Mineral Weathering as Related to Biogeochemical Processes in the Everglades

Willie Harris, Michael M. Reddy, and William Orem

Acknowledgments:

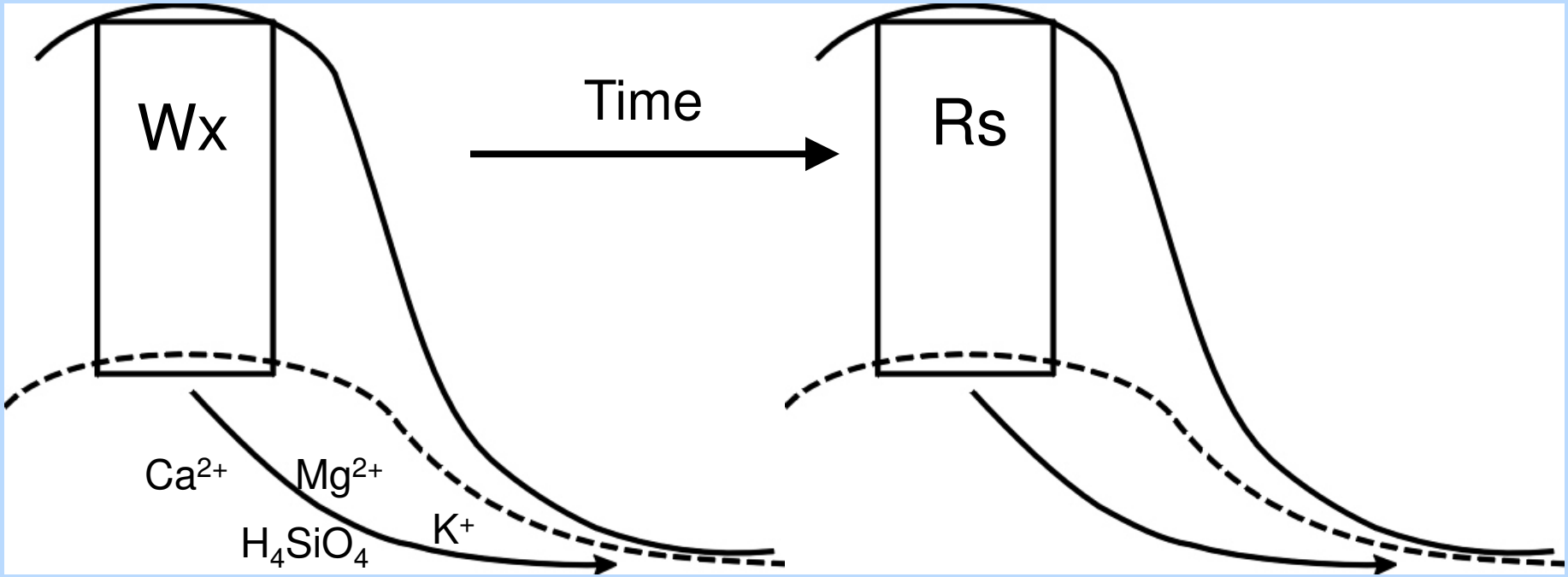
Personnel who contributed to the Florida Soil Survey Program. Data generated through their effort prompted research reported in this talk.

Outline

- Weathering – Everglades style
- Minerals of Everglades
- Mineral transformations & implications
- Inhibitors of crystalization
- Concluding ideas

“Weathering”, Everglades Style

“Weathering” as seen by typical soil mineralogists



Wx —(Acid Hydrolysis / Oxidation)→ Rs

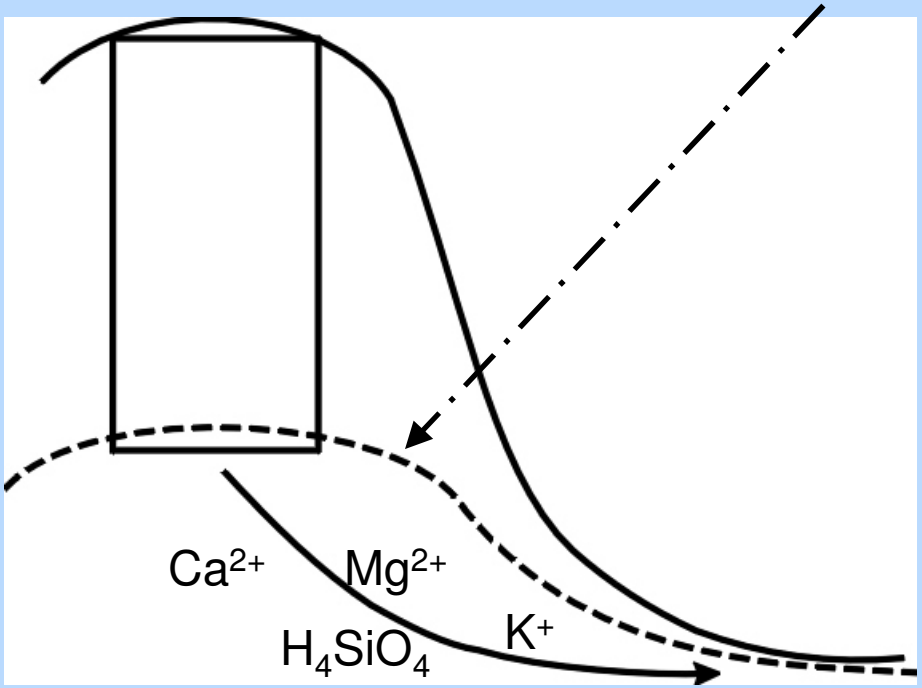
e.g.

