

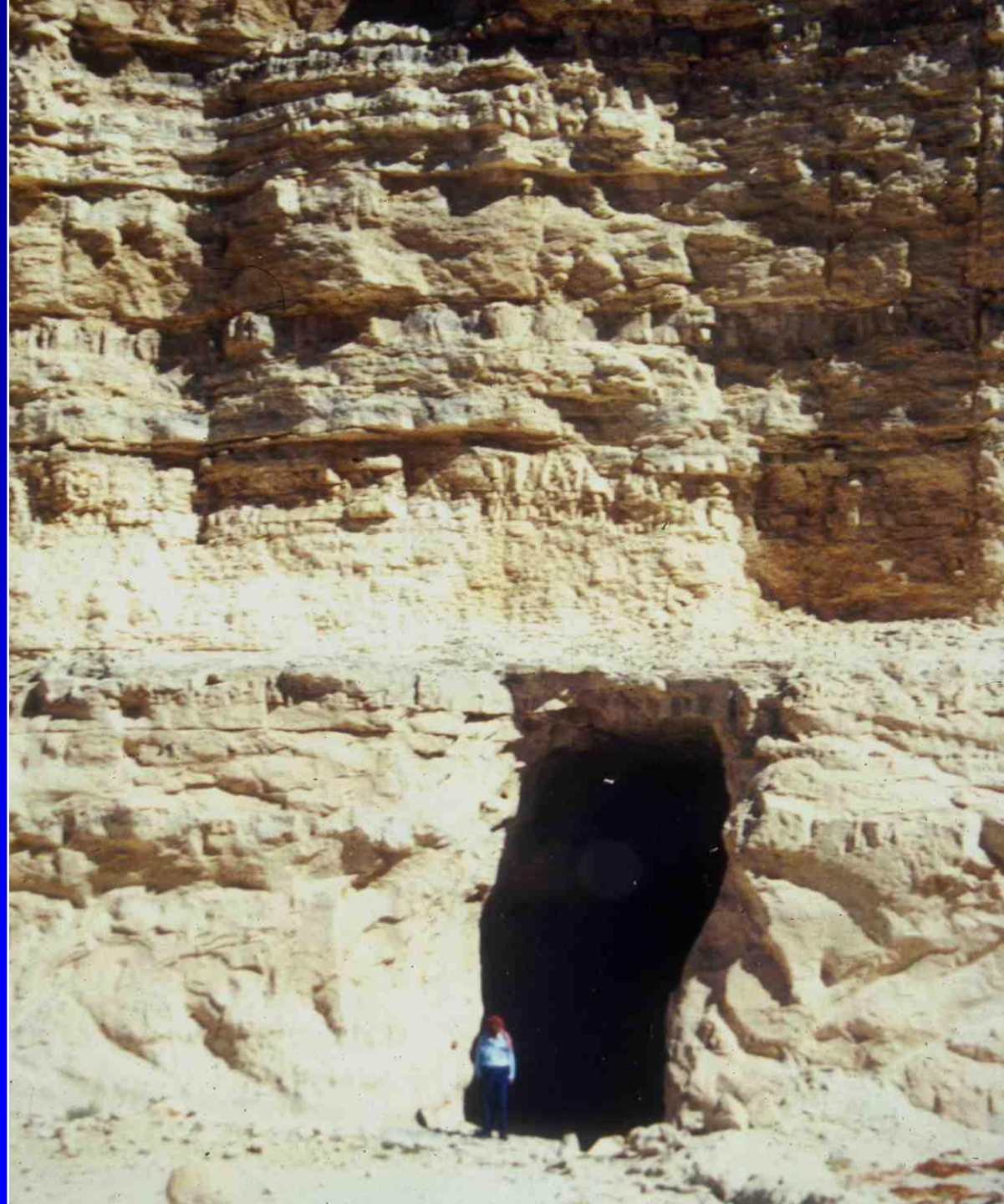
# Why are Precambrian economic phosphates so rare?

