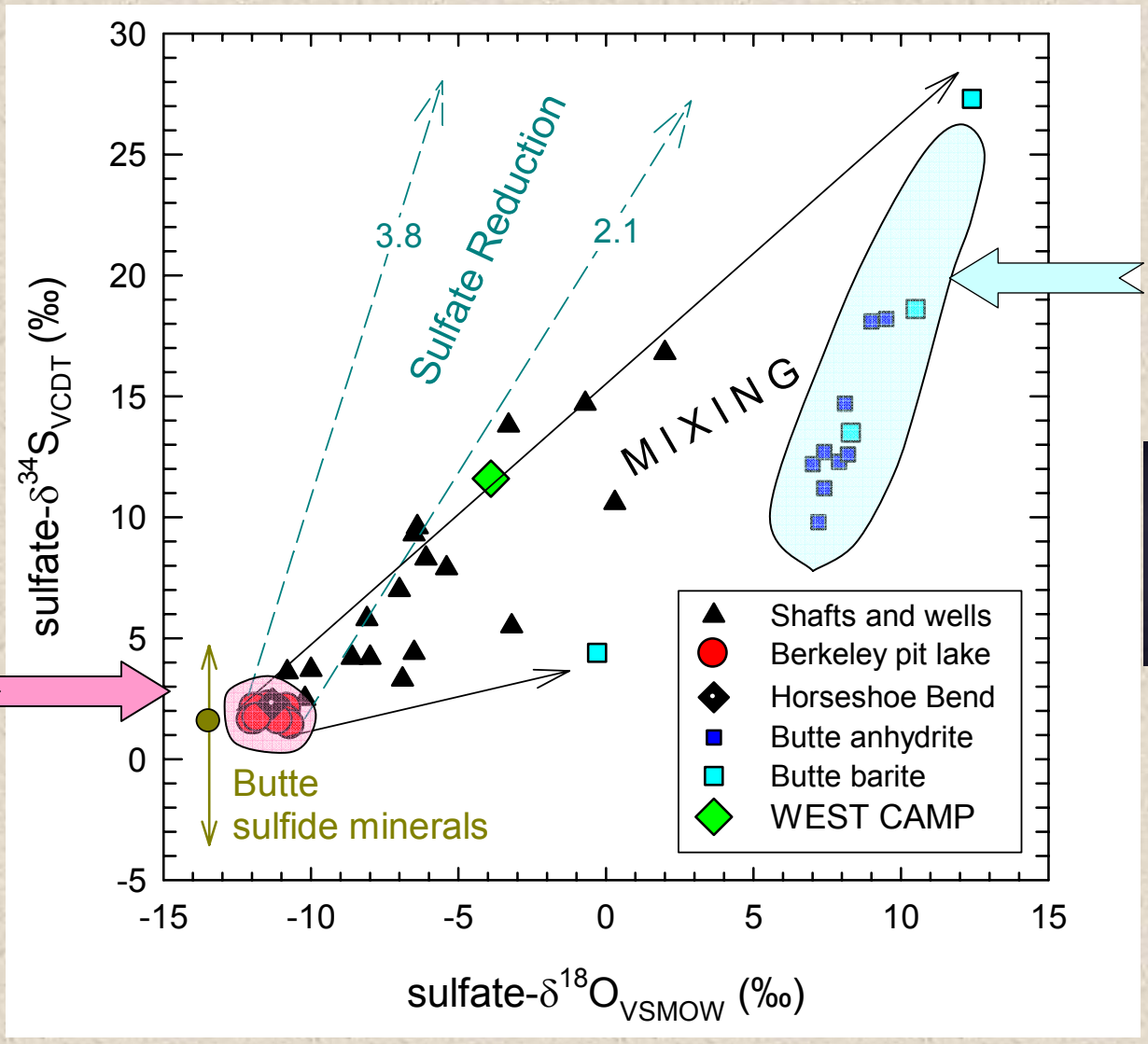
Organic carbon source?

15,000 km of wood-framed mine workings

Possible arsenic source?