Feldspar → Kaolinite

Unidirectional in Time and Space

Water Table

Upland Landscapes



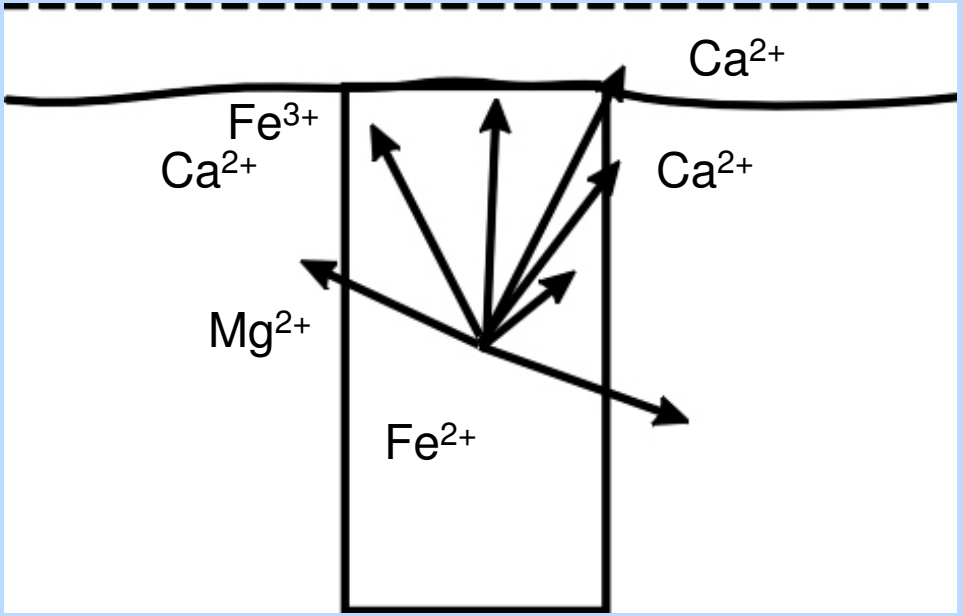
Flow Directional

Leaching Driven

Minerals that Die Stay Dead

Bio**geochemical**

Everglades



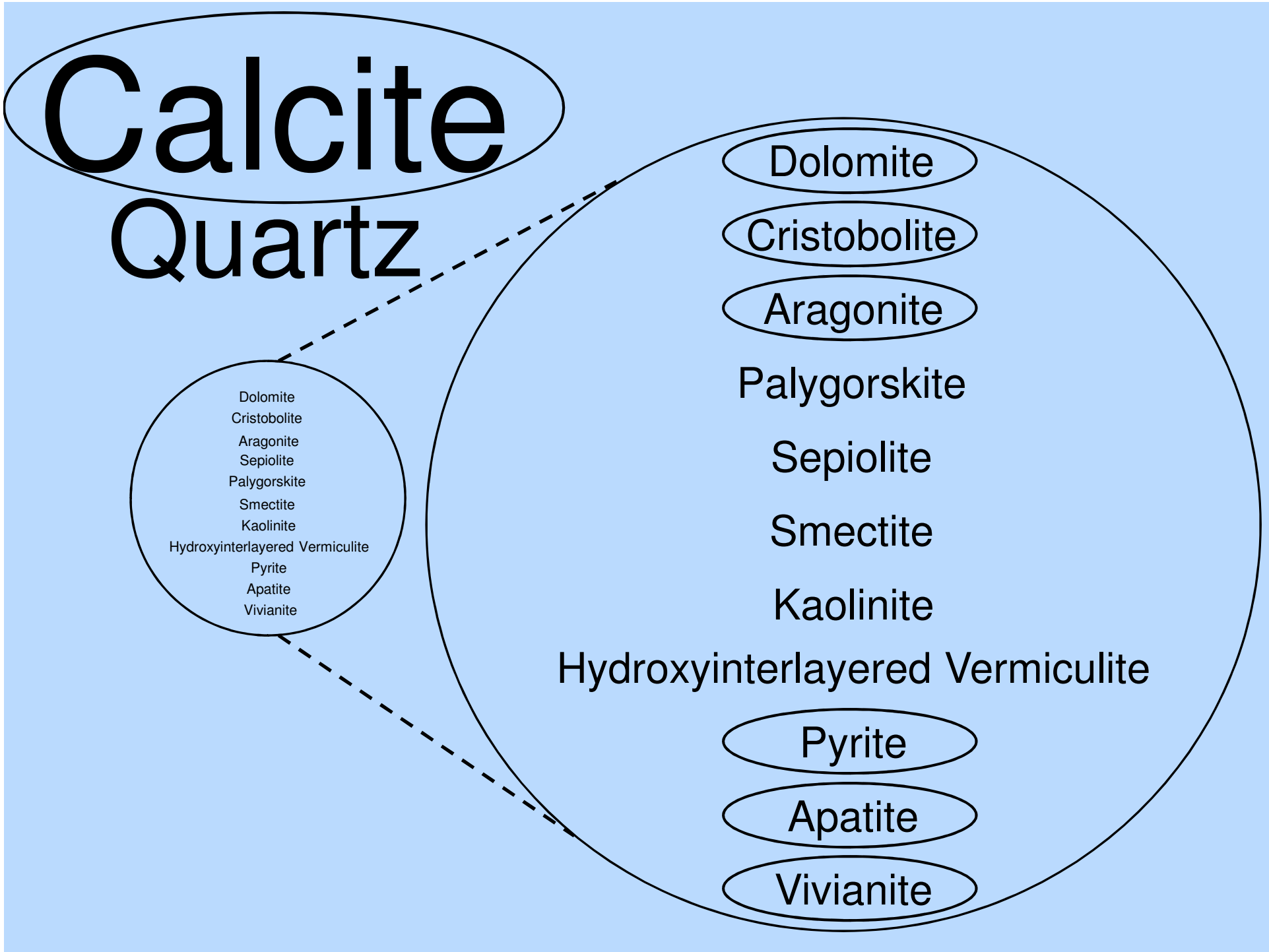
Life Directional

Diffusion Driven (“Life” Gradients)

Minerals that Die One Place are Reborn in Another

Biogeochemical

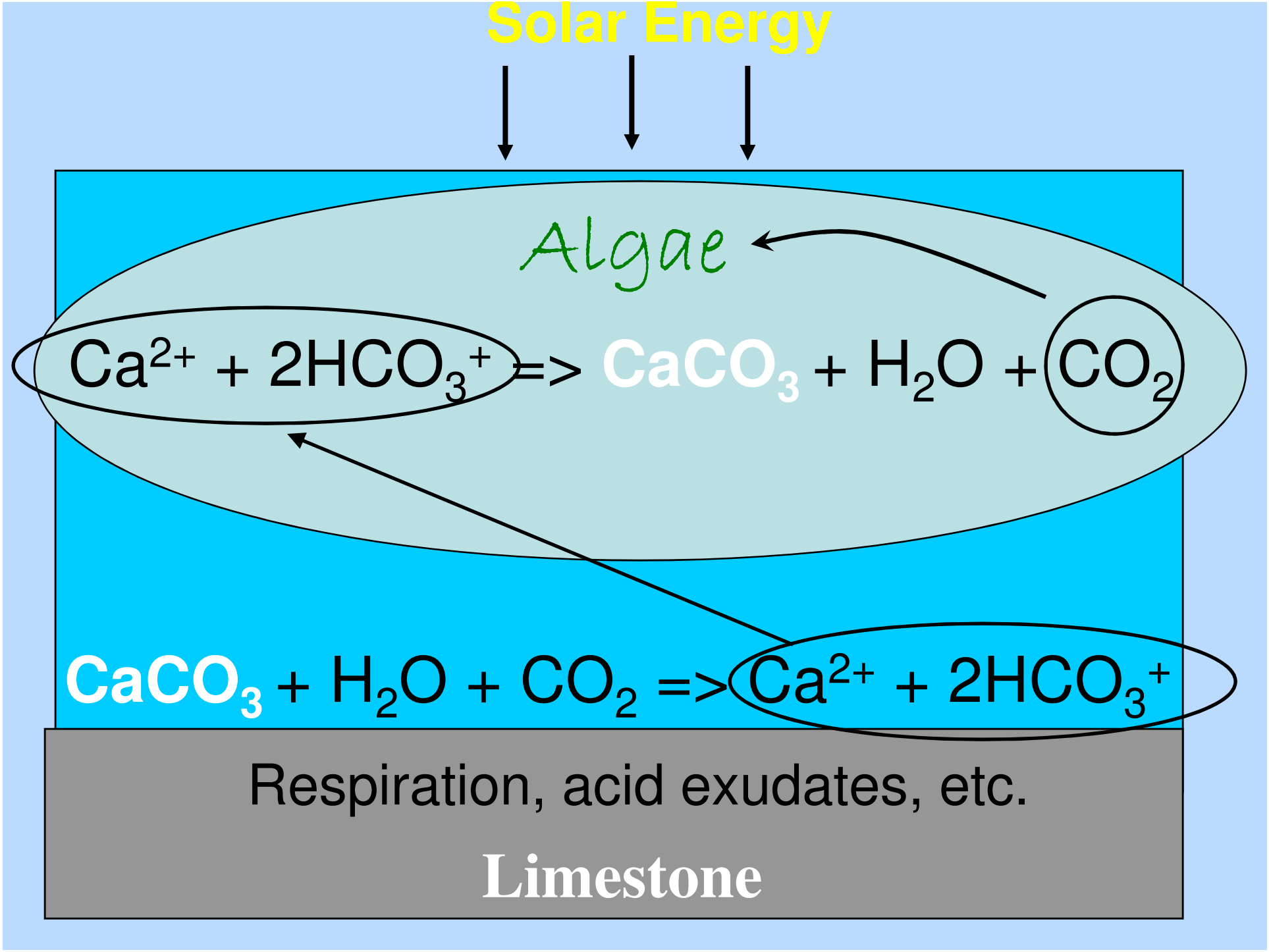
Minerals of the Everglades


Calcite
Quartz
Dolomite
Cristobolite
Aragonite
Sepiolite
Palygorskite
Smectite
Kaolinite
Hydroxyinterlayered Vermiculite
Pyrite
Apatite
Vivianite
Dolomite
Cristobolite
Aragonite
Palygorskite
Sepiolite
Smectite
Kaolinite
Hydroxyinterlayered Vermiculite
Pyrite
Apatite
Vivianite