Peir K. Pufahl



Wolfville, Nova Scotia, Canada

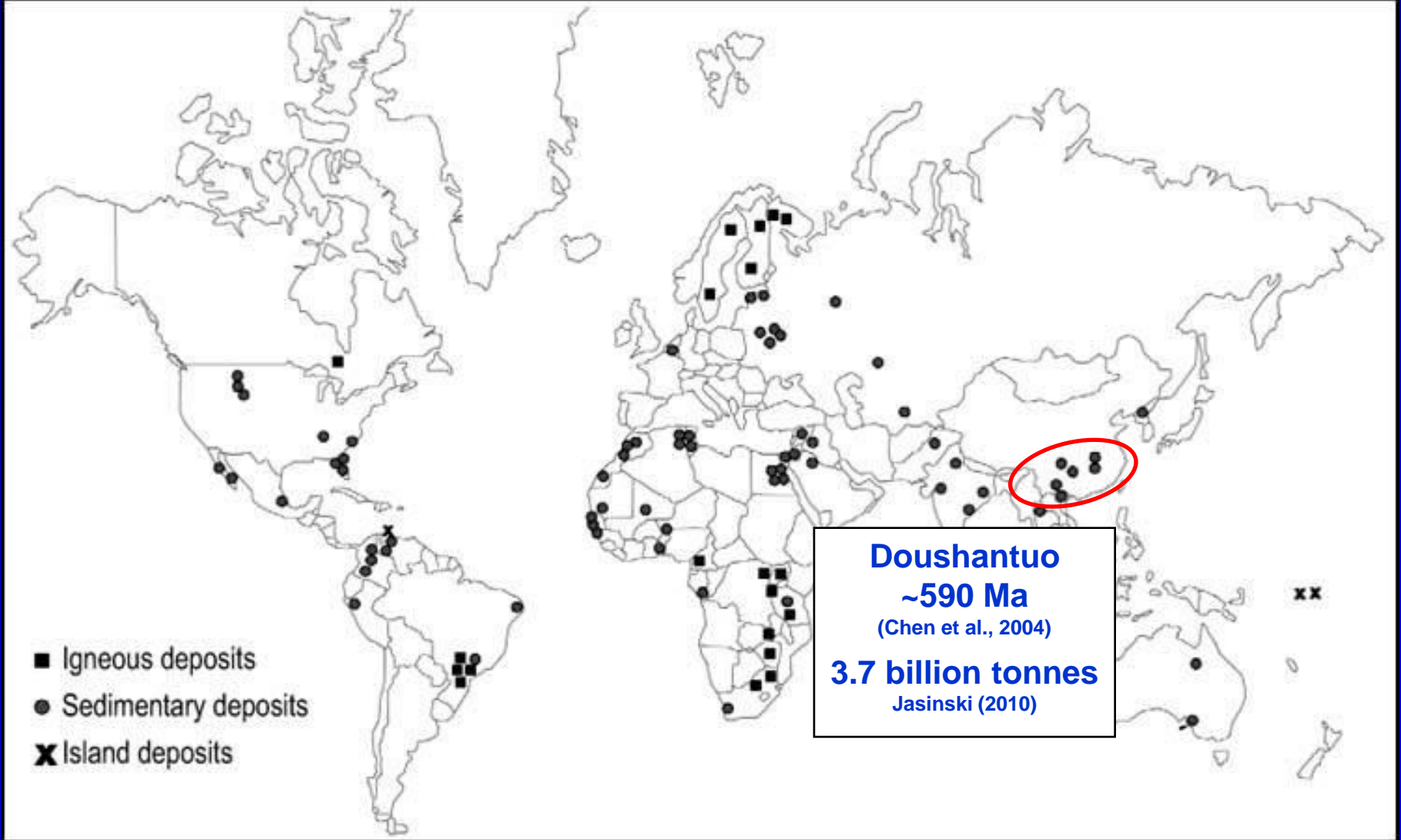
**WHY NOT IN THE  
PRECAMBRIAN?**





# Phosphorite

# Global Deposits

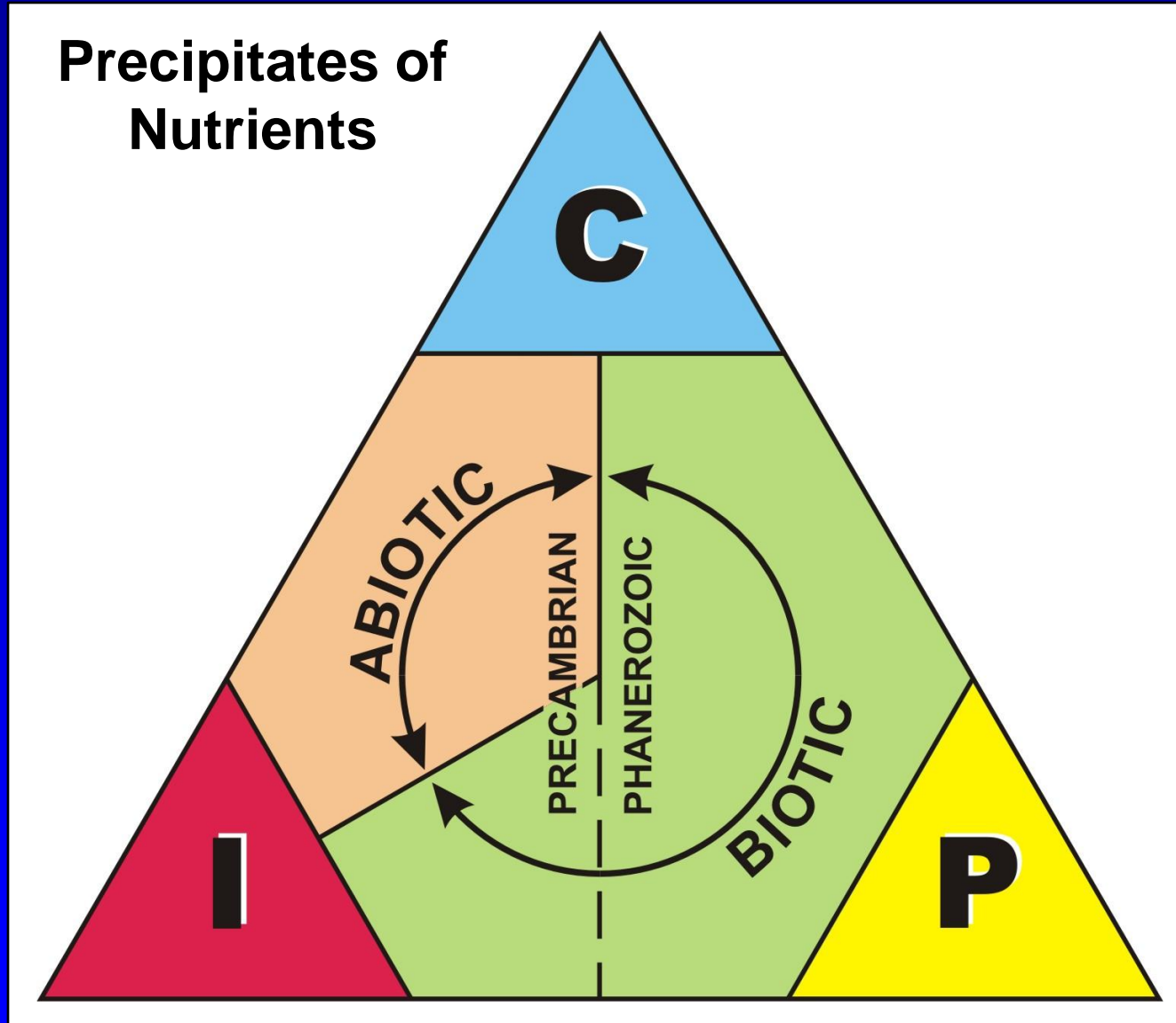


Zapata and Roy (2004)

*In the Precambrian different  
ocean and atmospheric  
compositions prevented the formation  
of large phosphorite deposits*

# Phosphorite

# Bioelemental Sediment



Pufahl (2010)

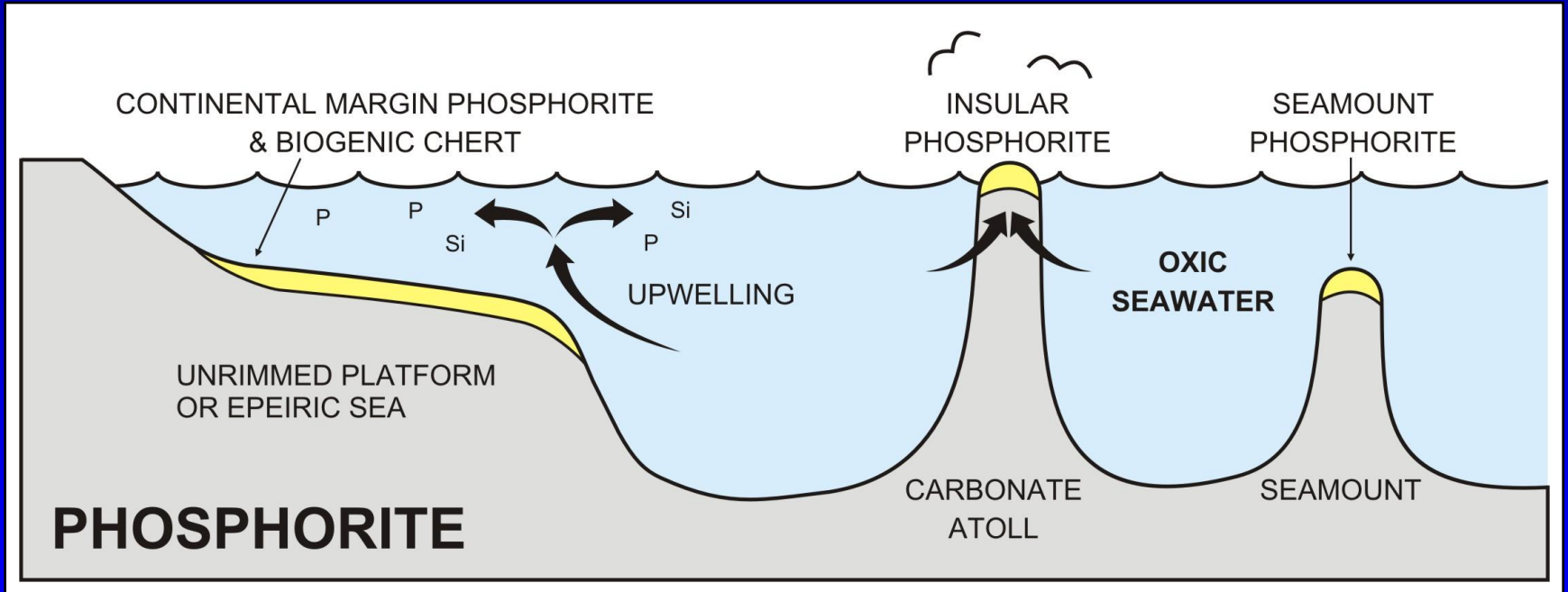
# Phosphorite

# Sedimentary

- P-rich rock with **> 18 wt. %  $P_2O_5$** , but can reach 40 wt. %  $P_2O_5$
- sedimentary phosphorite is a marine chemical sediment commonly associated with upwelling
- **francolite** or **carbonate-fluorapatite (CFA)** –  
 $Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_{x-y-z}(CO_3 \cdot F)_y(SO_4)_zF_2$
- provides **> 80% of the total** world production of phosphate rock
- annual consumption of phosphate rock ~150 million tons per year

# Phosphorite

# Sedimentary

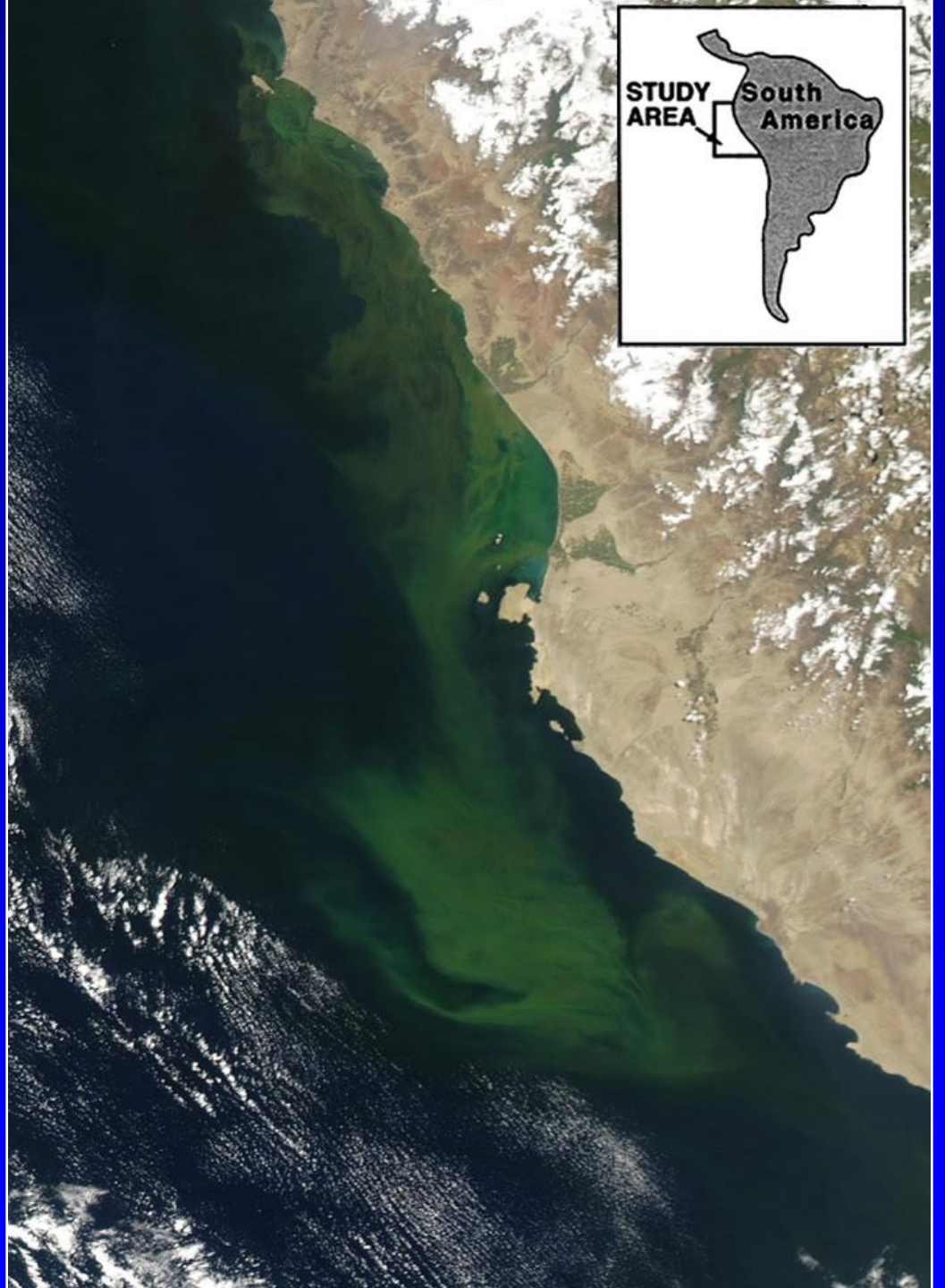


Pufahl (2010)