$\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate

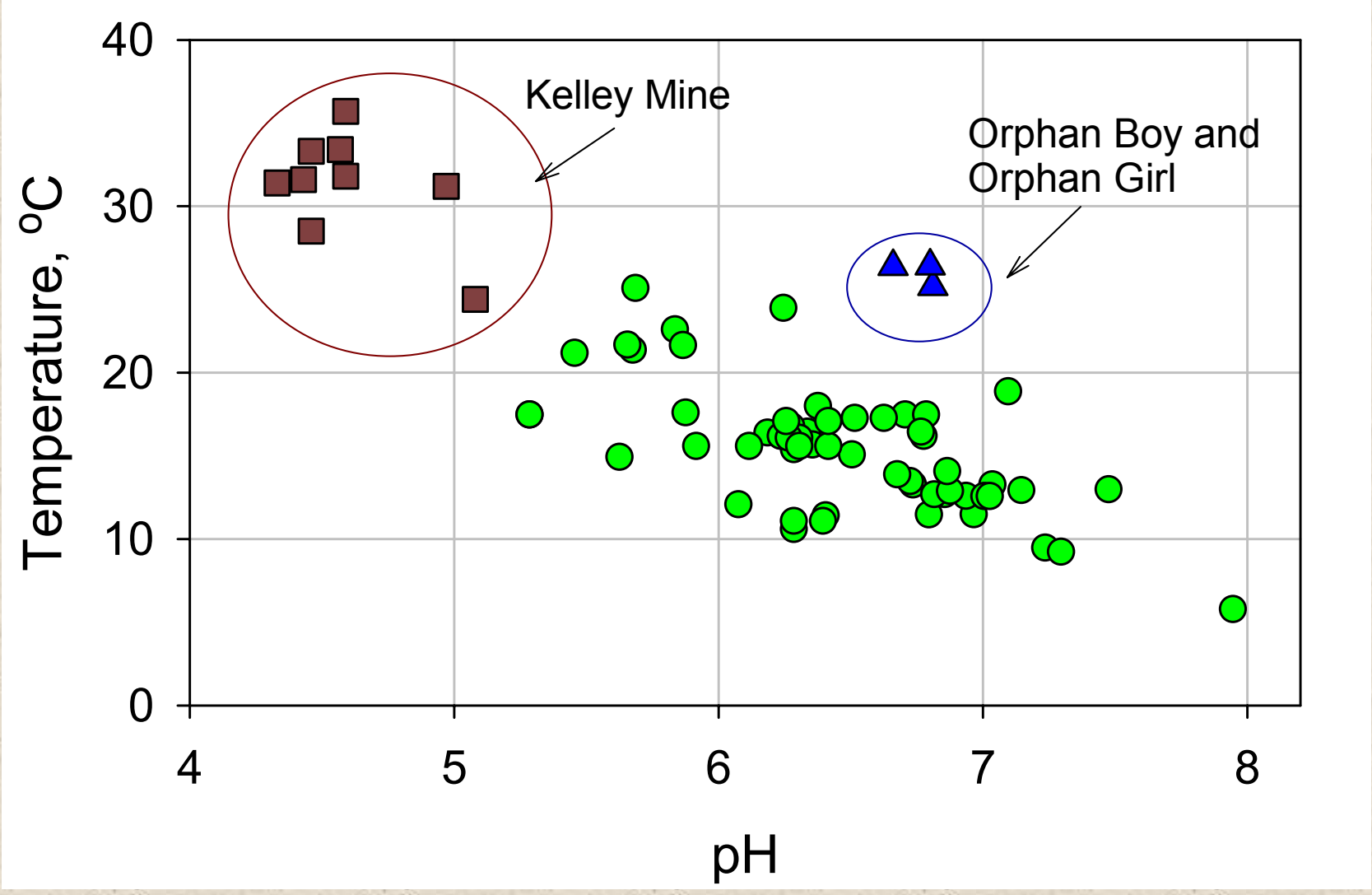
Sulfate from pyrite oxidation



Sulfate from dissolution of hydrothermal anhydrite

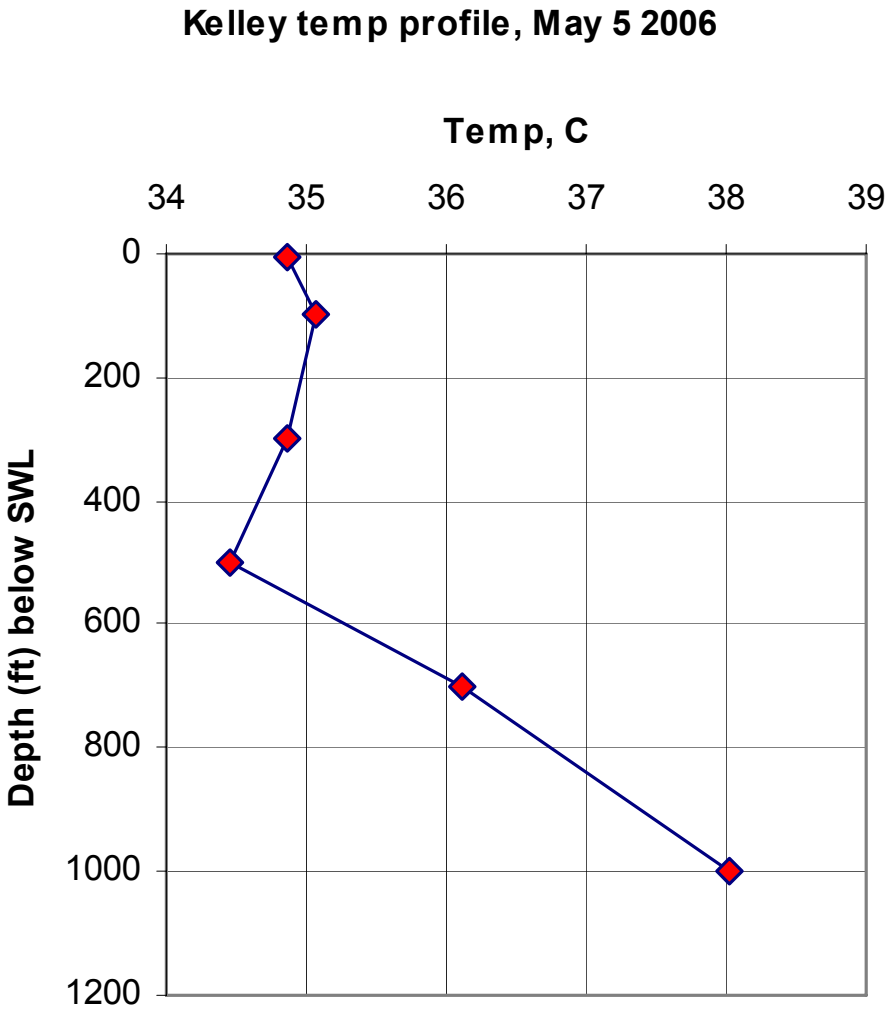
Pellicori et al., 2005: Applied Geochem. 20: 2116-2137