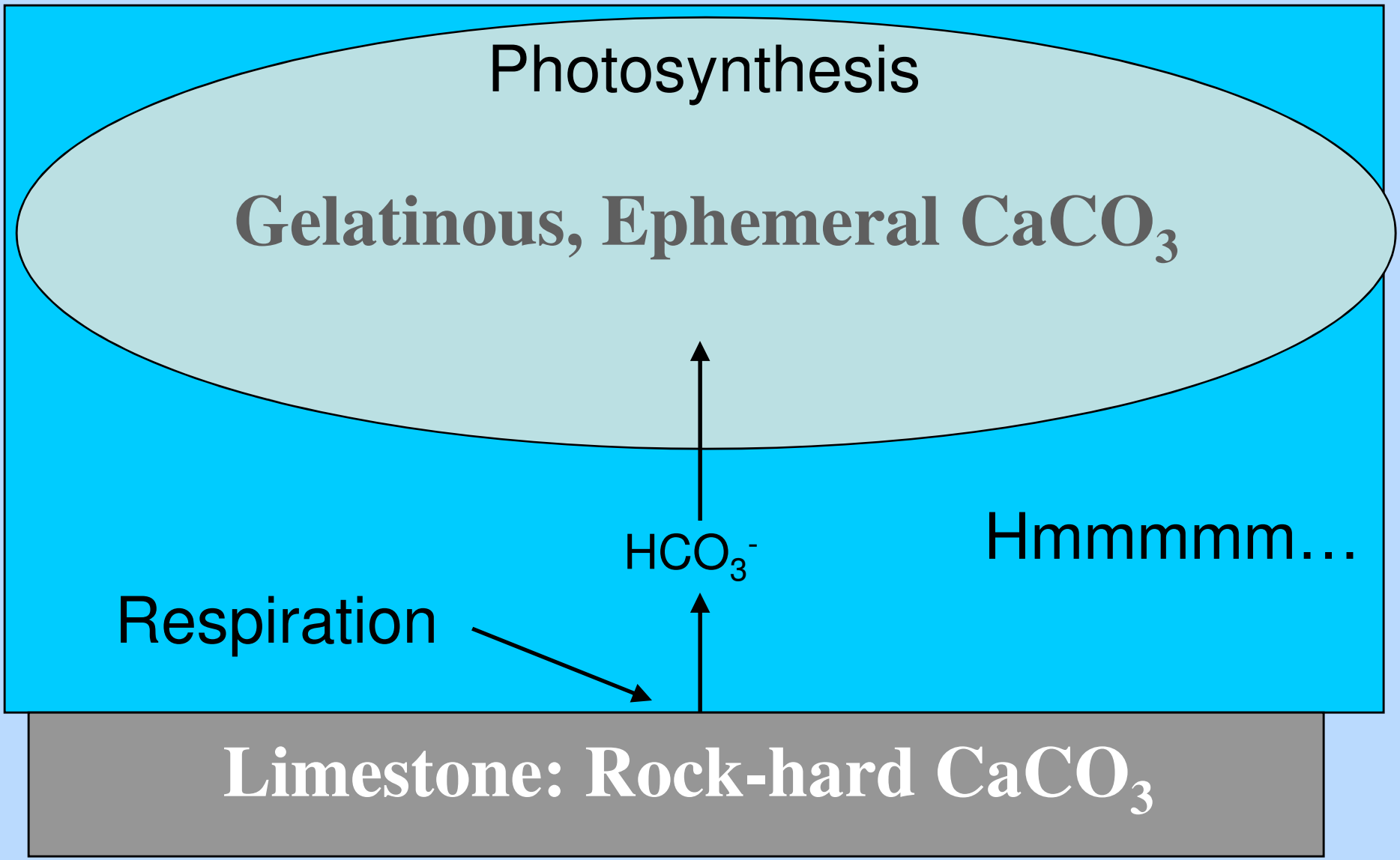
Mineral transformations & Implications

Calcite

- At the helm – strong buffer
- Ca-pH-HCO3 system


Solar Energy
Algae
$Ca^{2+} + 2HCO_3^+ \Rightarrow CaCO_3 + H_2O + CO_2$
$CaCO_3 + H_2O + CO_2 \Rightarrow Ca^{2+} + 2HCO_3^+$
Respiration, acid exudates, etc.
Limestone

Does Marl Formation Sequester C?

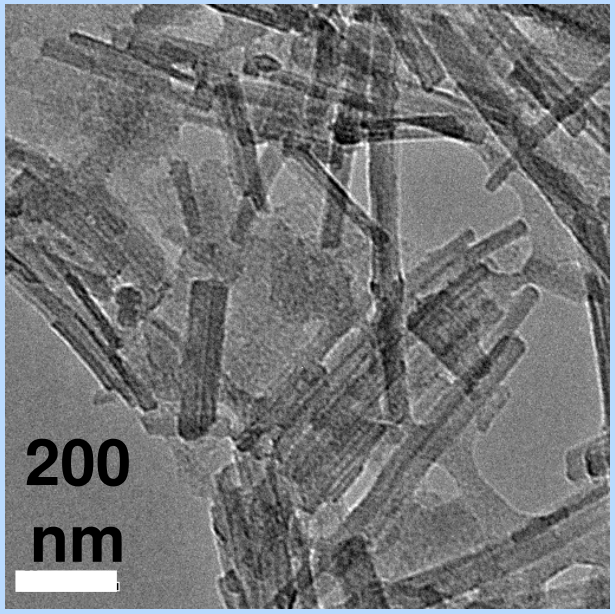


Mineral transformations & Implications

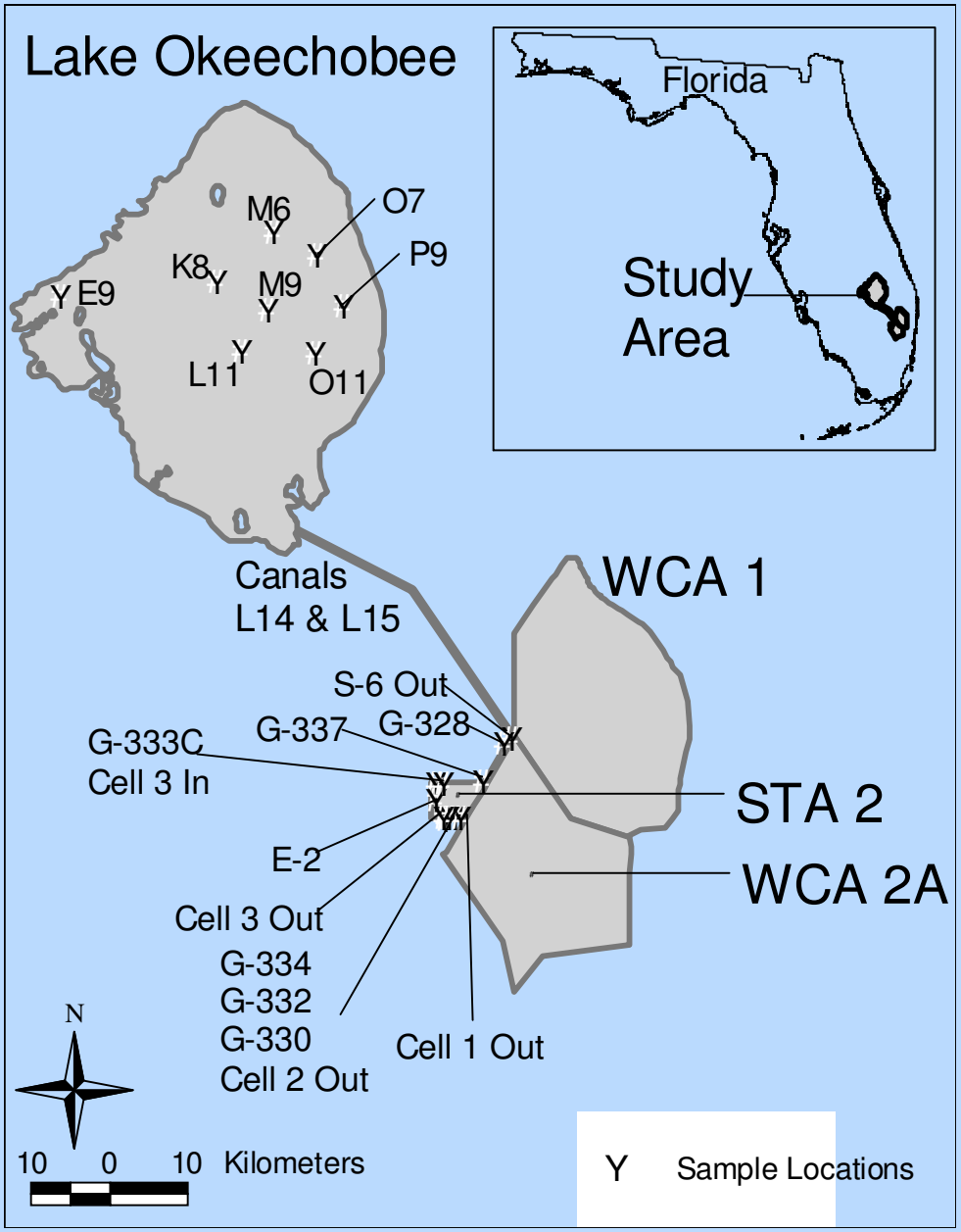
Silicates (except quartz)

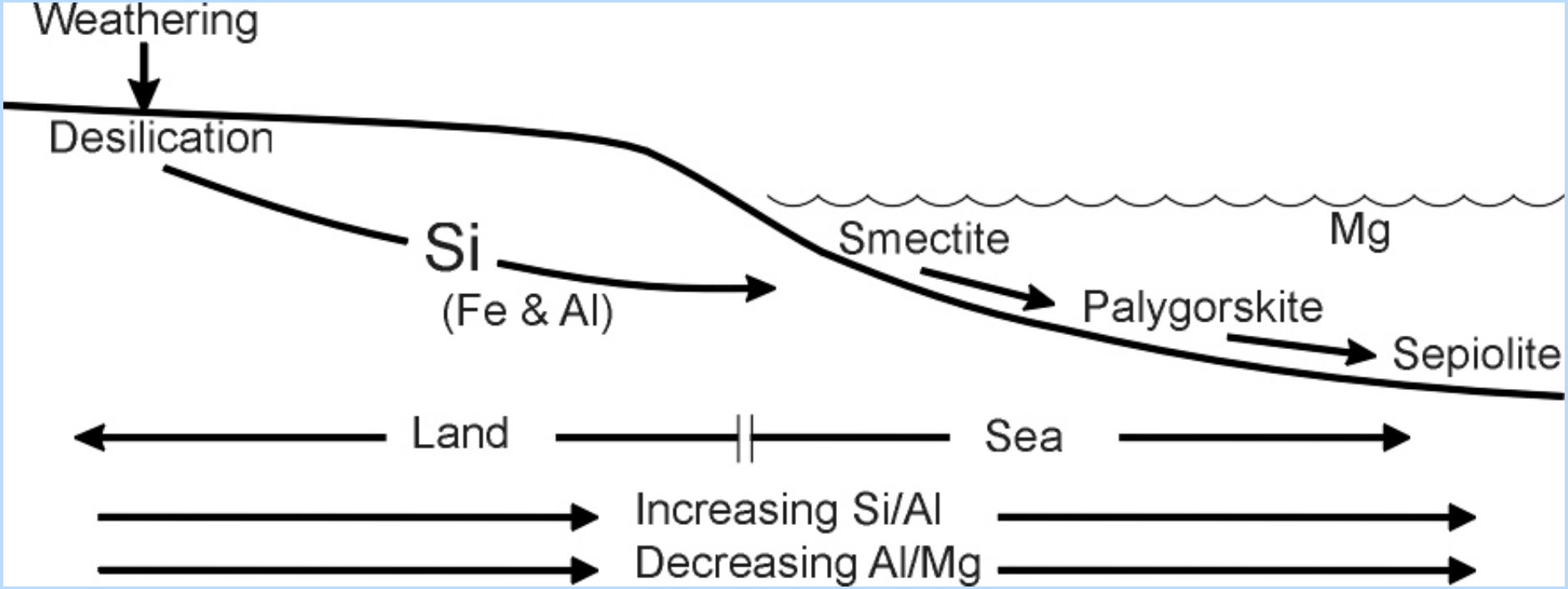
- Ubiquitous
- Of mysterious origin
- Stable in Everglades