# Phosphorite

- part of the upwelling triad

**Continental  
Margin**



# Phosphorite

# Continental Margin

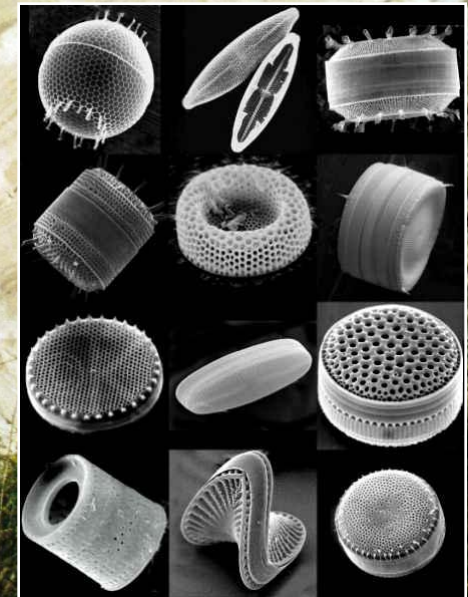
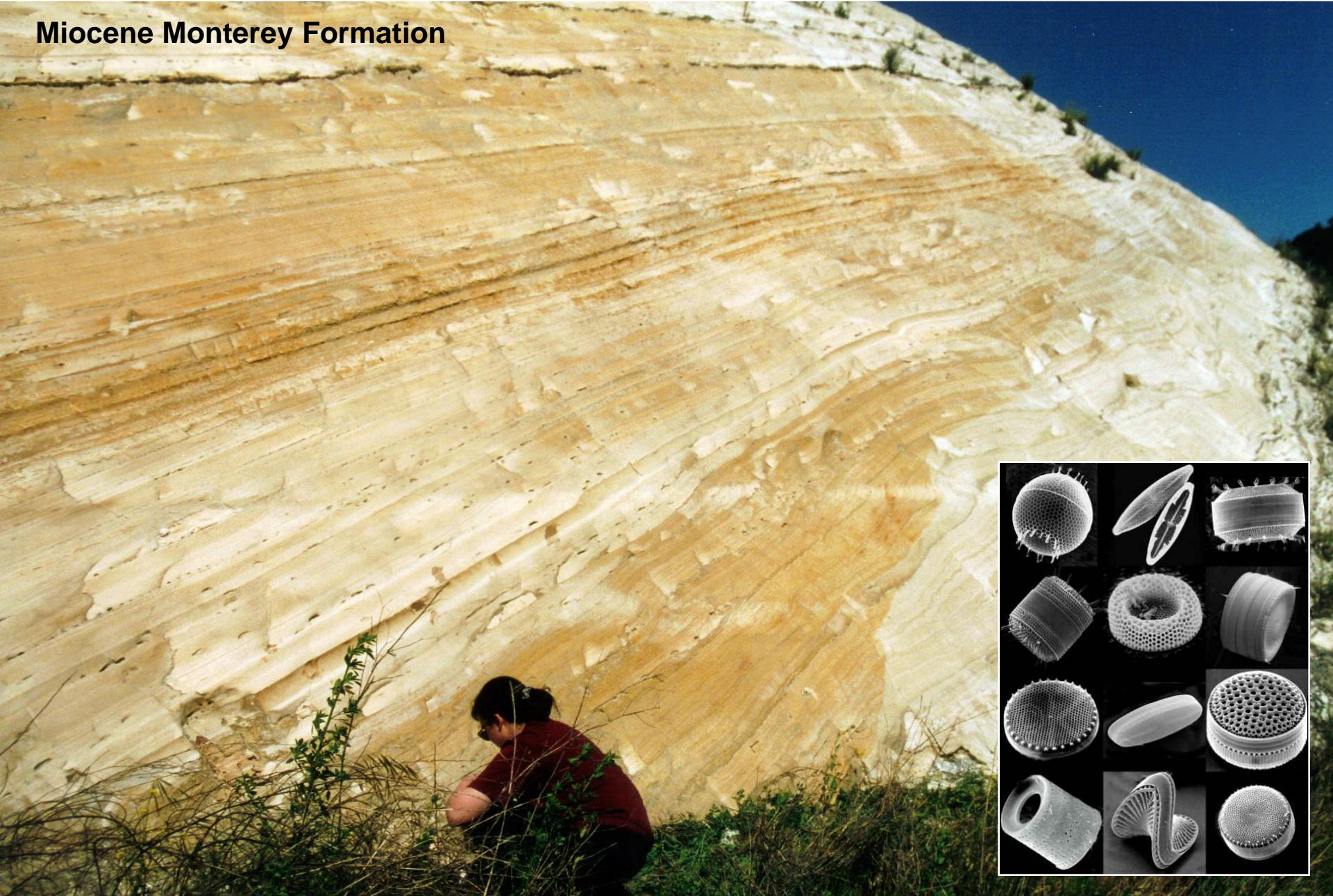
Campanian Alhisa Phosphorite Formation