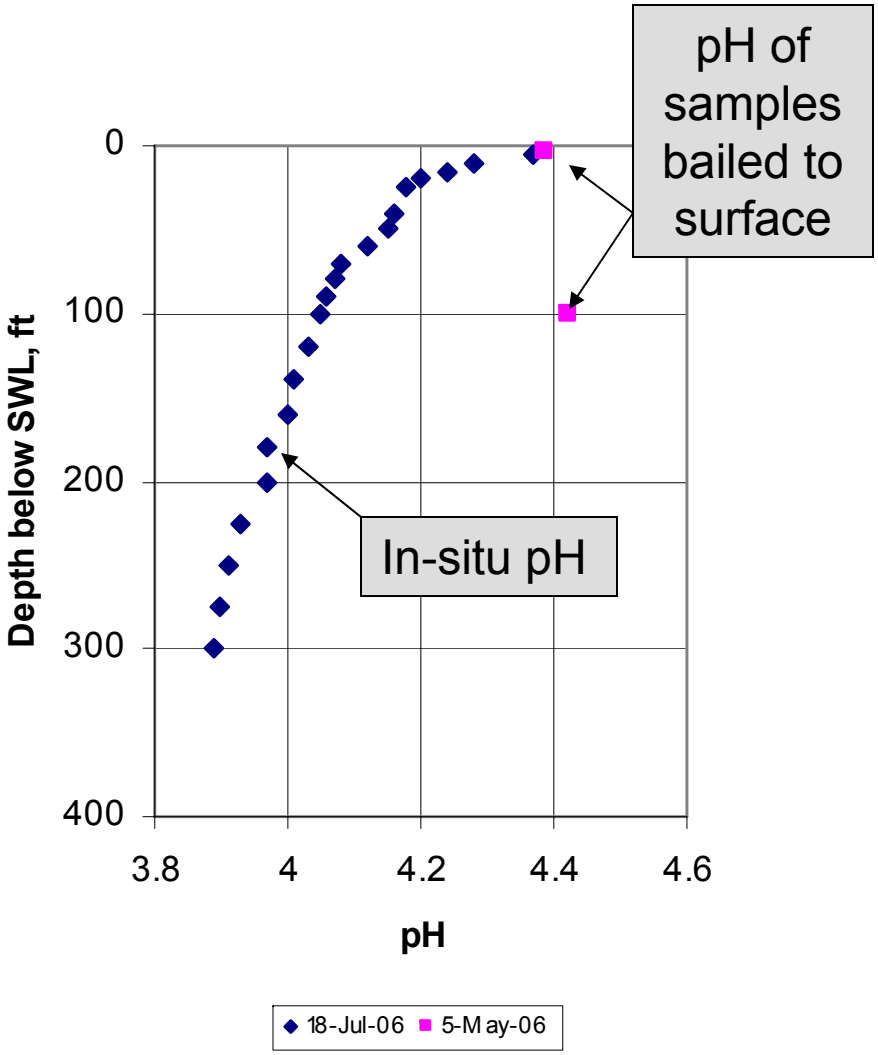
Temperature gradients



Gammons et al., 2006

Kelley Mine: A closer look



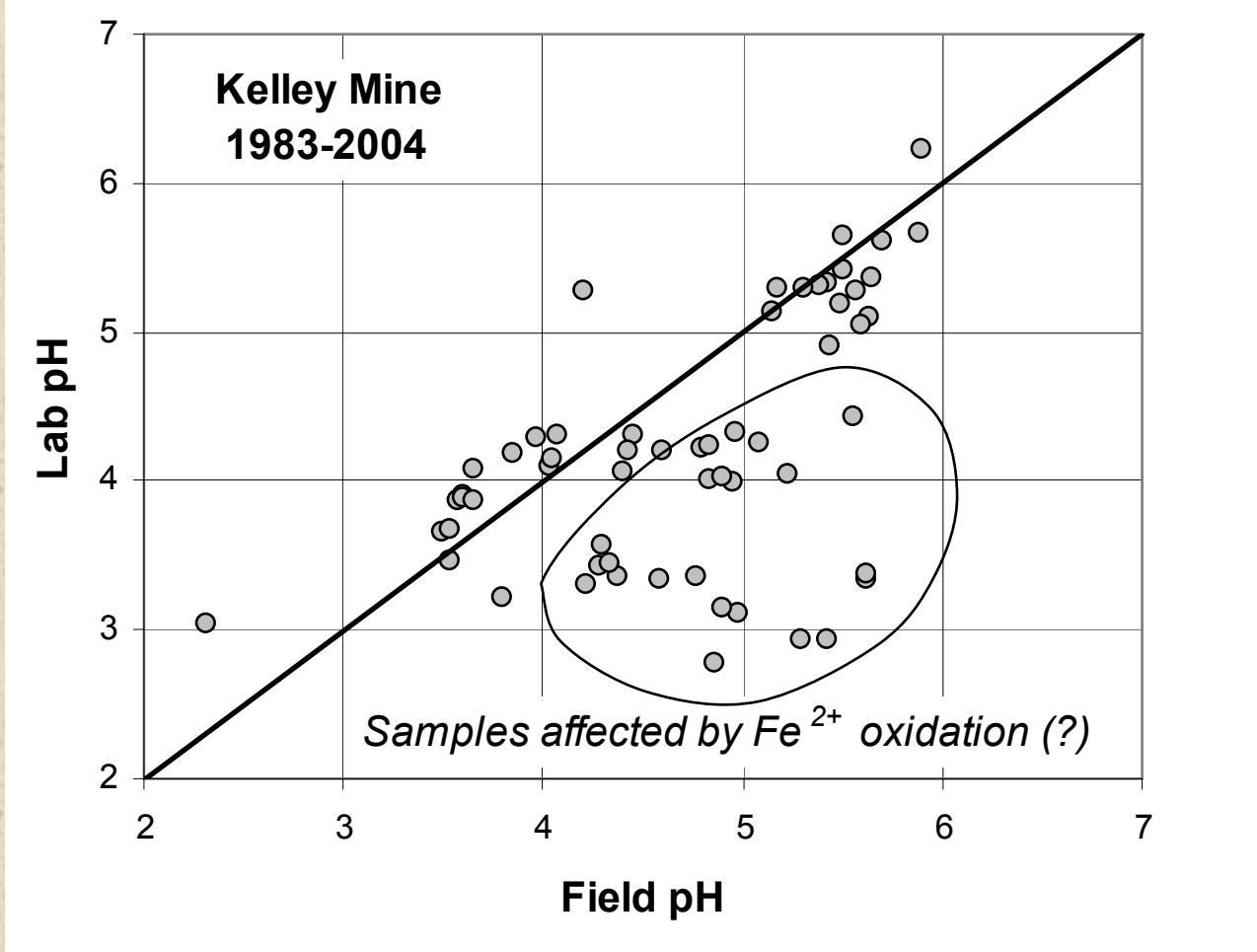


Snyder & Gammons, in prep.

Why is the water warm?

- Geothermal?
- Pyrite oxidation
  - Kelley Mine has lowest pH of any shaft