Mg-Bearing Silicates – Sepiolite, Palygorskite, and Smectite – Occur in Soils, Sediments, and Water Column

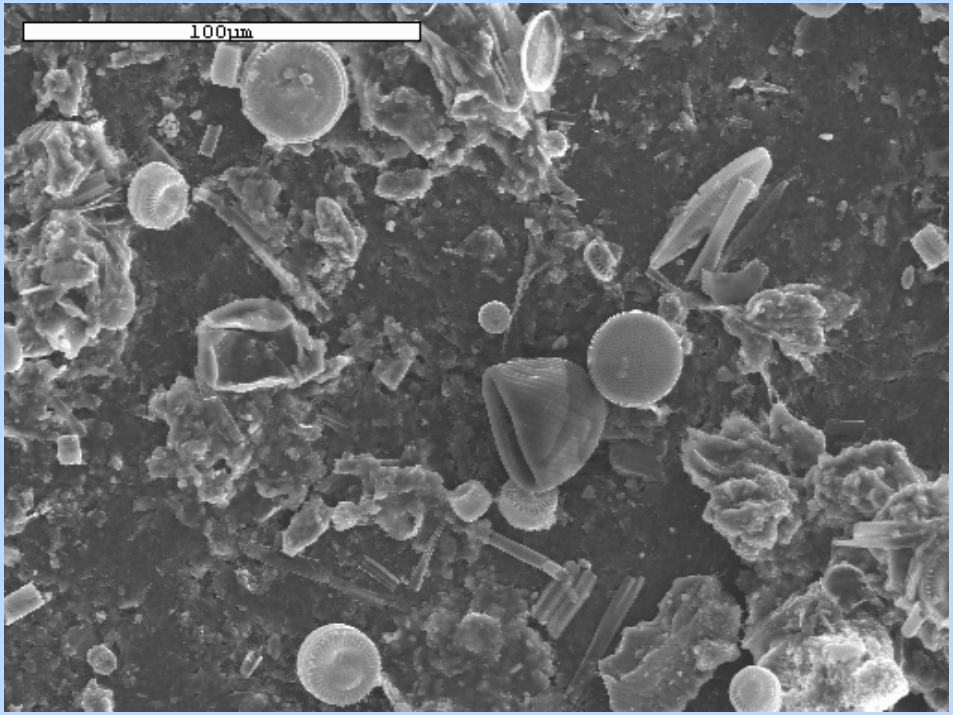


Sepiolite from Lake Okeechobee

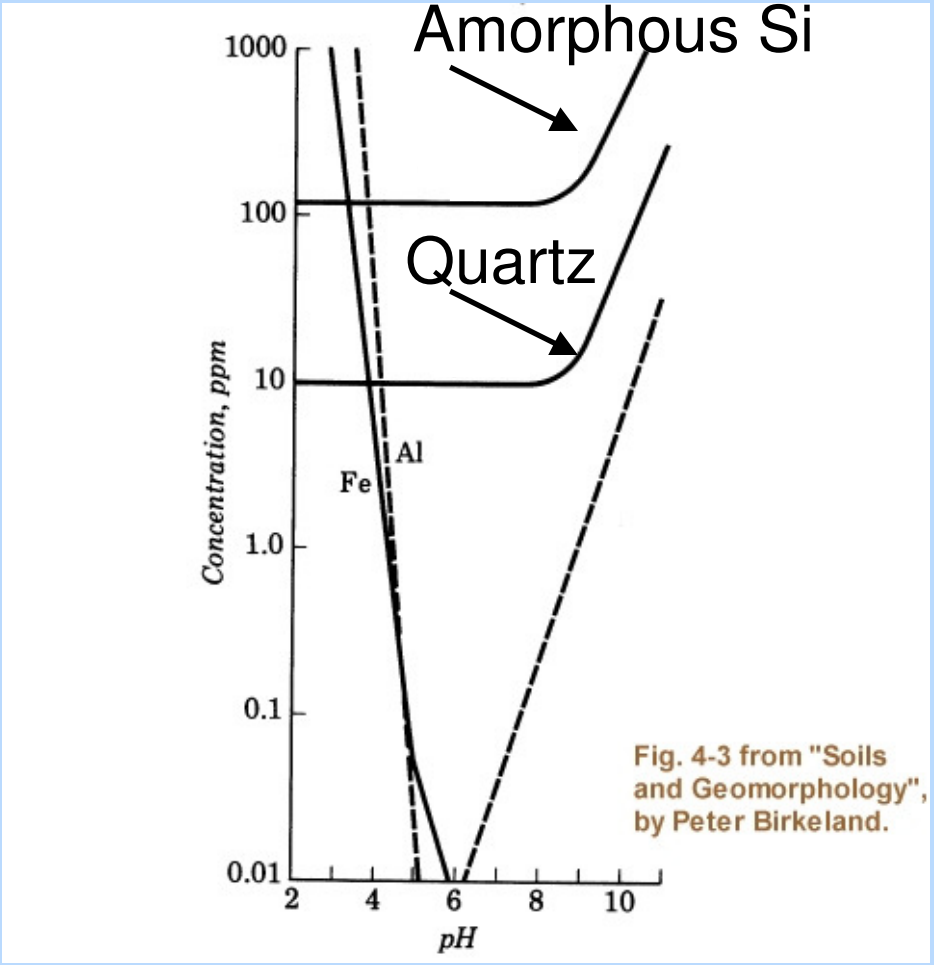




Are these minerals authigenic or detrital from phosphatic deposits?



Diatom frustules – pinnate and centric – ENR STA (Cell 4)



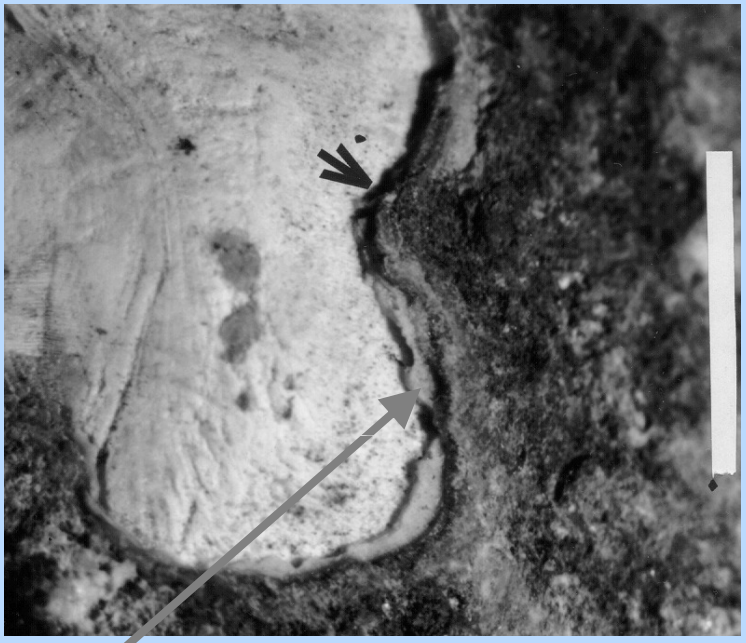
Wx of biogenic Si may help preserve quartz, smectite, sepiolite, and palygorskite

Mineral transformations & Implications

Phosphates

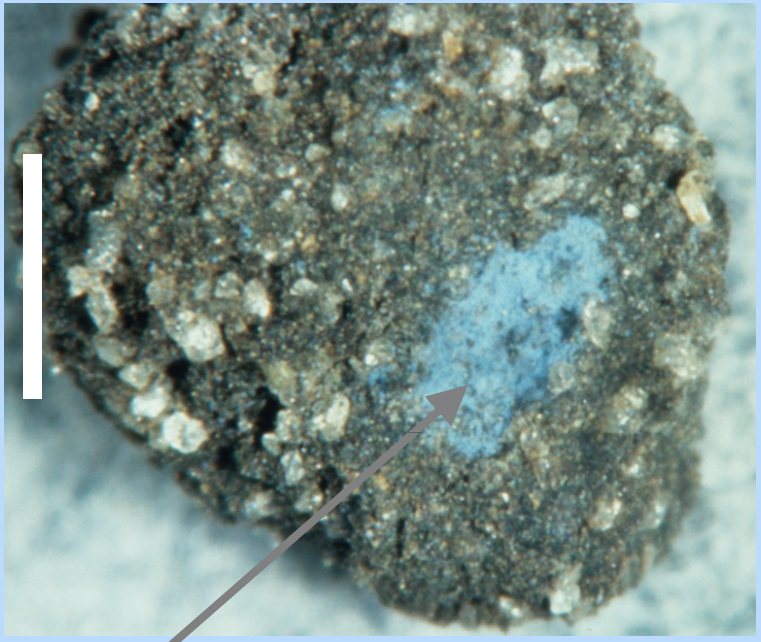
- Not much but too much
- Potential to be minimally soluble, but …