# Phosphorite

# Continental Margin

Miocene Monterey Formation



# Phosphorite

# Continental Margin

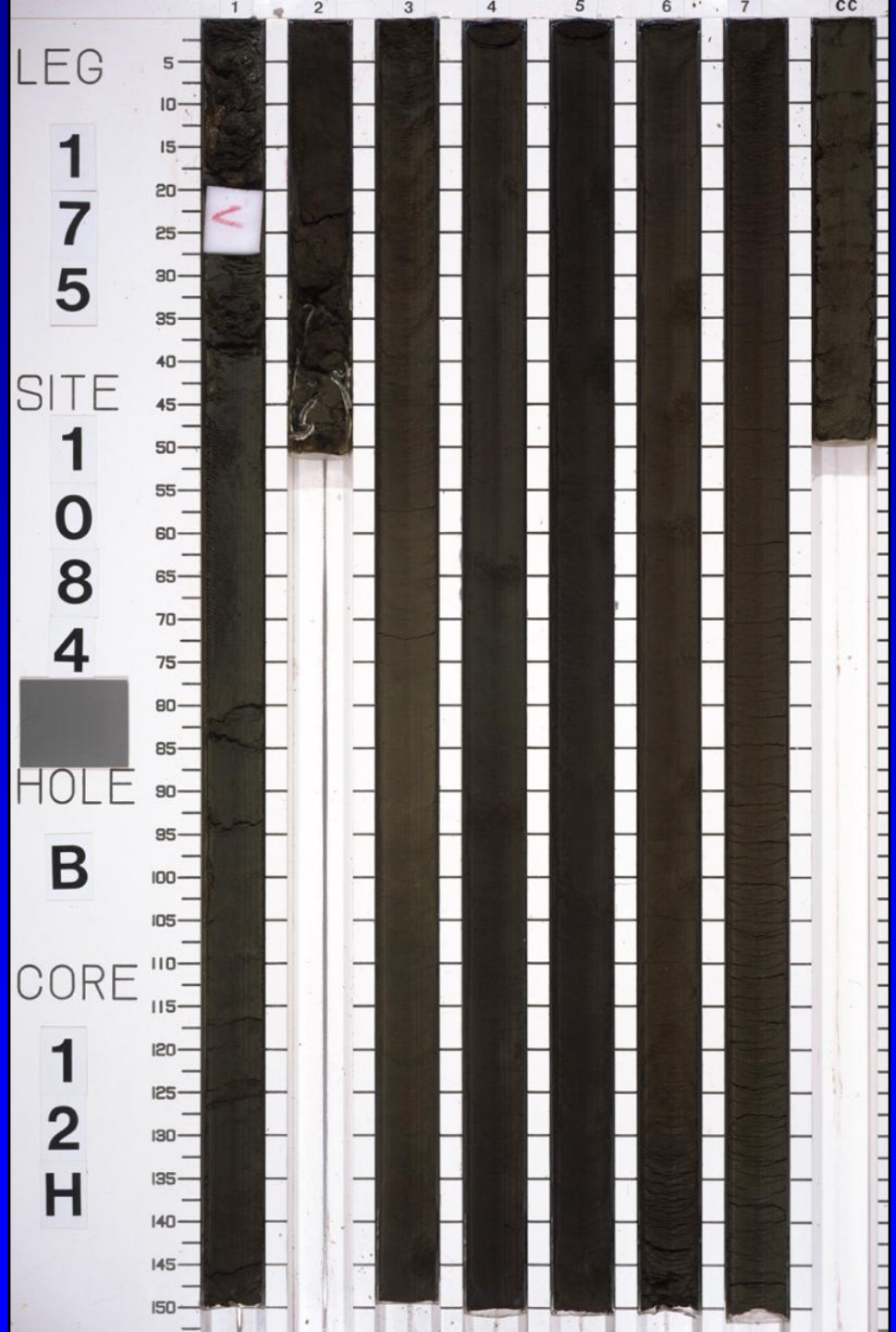
Late Devonian Exshaw Formation



# Phosphorite

- unbioturbated organic-rich mud

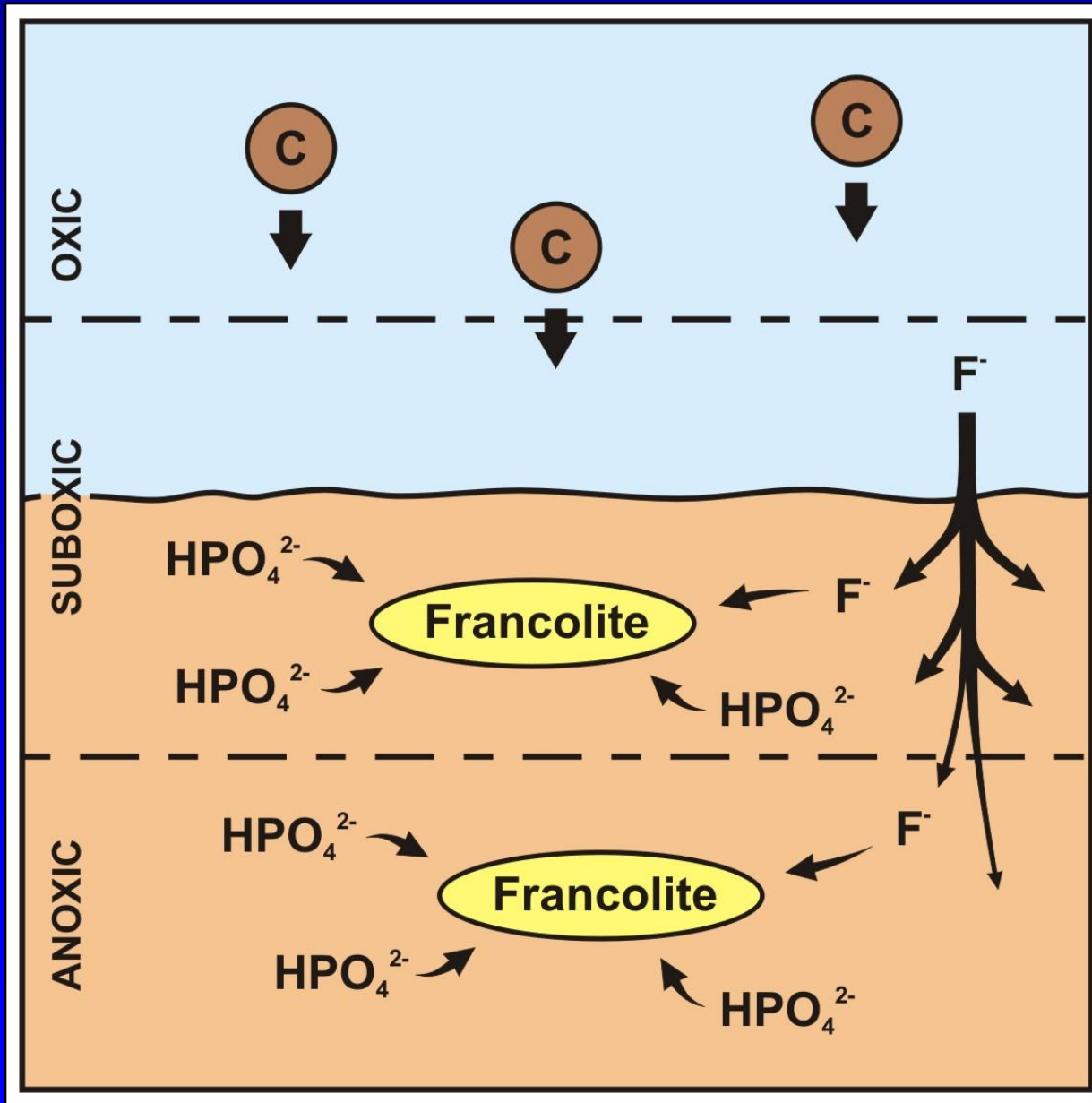
Phosphogenesis



# Phosphorite

# Phosphogenesis

MICROBIAL DEGRADATION

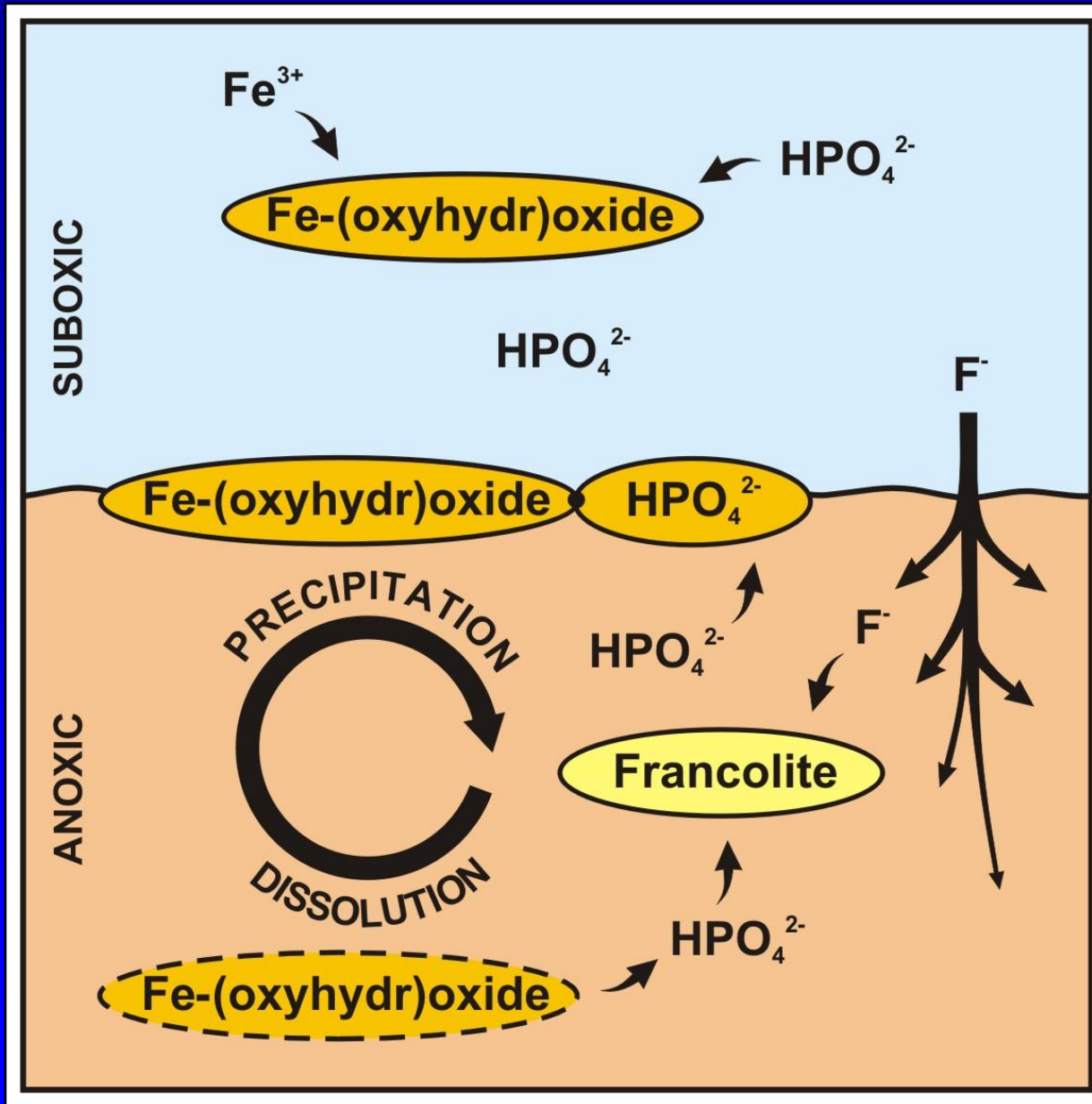


Pufahl (2010)

# Phosphorite

# Phosphogenesis

Fe-REDOX PUMPING



Pufahl (2010)