  - At pH < 4, oxidation of pyrite by Fe^{3+} may take place at significant rate
- Microbial activity
  - Orphan Girl and Orphan Boy have highest H_2S concentrations in district
  - Bacterial sulfate reduction is exothermic

NOTE: measure your pH and alkalinity of mine shaft water in-situ, or immediately after sampling



Fe^{2+} oxidation and precipitation of ferrihydrite will result in drop in pH and alkalinity

Vertical gradients in mine shaft chemistry

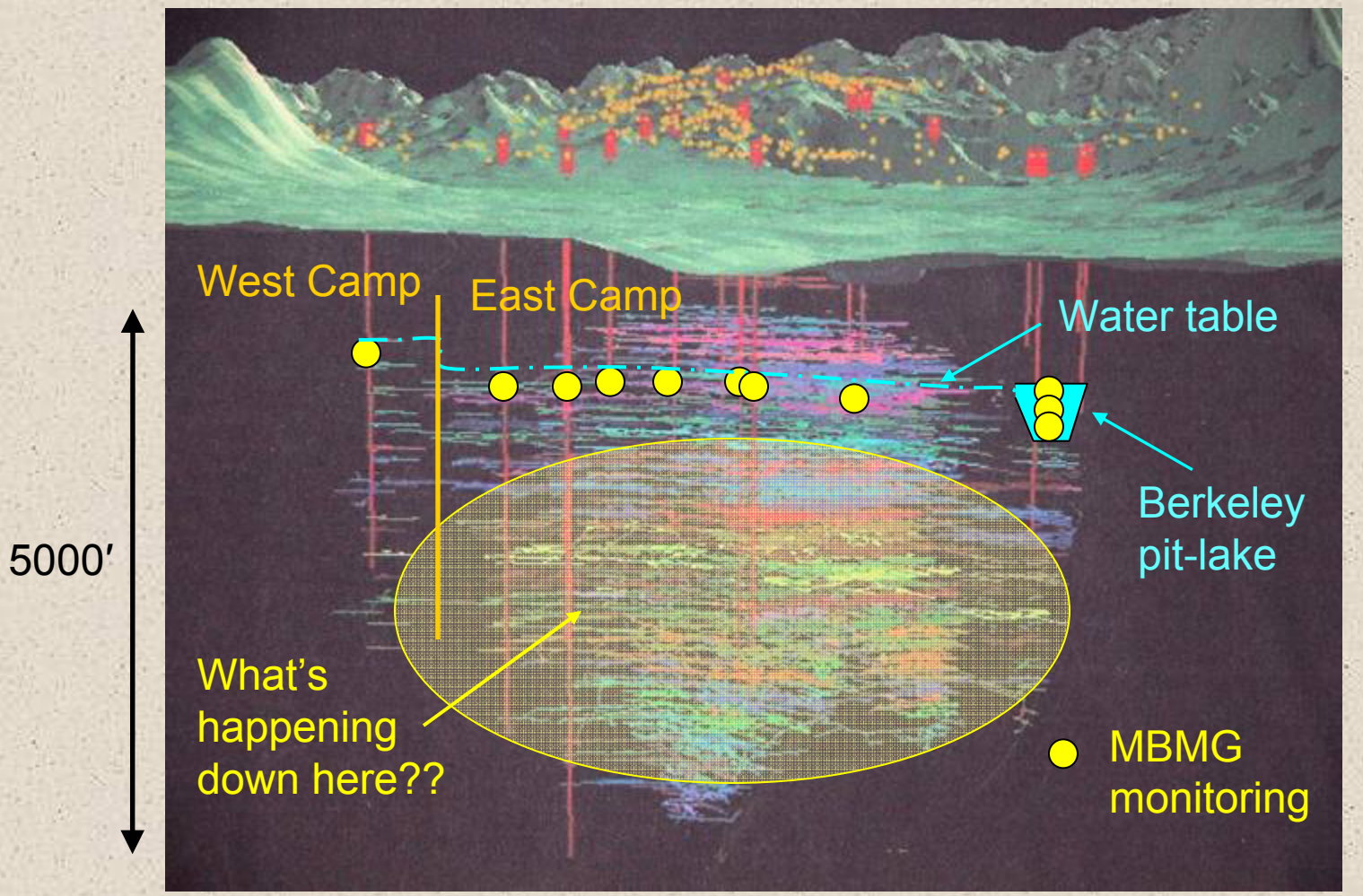
- Project is in progress
- Some preliminary data shown here