“Quaint” Anthropogenic P



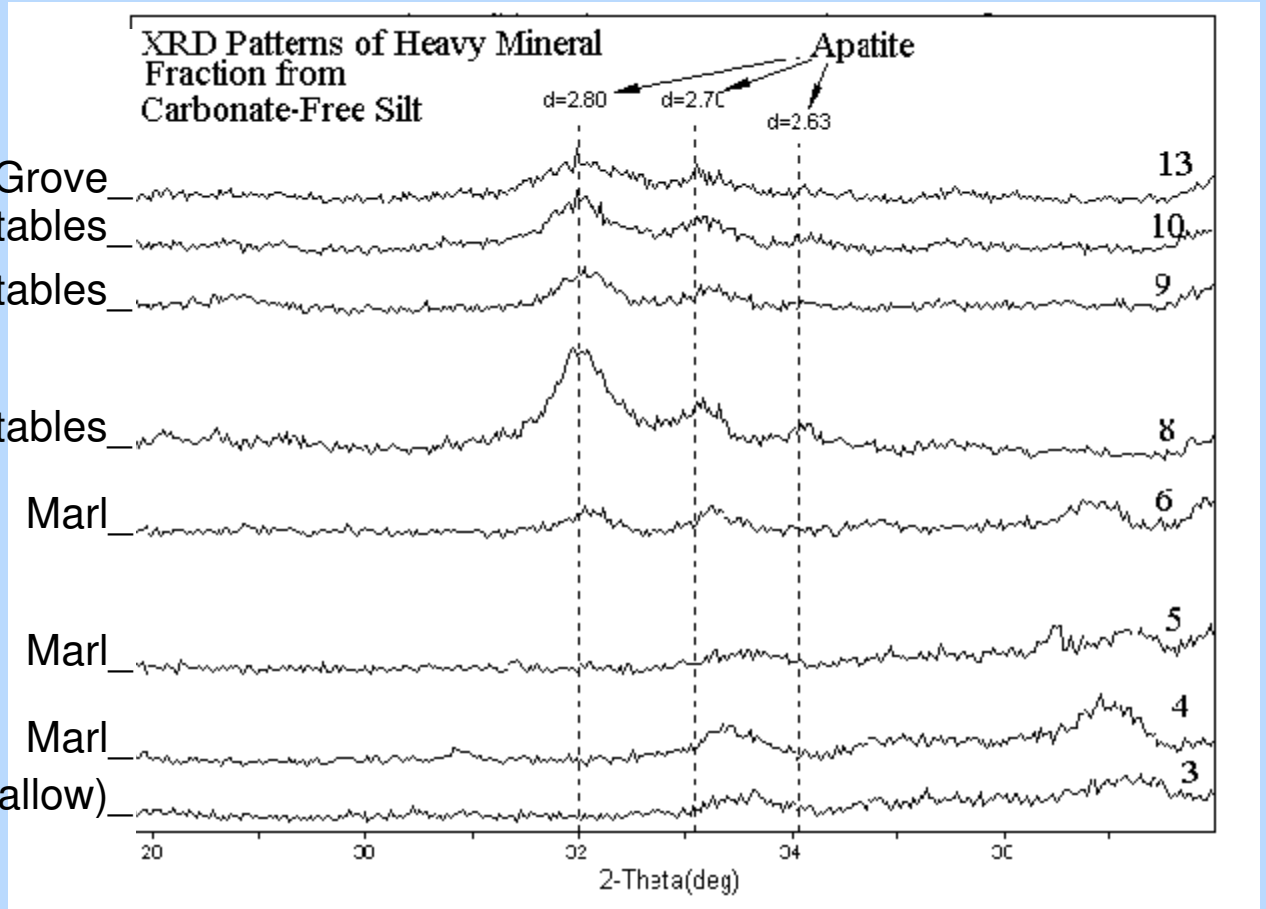
Apatite patina on oyster shell from shell mound midden

“Un-Quaint” Anthropogenic P

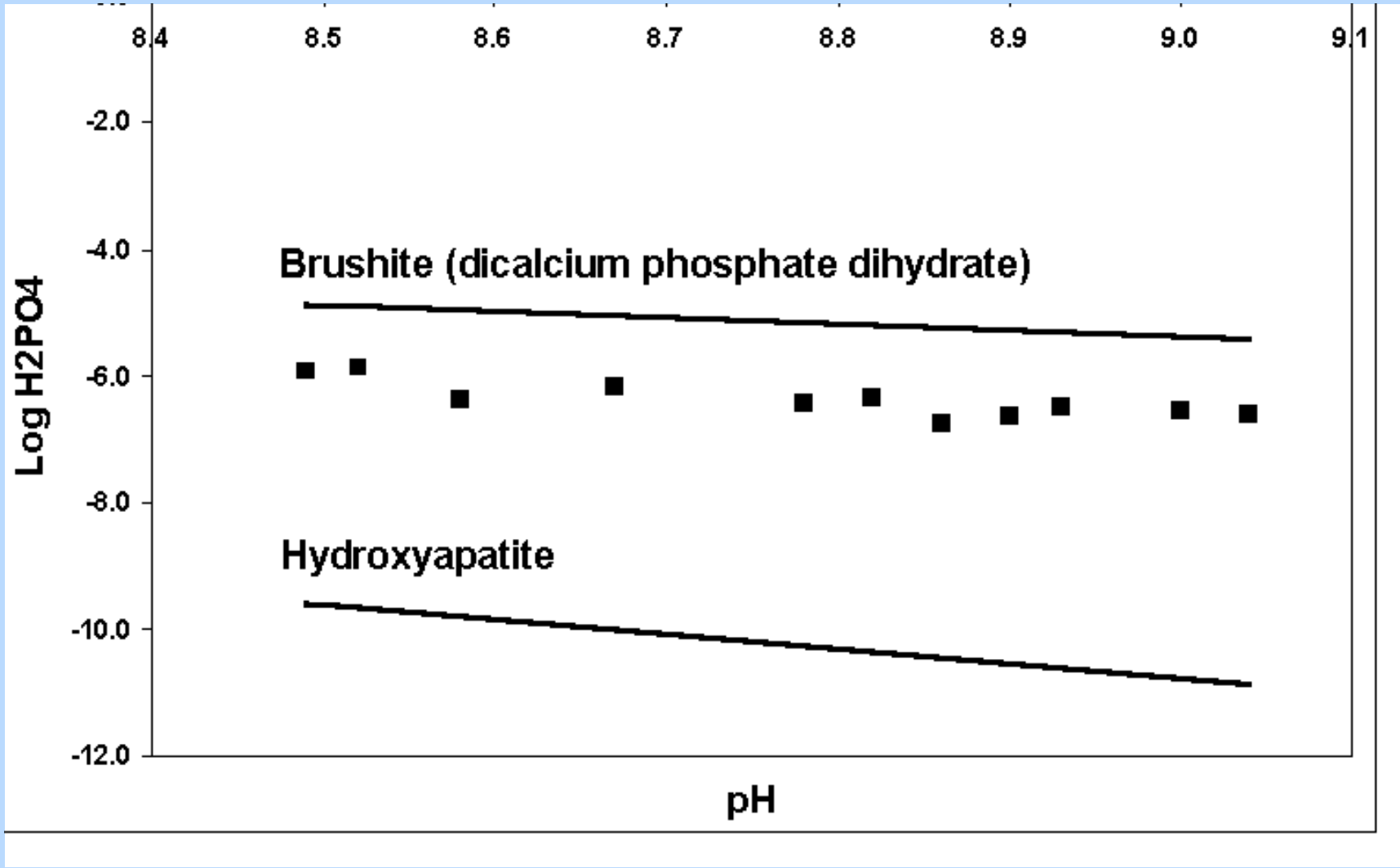


Vivianite - $Fe_3(PO_4)_2 \cdot 8H_2O$ downstream from dairy barn

More Anthropogenic P – Apatite formed in “Hole in the Donut” (work of M. Zhang, Y. Li, & W. Harris)



	P (mg kg^{-1})
Rockplowed, Grove	4055
Rockplowed, Vegetables	2916
Rockplowed, Vegetables	4090
Rockplowed, Vegetables	2257
Marl	573
Marl	138
Marl	125
Pineland (shallow)	251