# Phosphorite

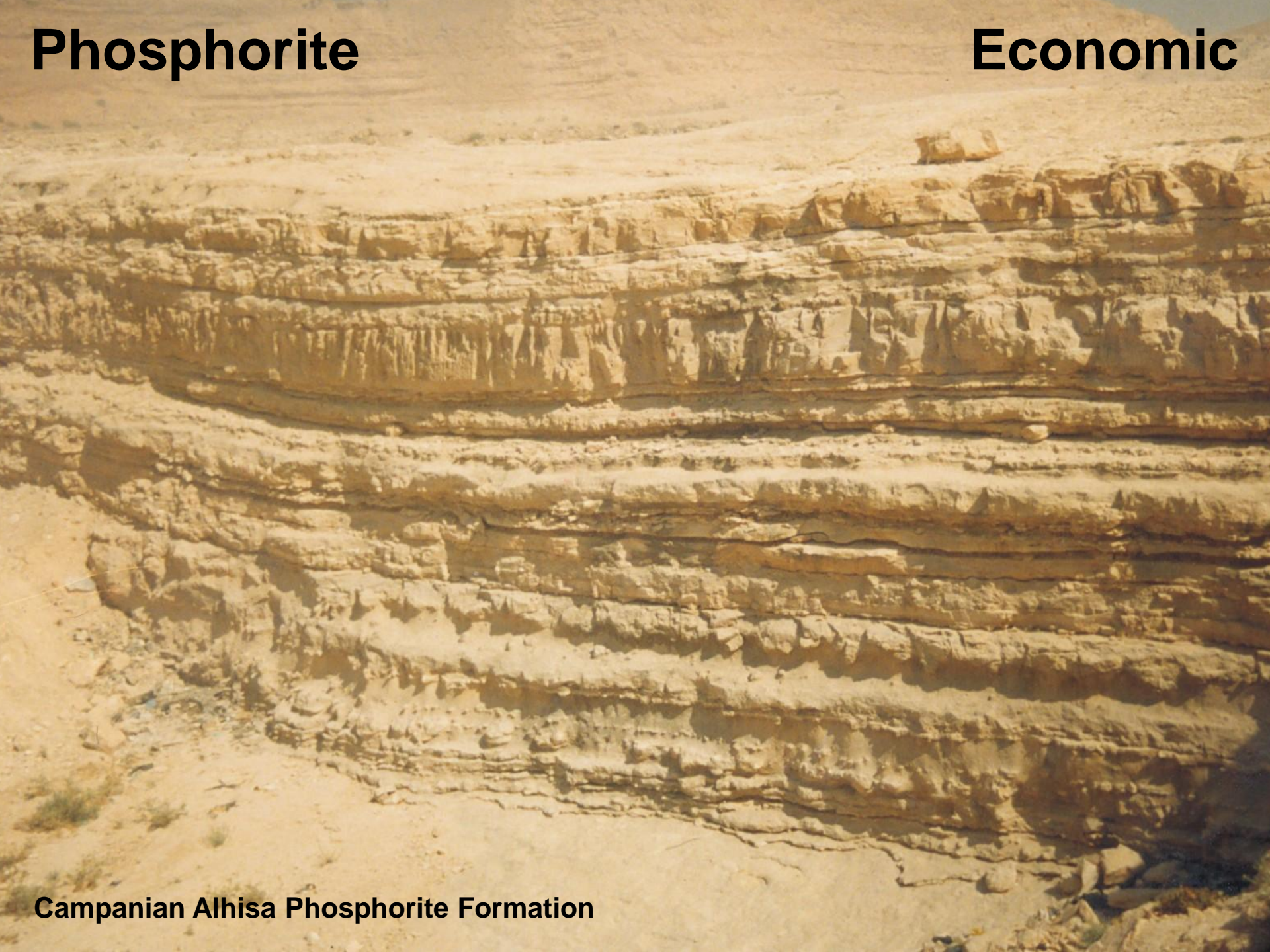
# Phosphogenesis

LAMINATED PRISTINE PHOSPHORITE – MIOGENE MONTEREY FORMATION



**Phosphorite**

**Economic**

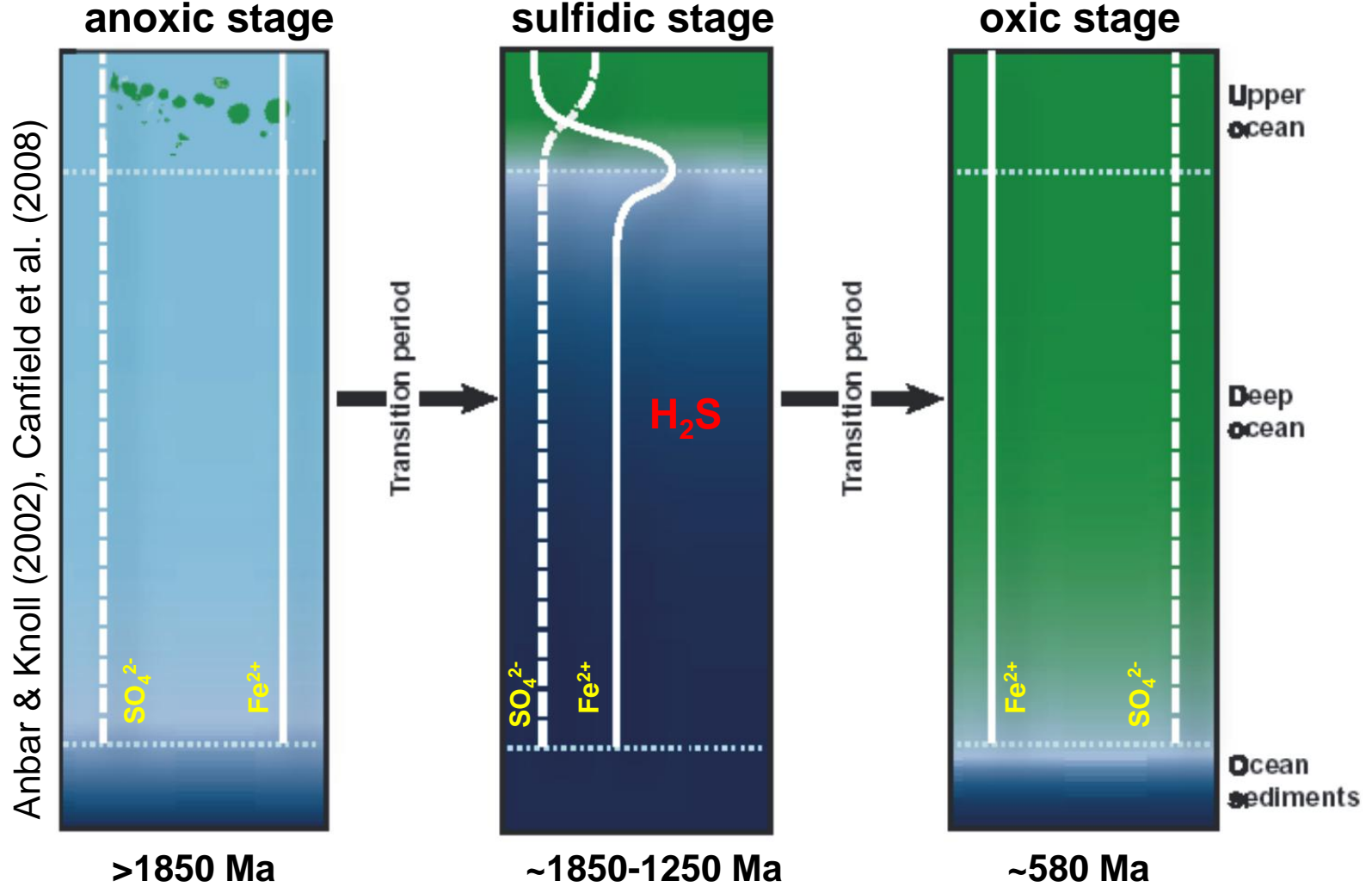


**Campanian Alhisa Phosphorite Formation**

*What were the differences in the compositions of the atmosphere and oceans that prevented the formation of economic phosphorite?*

# Phosphorite

# Precambrian



**LOW OXYGEN LEVELS IN ATMOSPHERE & OCEAN**

# Phosphorite

# Precambrian

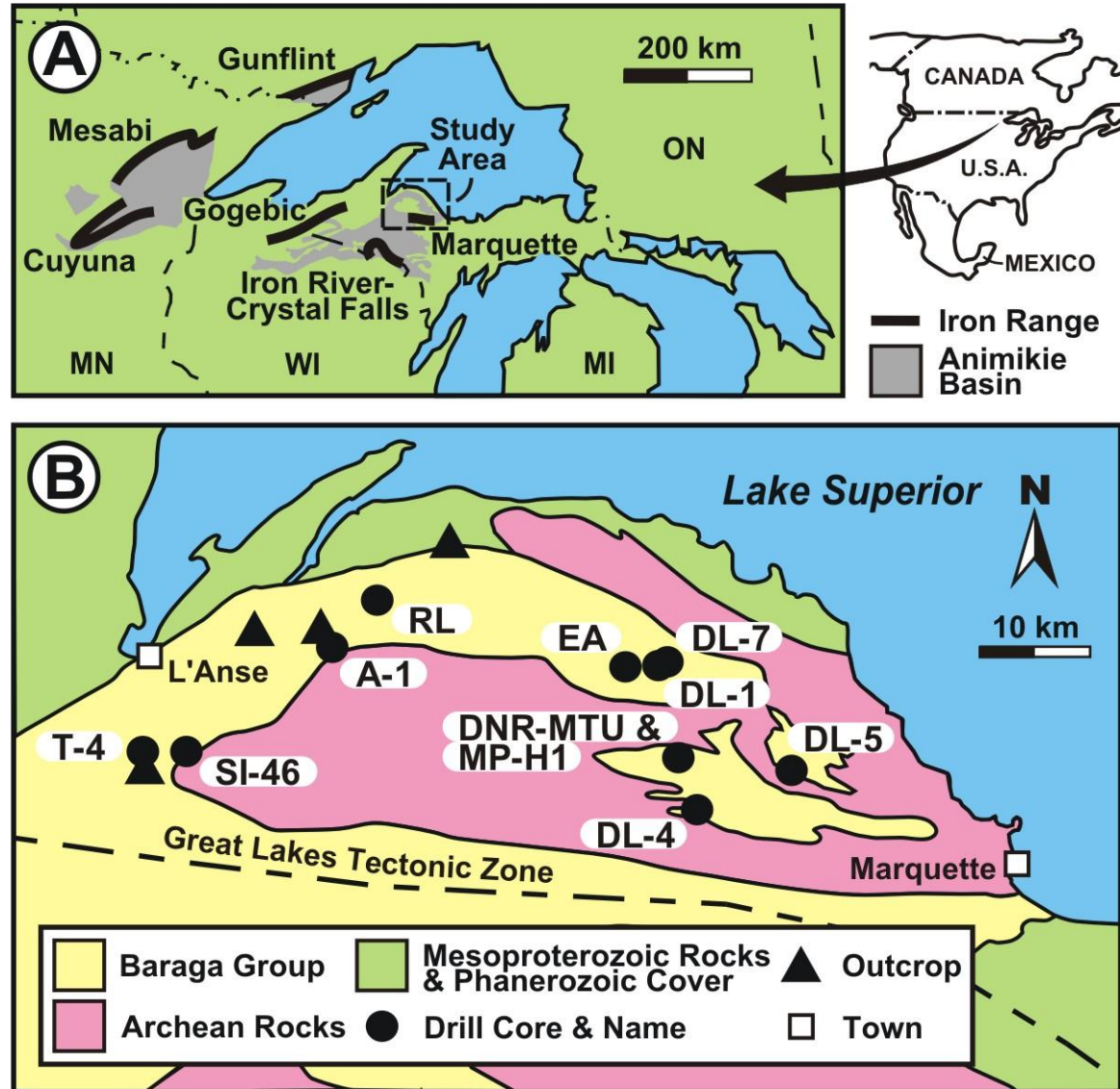
RESULT OF LOW ATMOSPHERIC  $O_2$  =  
LOW  $SO_4^{2-}$  IN PRECAMBRIAN SEAWATER (<2.4mM)