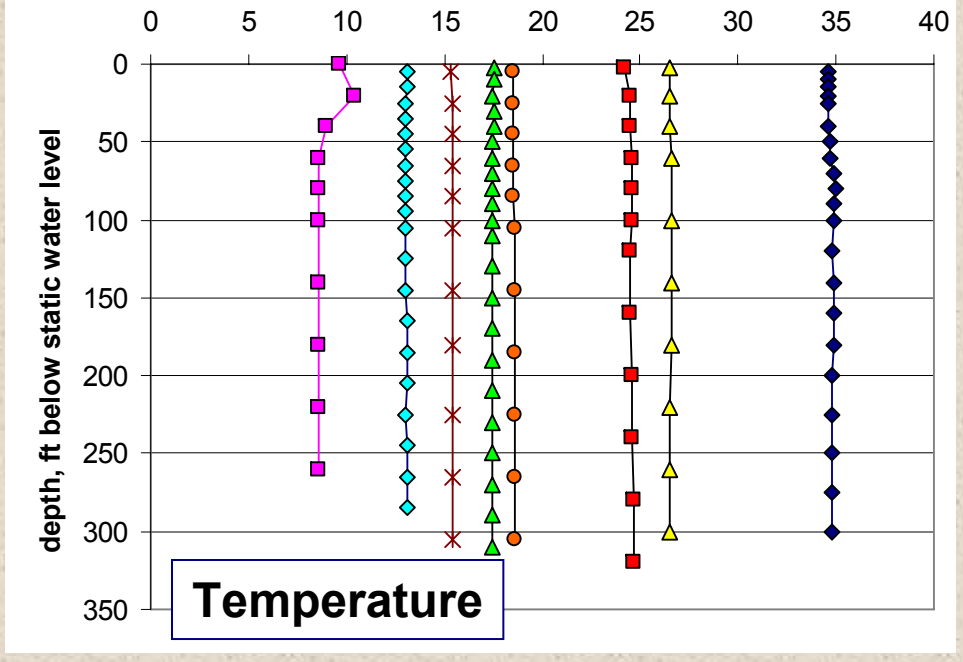
  (we have lots more!)