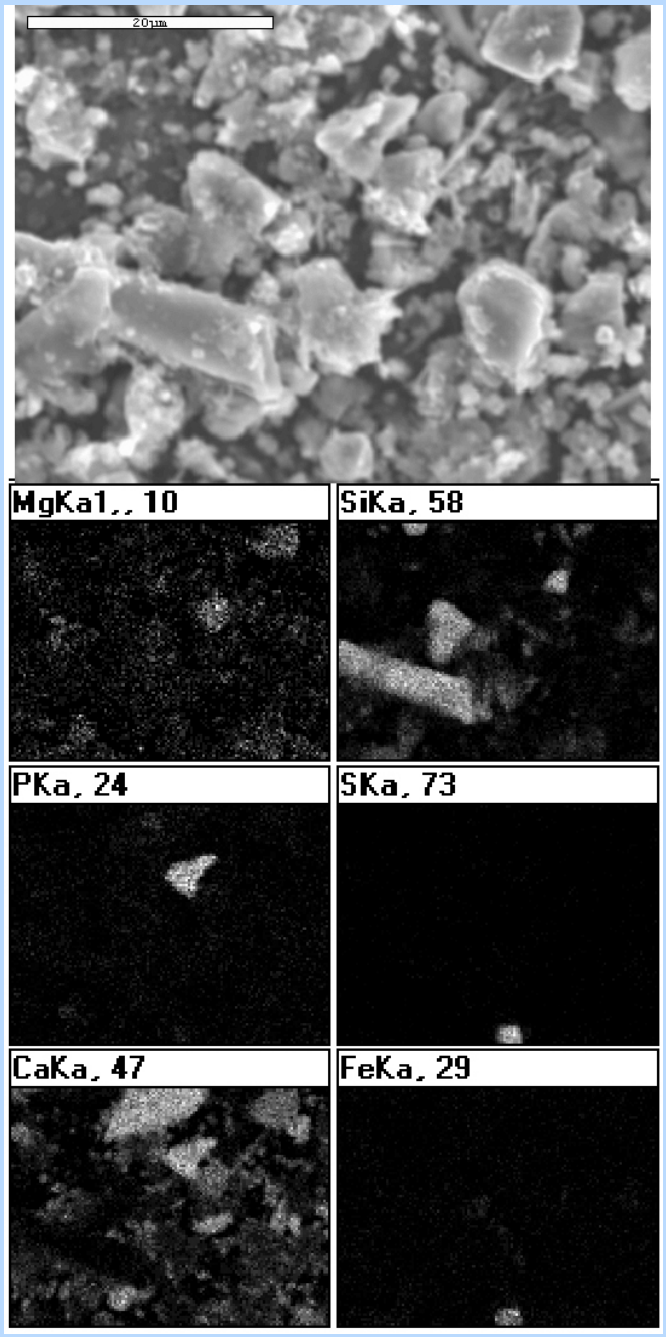


Solubility lines for brushite and hydroxyapatite with points plotted for Lake Okeechobee porewater samples.

SEM/EDS images

SEM secondary image

EDS elemental dot maps

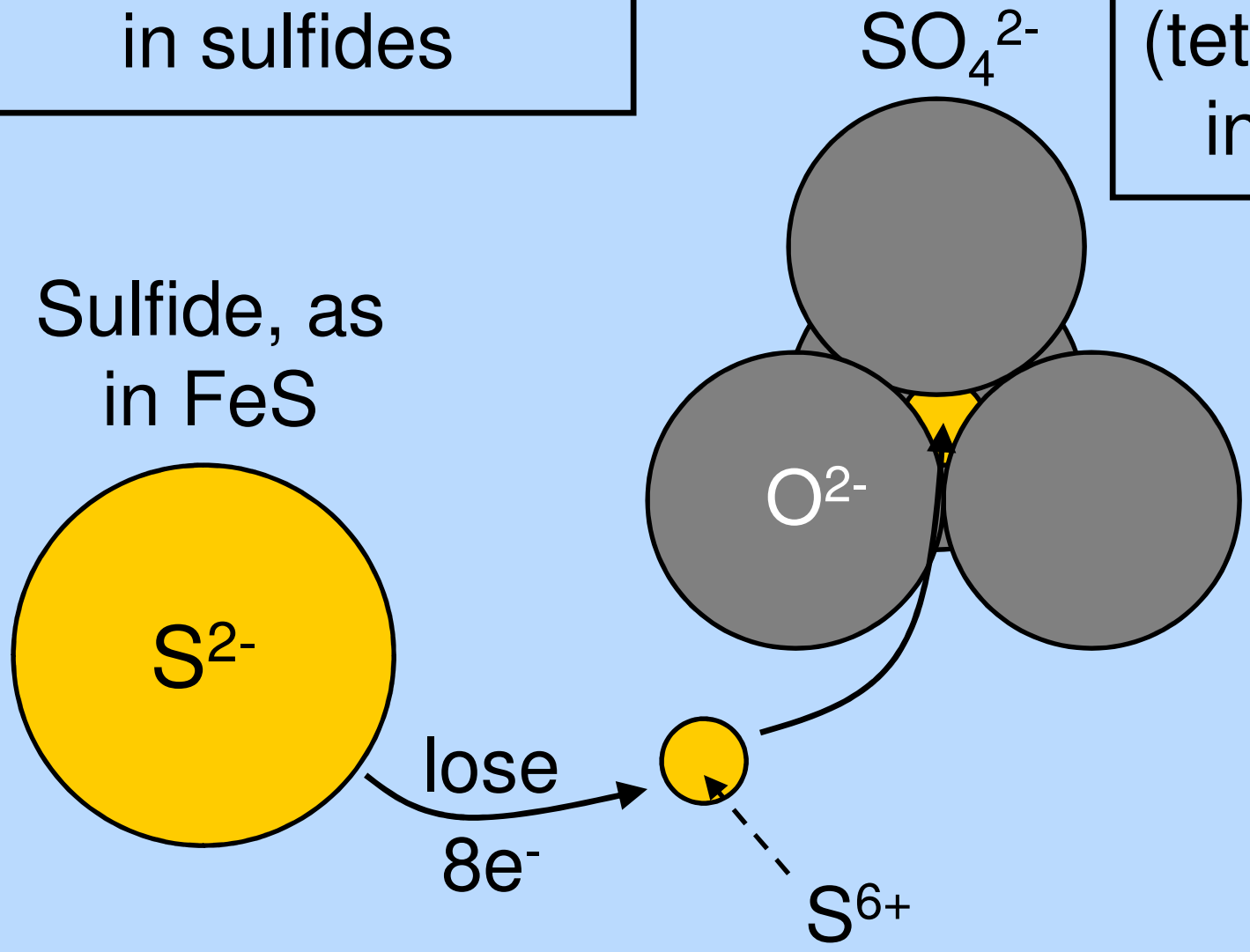


Mineral transformations & Implications

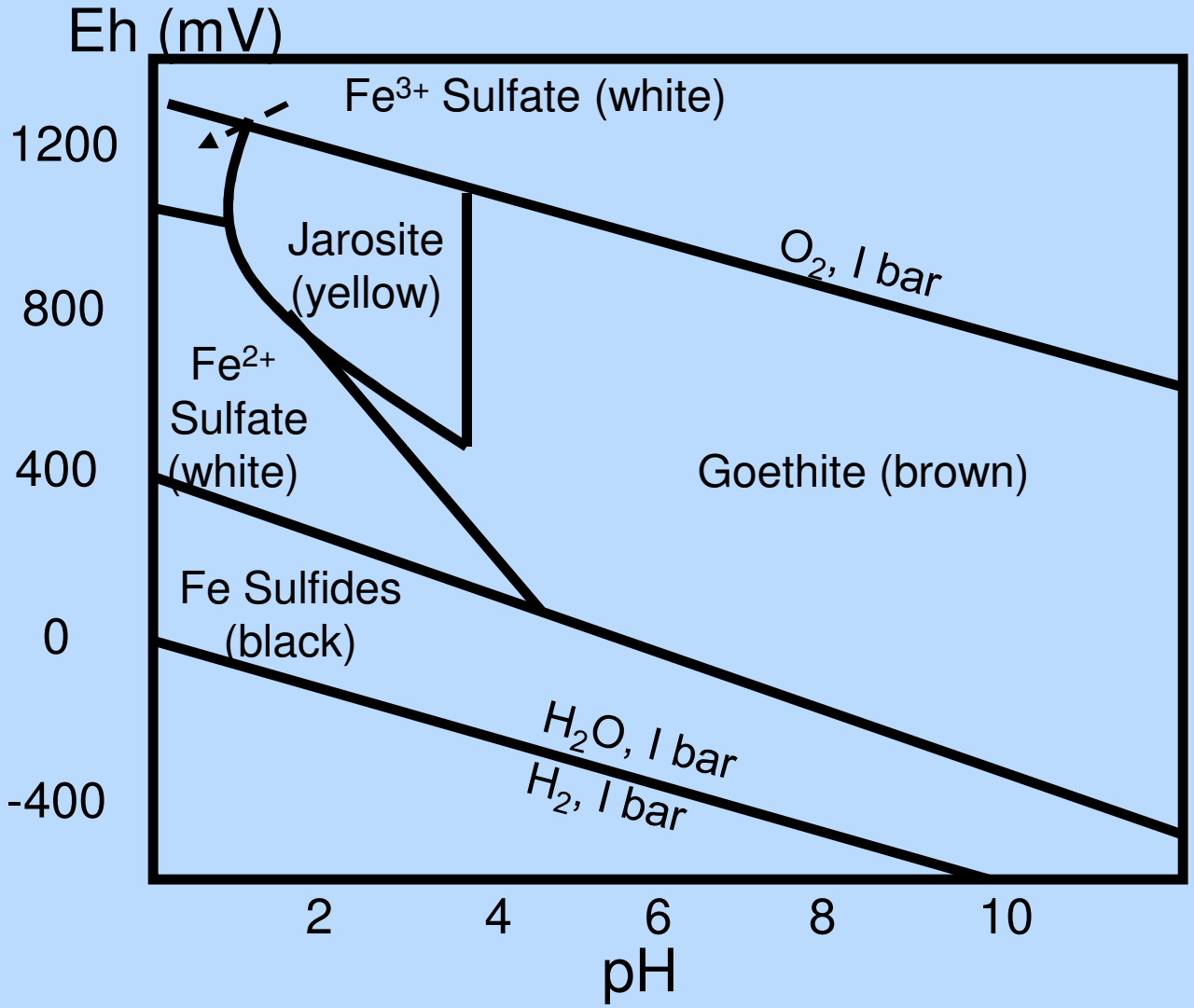
S Minerals

S is “coordinator” (octahedral with Fe) in sulfides

S is “coordinatee” (tetrahedrally) in sulfates



After Fanning et al., 2002



Goethite:
$FeOOH$

Jarosite:
$KFe_3(SO_4)_2(OH)_6$

After van Breeman
(1982)