# Phosphorite

# Precambrian

## BARAGA GROUP



Nelson et al. (2010)

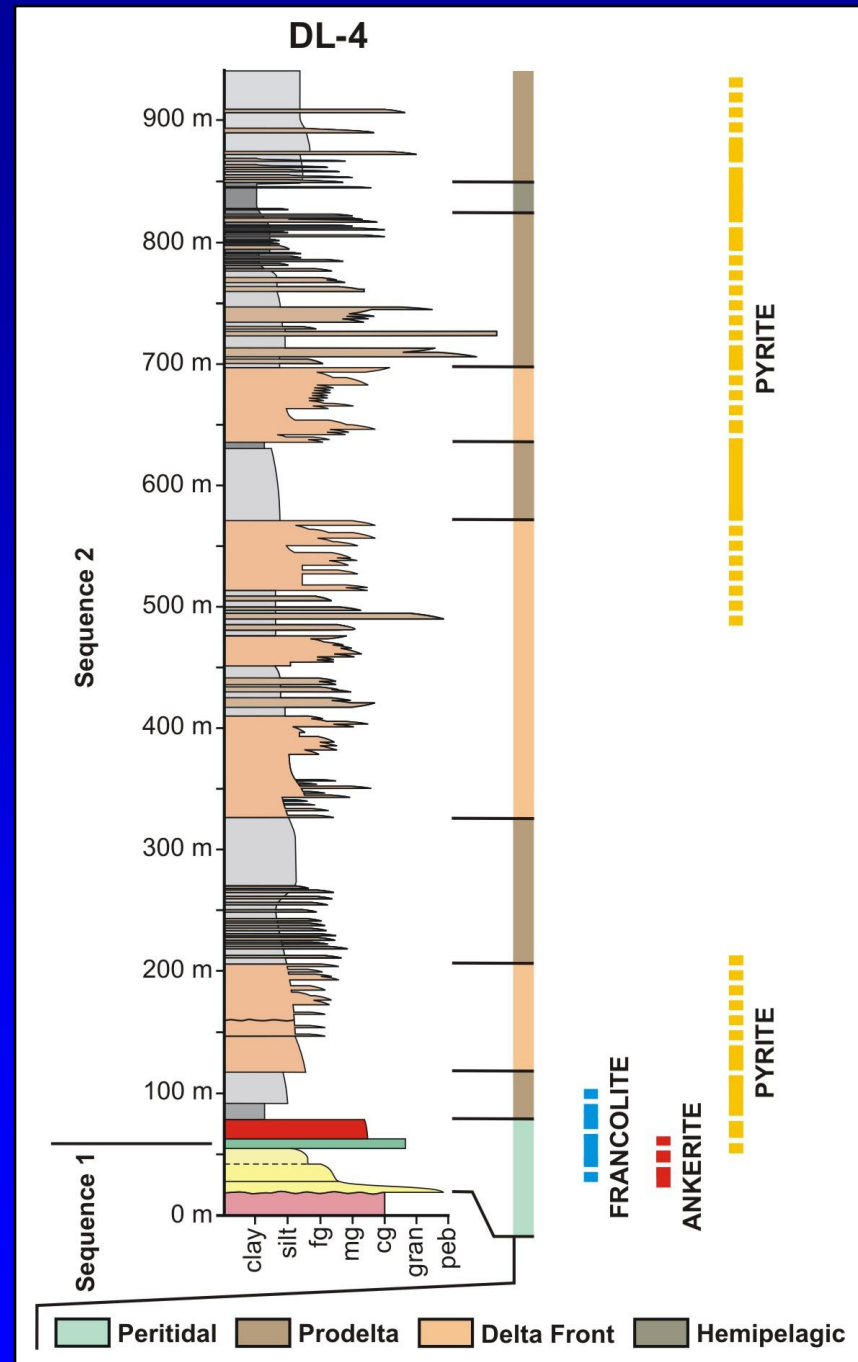




# Phosphorite

- phosphatic sediments formed only in nearshore environments

Precambrian



Nelson et al. (2010)