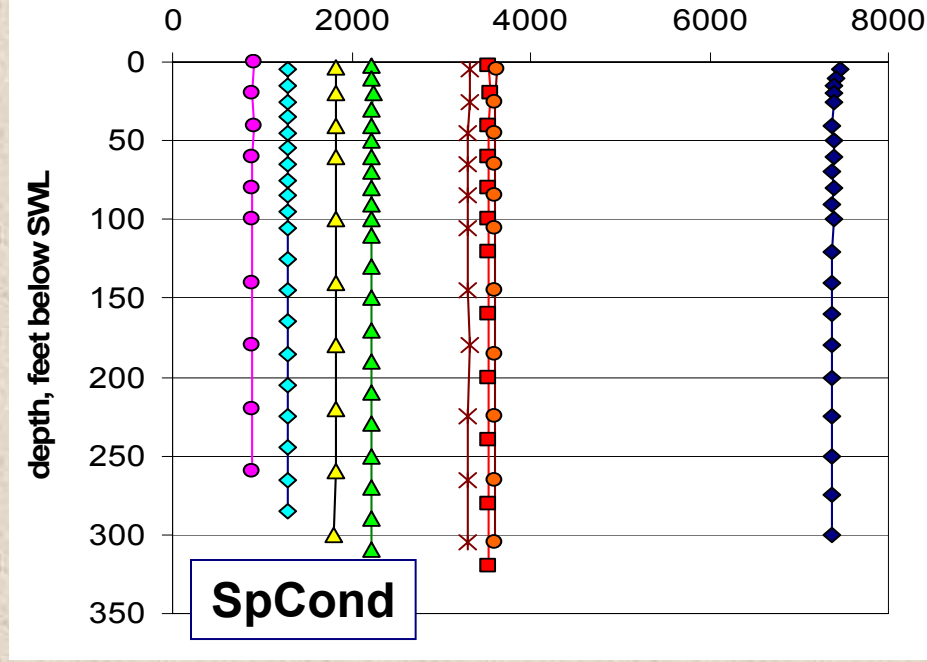
Grad student Dean Snyder sampling the Orphan Girl shaft