Hg^{2+} - S - DOC

- Hg methylation & bioaccumulation a problem
- Sulfate reducing bacteria are methylators
- Agricultural S has been implicated as enhancer of methylation
- Organic complexation may limit methylation under some circumstances

Inhibition

Inhibition of Calcite & Apatite Crystalization by DOC

- Complexation of Ca^{2+} in solution
- Inhibited nucleation
- Blocked growth sites

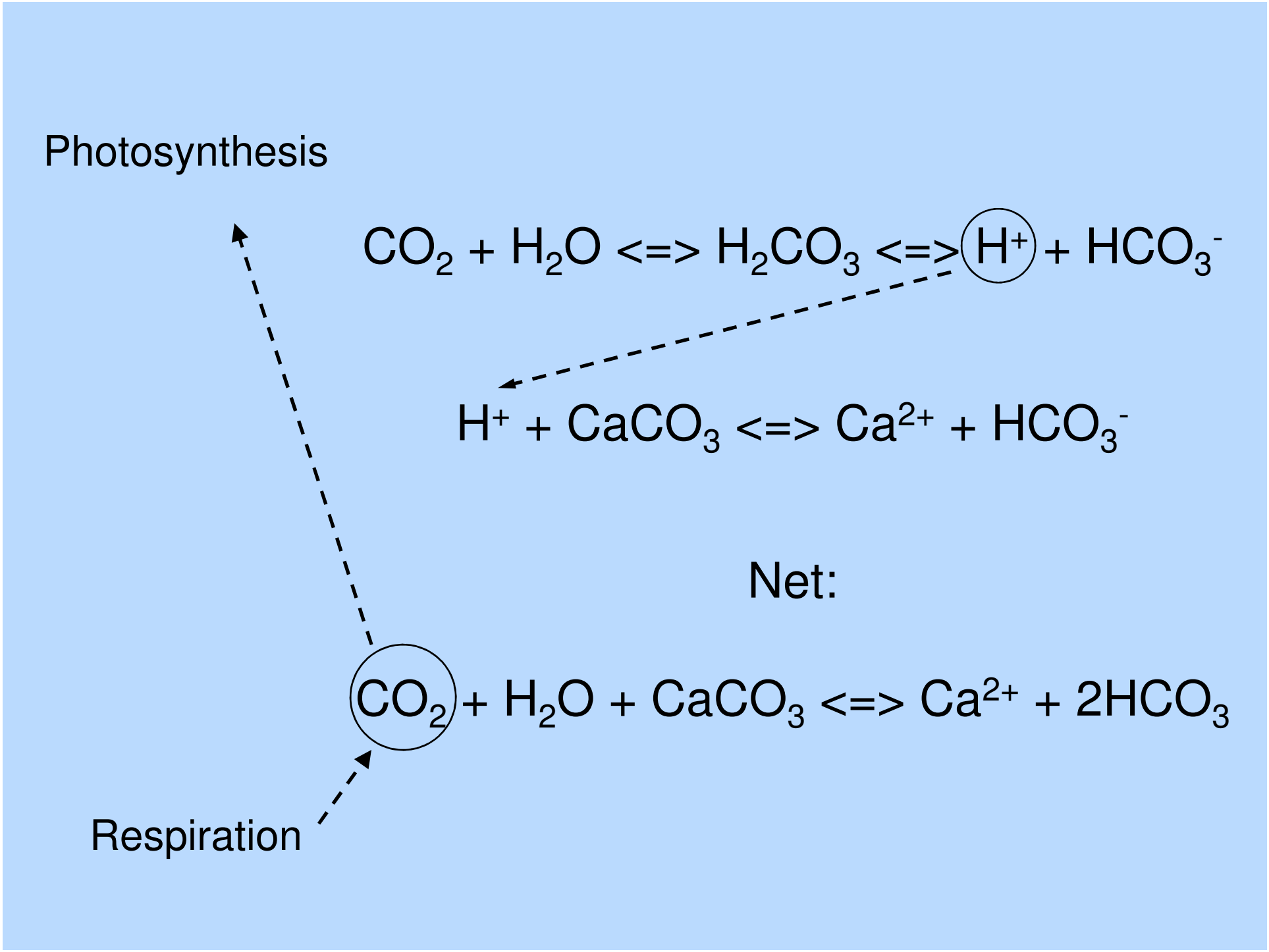
Other Inhibitors

- Mg^{2+} - Misfit substitute for Ca^{2+}
- PO_4^{3+} - Misfit substitute for CO_3^{2-}

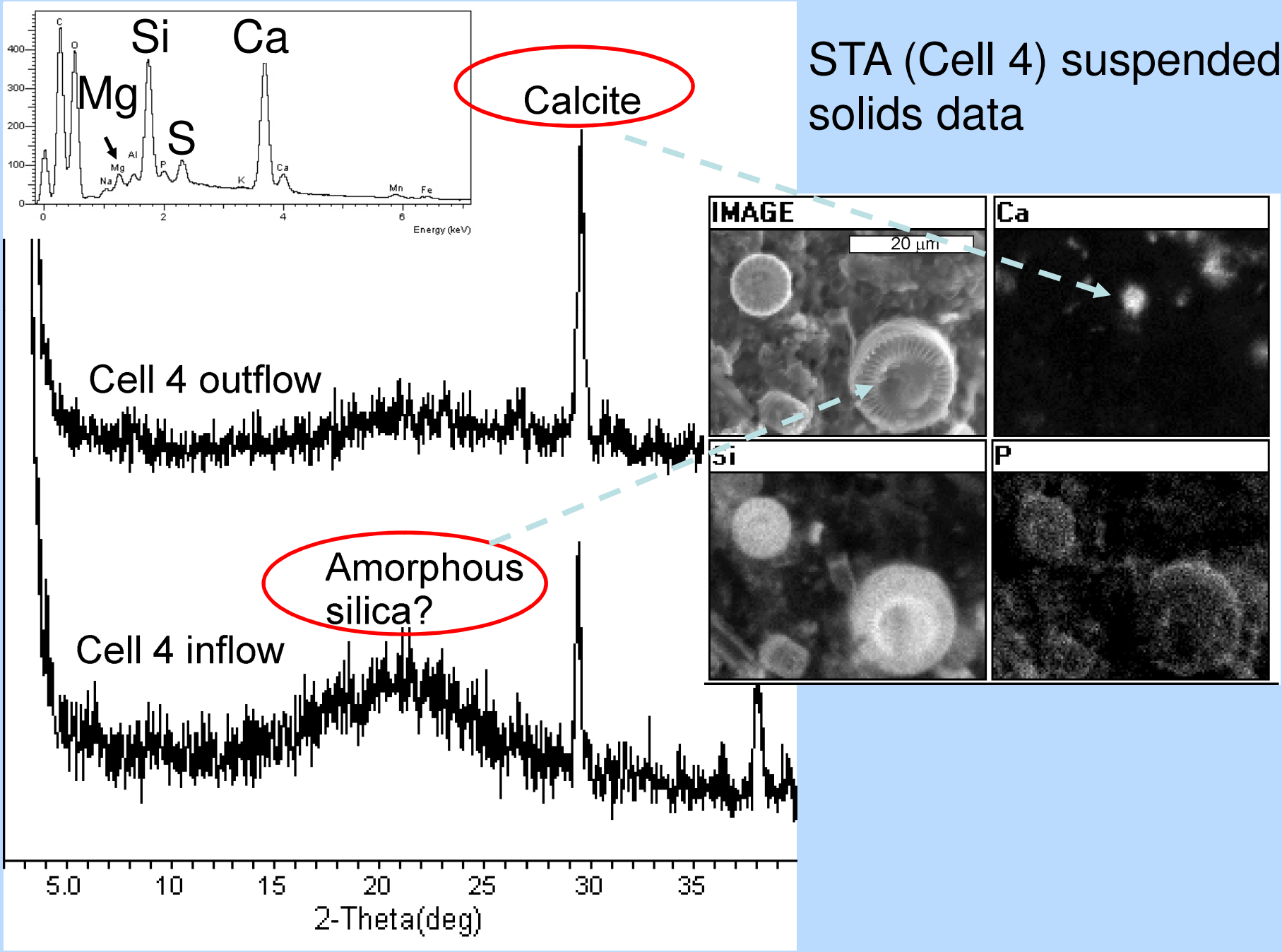
Concluding Ideas

- Distributions of carbonates, sulfides, & phosphates strongly influenced by organisms.
- Weathering driven by biologically-induced gradients.
- Photosynthesis promotes limestone weathering =>ephemeral periphton $CaCO_3$.
- S minerals & DOC affect Hg methylation & bioaccumulation.
- DOC, Mg, & PO_4 inhibit calcite & phosphate precipitation.
- Everglades weathering is …