# Phosphorite

Precambrian

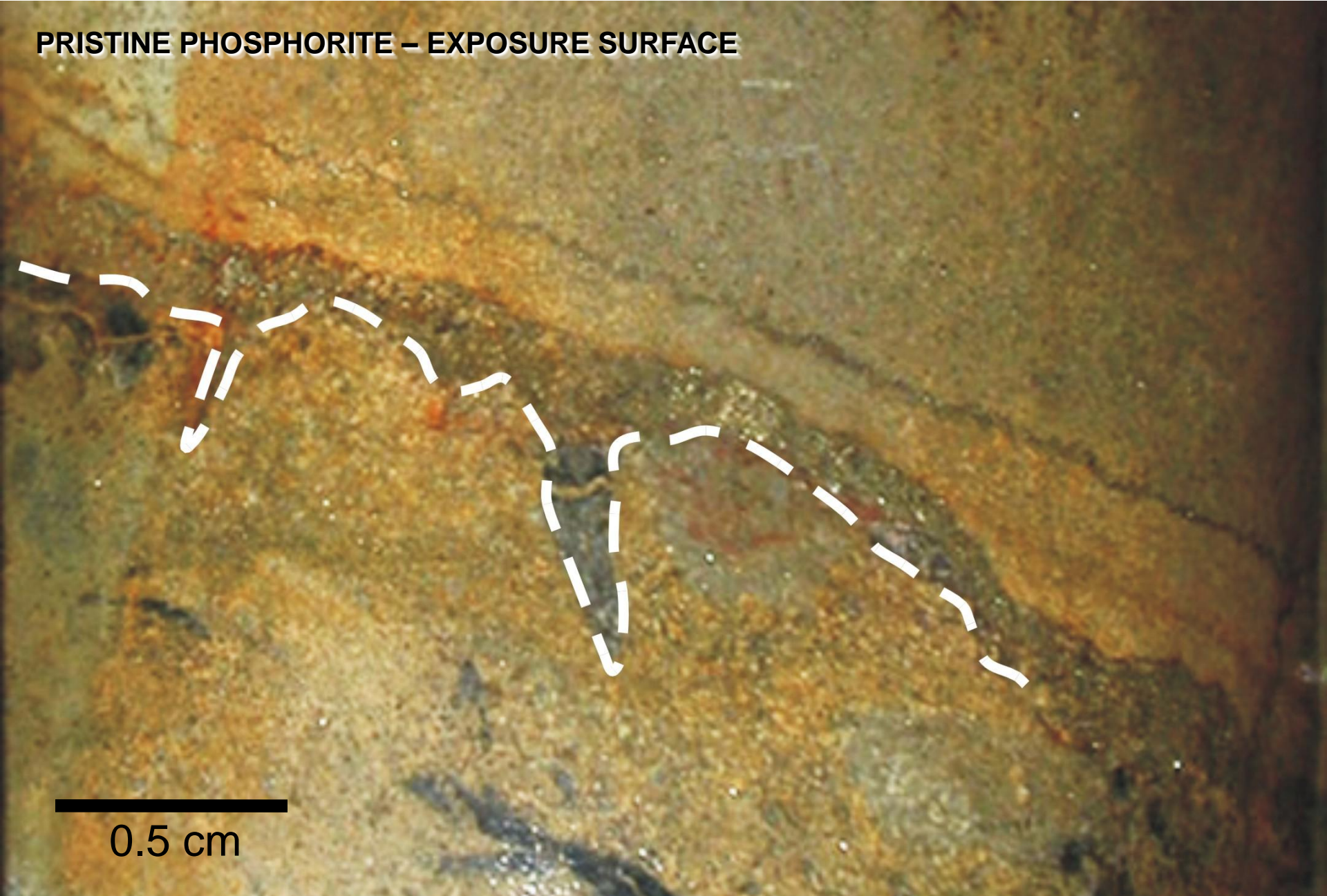
PHOSPHATIC STROMATOLITES – PALEOPROTEROZOIC BARAGA GROUP, MICHIGAN



# Phosphorite

Precambrian

PRISTINE PHOSPHORITE – EXPOSURE SURFACE



0.5 cm

# Phosphorite

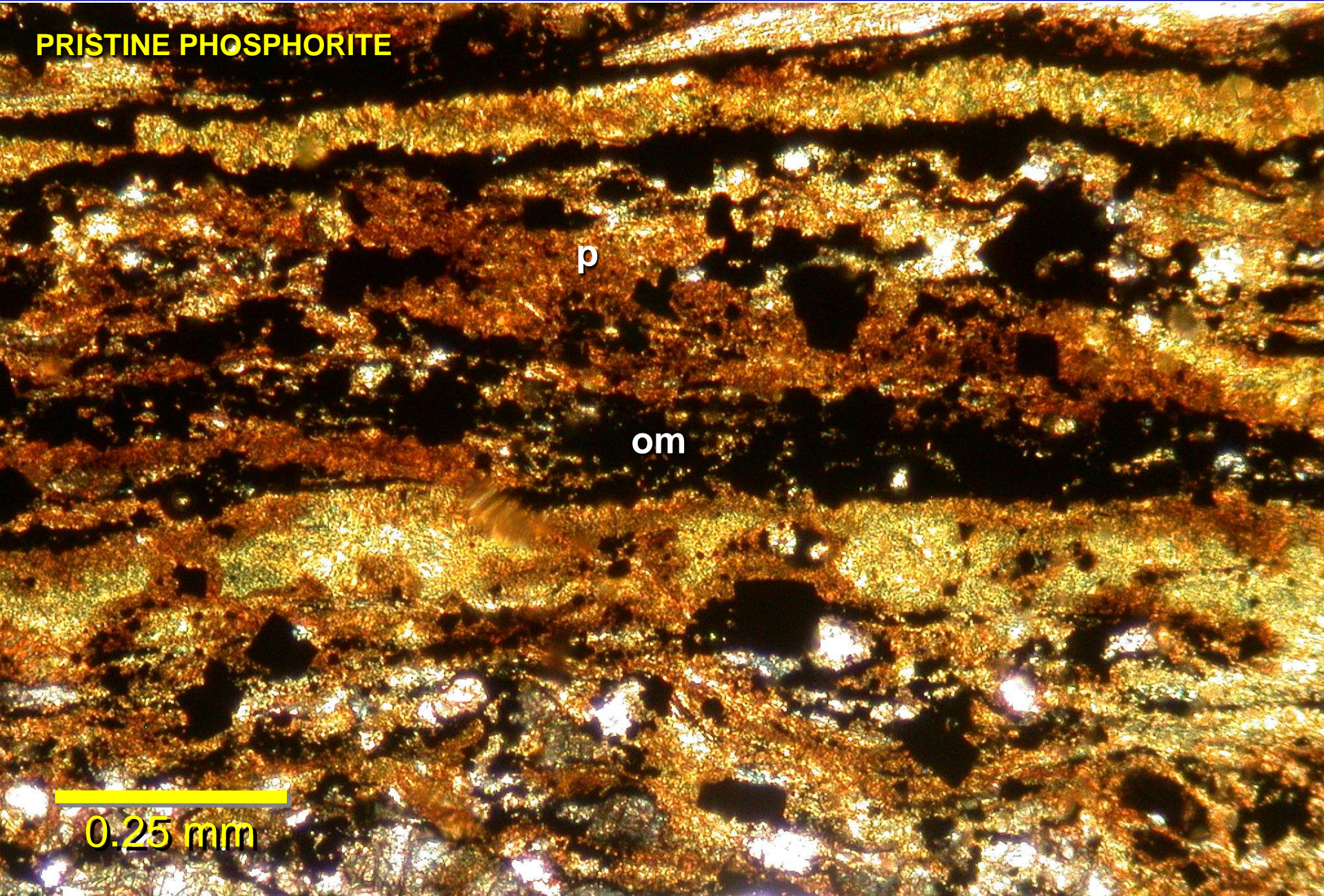
Precambrian

PRISTINE PHOSPHORITE

p

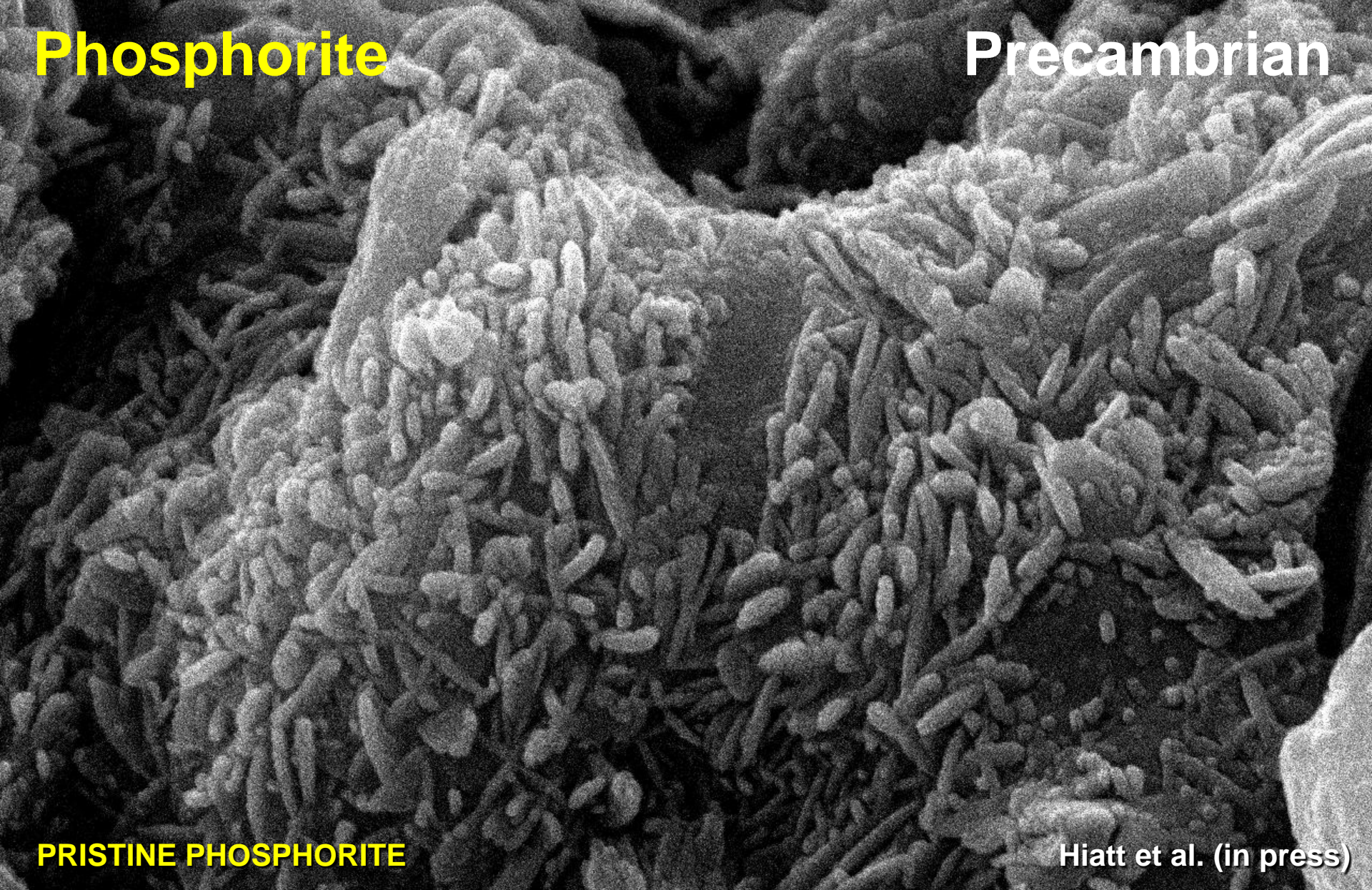
om

0.25 mm



**Phosphorite**

**Precambrian**



**PRISTINE PHOSPHORITE**

Hiatt et al. (in press)