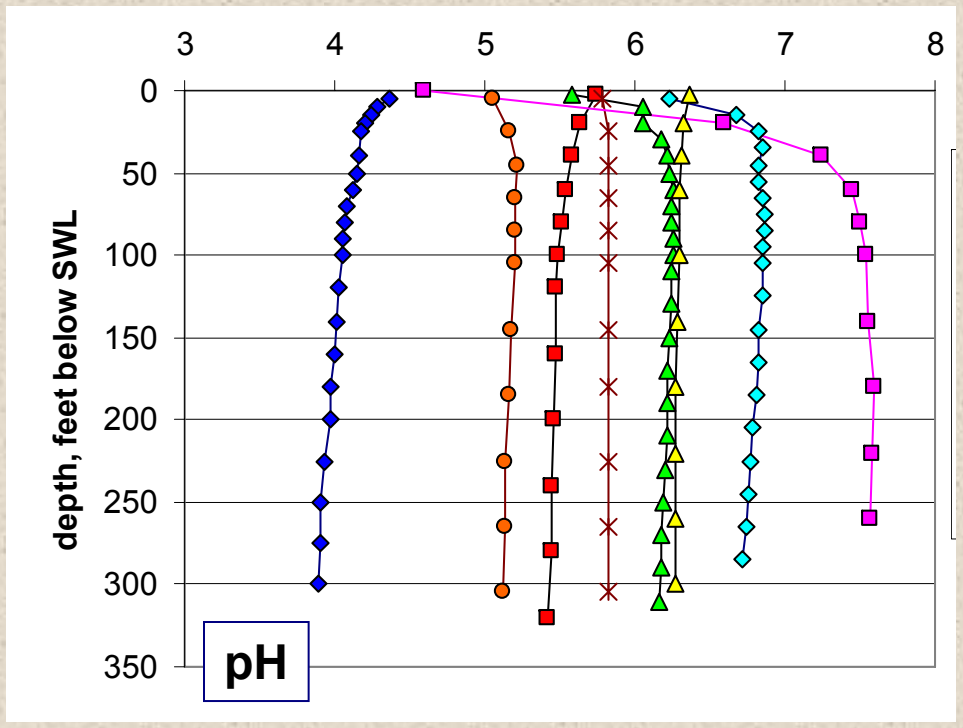
“Kemmerer-type” point source sampler

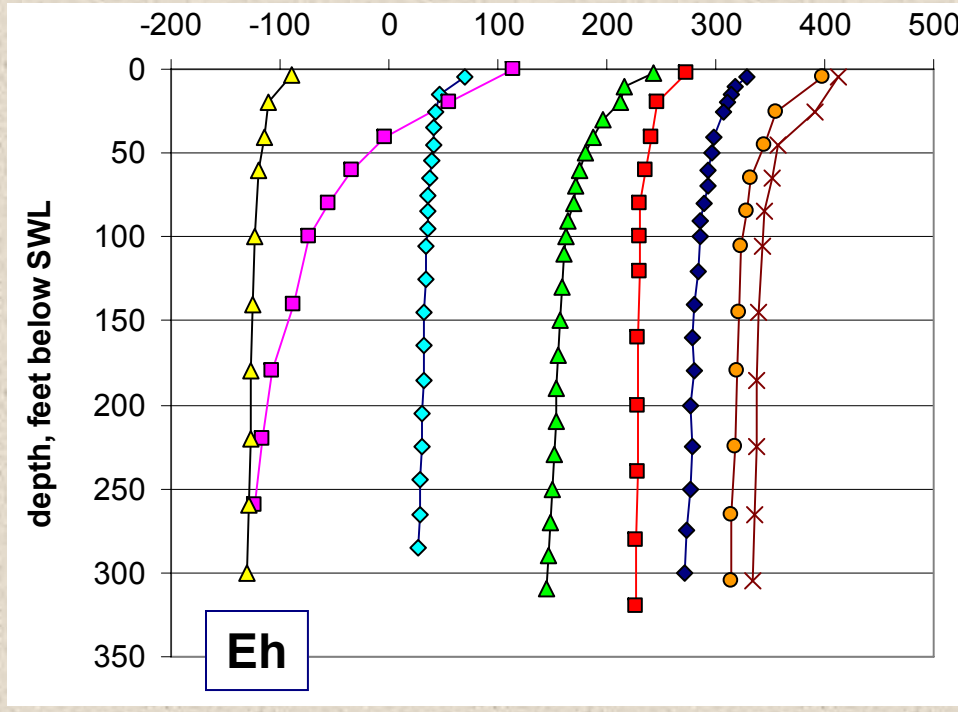
Butte flooded mine complex: geochemical gradients with depth?




0
5
10
15
20
25
30
35
40
depth, ft below static water level
0
50
100
150
200
250
300
350
Temperature


0
2000
4000
6000
8000
depth, feet below SWL
0
50
100
150
200
250
300
350
SpCond


3
4
5
6
7
8
depth, feet below SWL
0
50
100
150
200
250
300
350
pH


-200
-100
0
100
200
300
400
500
depth, feet below SWL
0
50
100
150
200
250
300
350
Eh

Findings

- Butte mine shaft waters have tremendous variety in chemistry
- Overall chemical trends are largely controlled by changes in mineralogy of veins
- West Camp and Outer Camp are rich in biogenic H_2S
- With the exception of the Kelley Mine, vertical gradients in chemistry of the mine shafts are minimal, especially below a depth of 100 ft.
- Water in each deep shaft appears to be vertically mixed, possibly due to thermal convection
- Some shaft waters are anomalously warm, possibly due to ongoing pyrite oxidation or bacterial reactions
- Deep mine shaft sampling is difficult, time-consuming, and expensive (lost equipment)!

Acknowledgments

- US-EPA, US-DOE
- MT Tech Mine Waste Technology Program
- ARCO, Montana Resources
- Simon Poulson (UNev-Reno)
- Montana Bureau of Mines and Geology
- Montana Tech Students
  - Amber Henne Roesler
  - Dean Snyder

Nick Tucci, MBMG Hydrogeologist

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Gammons C. H., Poulson S. R., Pellicori D. A., Roesler A., Reed P. J., Petrescu E. M. (2006) The hydrogen and oxygen isotopic composition of precipitation, evaporated mine water, and river water in Montana, USA. *Journal of Hydrology* 328, 319-330.

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Metesh J. J. (2006) Using a water balance to determine the source of water in a flooding mine complex, Butte, Montana. *Mine Water and the Environment* 25(2), 108-113.

Pellicori D. A., Gammons C. H., and Poulson S. R. (2005) Geochemistry and stable isotope composition of the Berkeley pit lake and surrounding mine waters, Butte, Montana. *Applied Geochemistry* 20, 2116-2137.

Roesler A.J., Gammons C. H., Druschel G.K., Oduro H., and Poulson S.R. (in review) Geochemistry of flooded underground mine workings influenced by bacterial sulfate reduction

References in **bold** are included on the MEND workshop CD

Questions?

Ice formations in Lexington Tunnel
C. Gammons, 2002