Bio geochemical

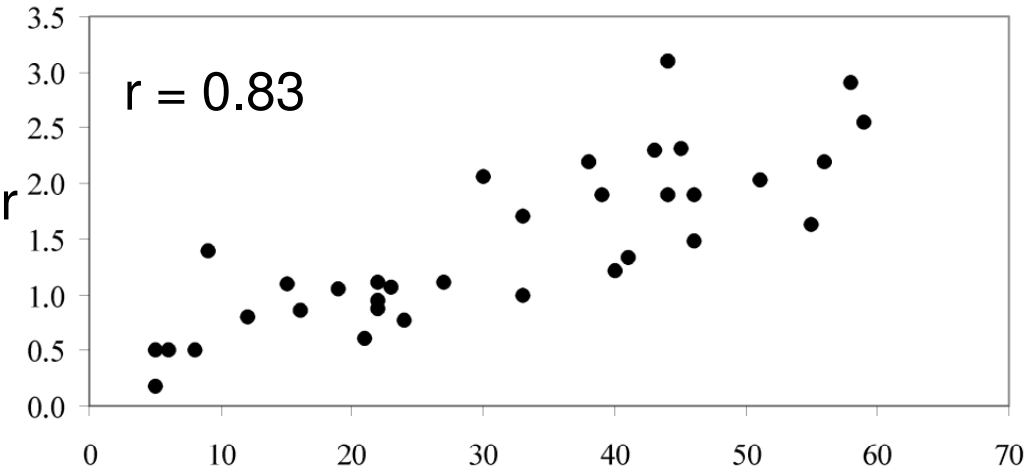

Photosynthesis
$CO_2 + H_2O <=> H_2CO_3 <=> H^+ + HCO_3^-$
$H^+ + CaCO_3 <=> Ca^{2+} + HCO_3^-$
Net:
$CO_2 + H_2O + CaCO_3 <=> Ca^{2+} + 2HCO_3$
Respiration

STA (Cell 4) suspended solids data

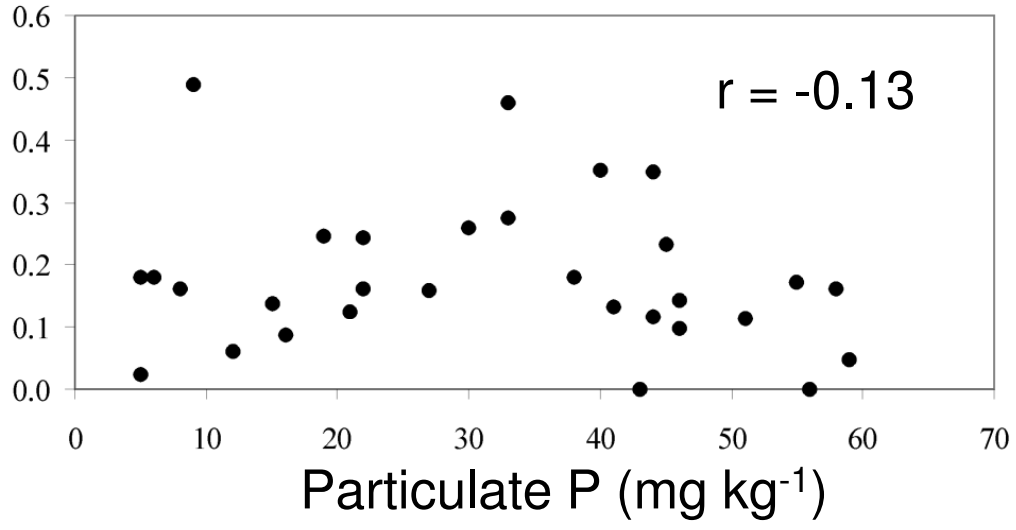


Data for Cell 4, Summer & Early Fall

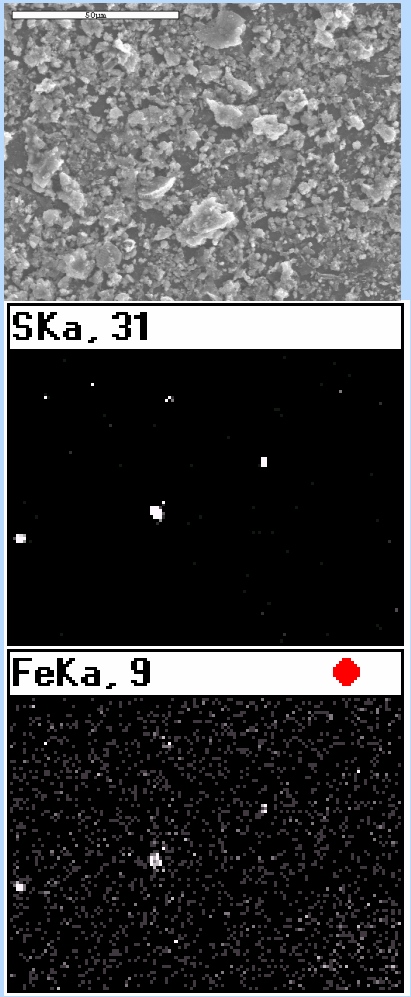
Organic Matter (mg kg^{-1})



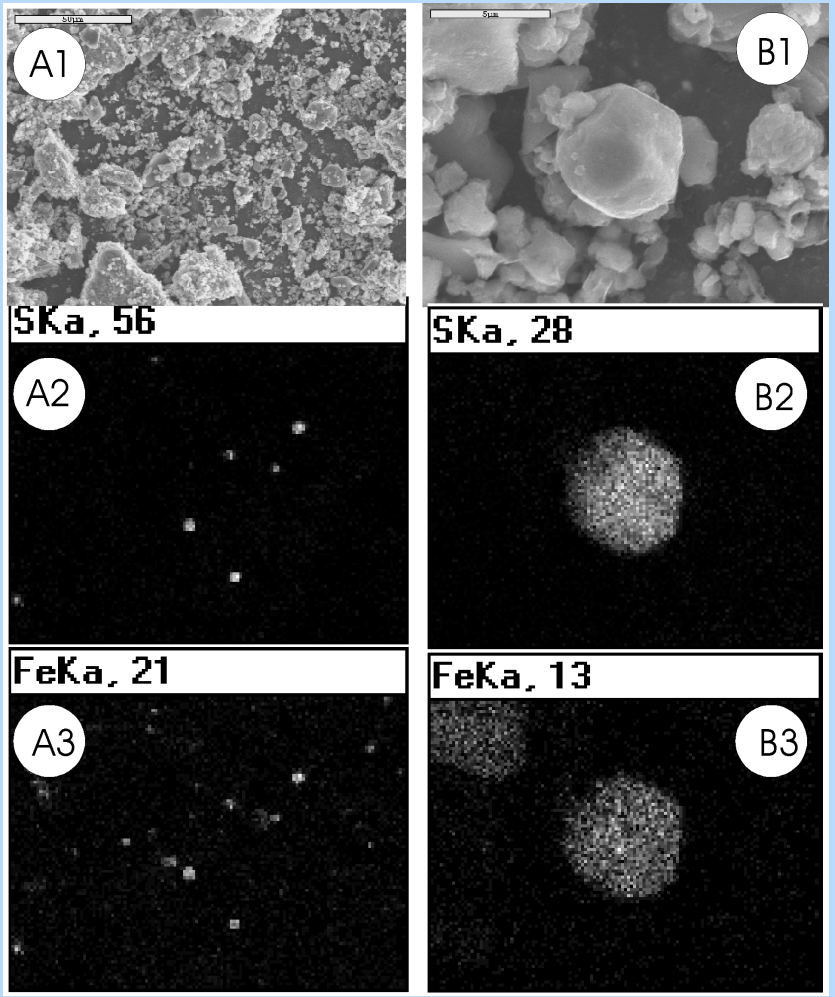
Calcite (mg kg^{-1})



Fe-S associations – consistent!



ENR canal



Okeechobee sediment
Station O, 20-30 cm

“BIO” goes beyond microbial- and weathering-related mineral redistribution!

- Roosting birds enriching P on tree islands
- Humans digging canals that expose minerals and increase sediment load

Saturation indices for Okeechobee porewater.

+ number = Supersaturation.
"**E**" = Found in Everglades
"**M**" = Found in Dairy Manure

Station	Depth	Sepiolite	Aragonite	Calcite	Dolomite	Apatite	Whitlockite	Brushite
	(cm)	**E**	**E**	**EM**	**E**	**EM**	**M**	
K8	10-20	1.51	1.22	1.36	1.97	12.41	2.81	-1.31
K10	0-10	1.59	1.41	1.56	2.37	13.51	3.48	-1.08
K10	30-40	1.93	1.17	1.32	1.83	13.27	3.40	-0.99
L11	30-44	1.31	0.87	1.01	1.27	13.11	3.39	-0.84
M6	10-20	1.87	1.49	1.63	2.48	12.83	3.00	-1.34
M9	30-40	0.88	0.83	0.98	1.25	11.28	2.18	-1.43
O7	0-10	2.07	1.69	1.83	2.92	13.15	3.15	-1.37
O7	20-30	2.28	1.36	1.51	2.31	11.95	2.46	-1.55
O11	0-10	2.10	1.57	1.71	2.68	13.53	3.44	-1.16
O11	10-20	1.12	0.76	0.9	1.09	12.55	3.06	-0.95
P9	0-10	2.28	1.66	1.80	2.87	13.66	3.50	-1.18
P9	10-20	2.93	1.72	1.86	3.03	13.68	3.49	-1.22