25kV

X16,000

1  $\mu$ m

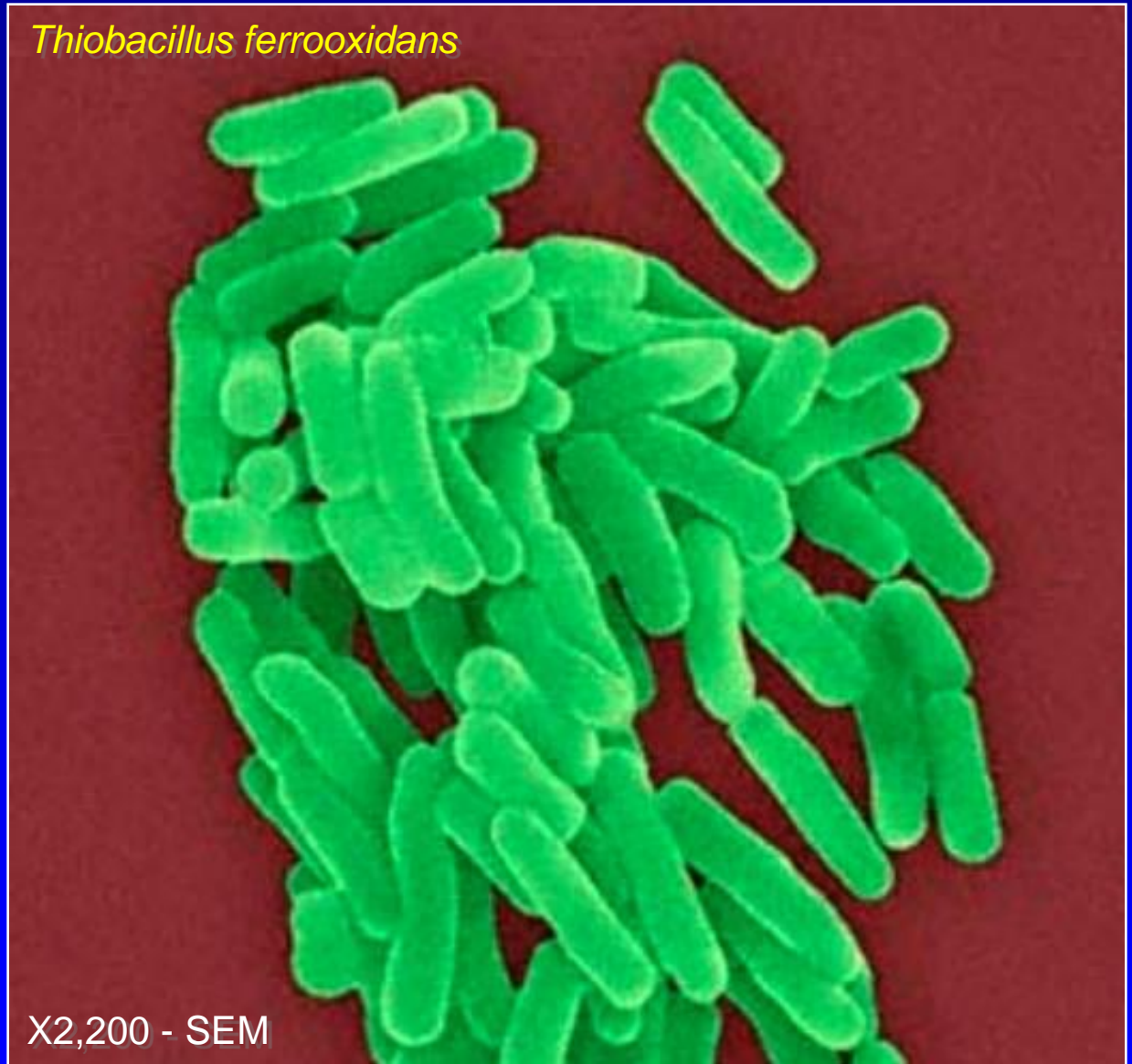
10 16 SEI

# Phosphorite

Precambrian

- modern equivalent?

*Thiobacillus ferrooxidans*



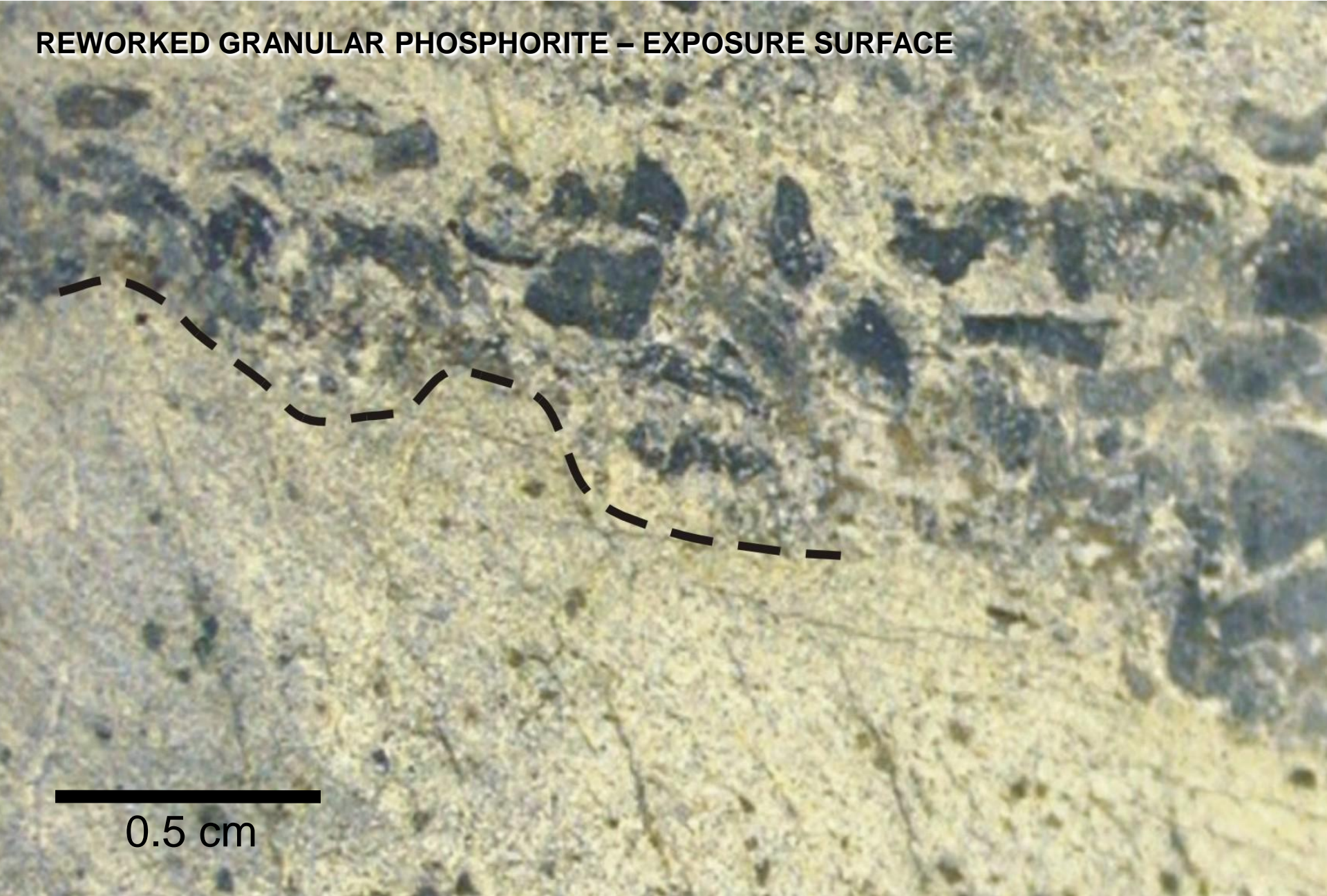
X2,200 - SEM

Photo by Dennis Kunkel

# Phosphorite

Precambrian

REWORKED GRANULAR PHOSPHORITE – EXPOSURE SURFACE



0.5 cm

# Phosphorite

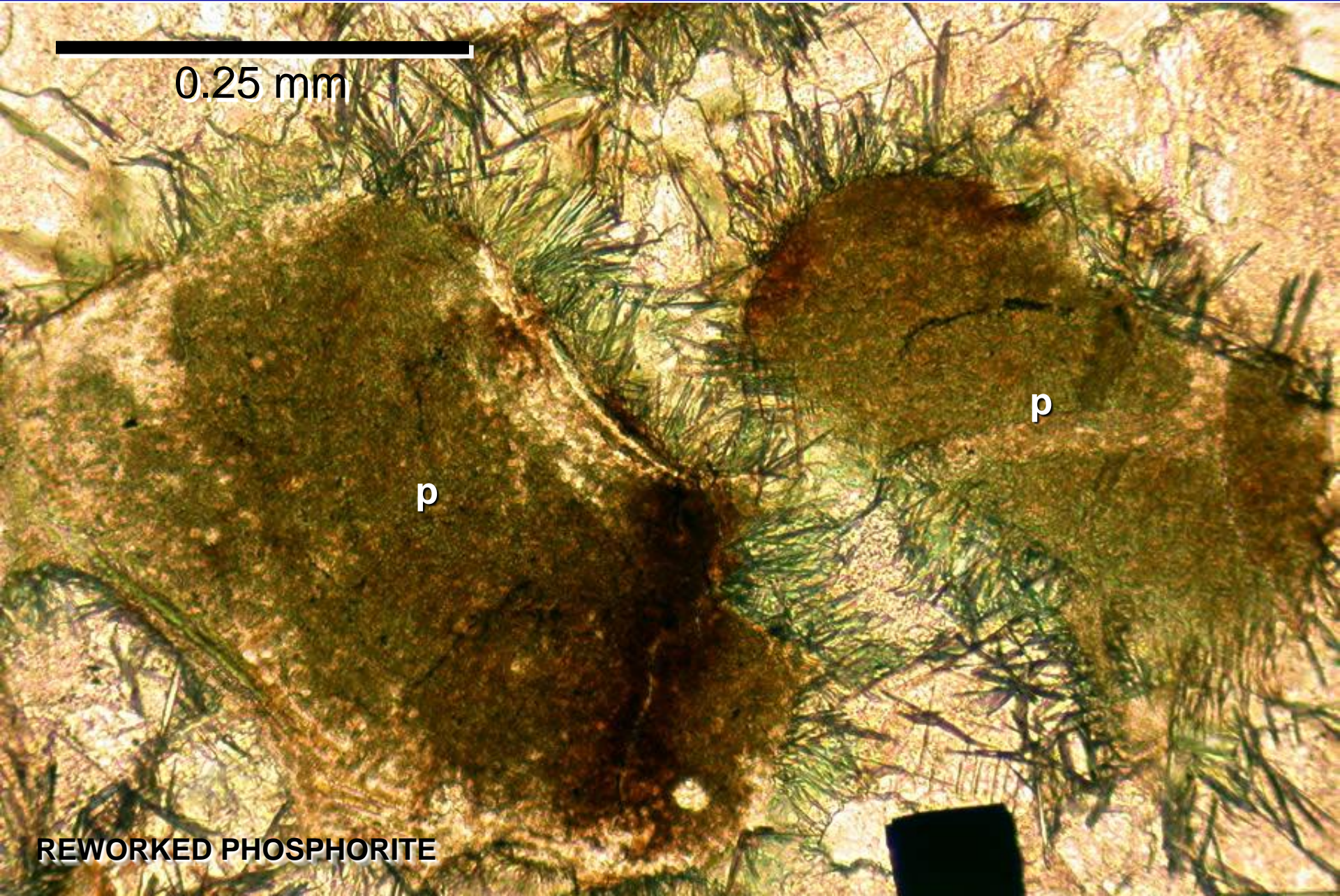
Precambrian

0.25 mm

p

p

REWORKED PHOSPHORITE



# Phosphorite

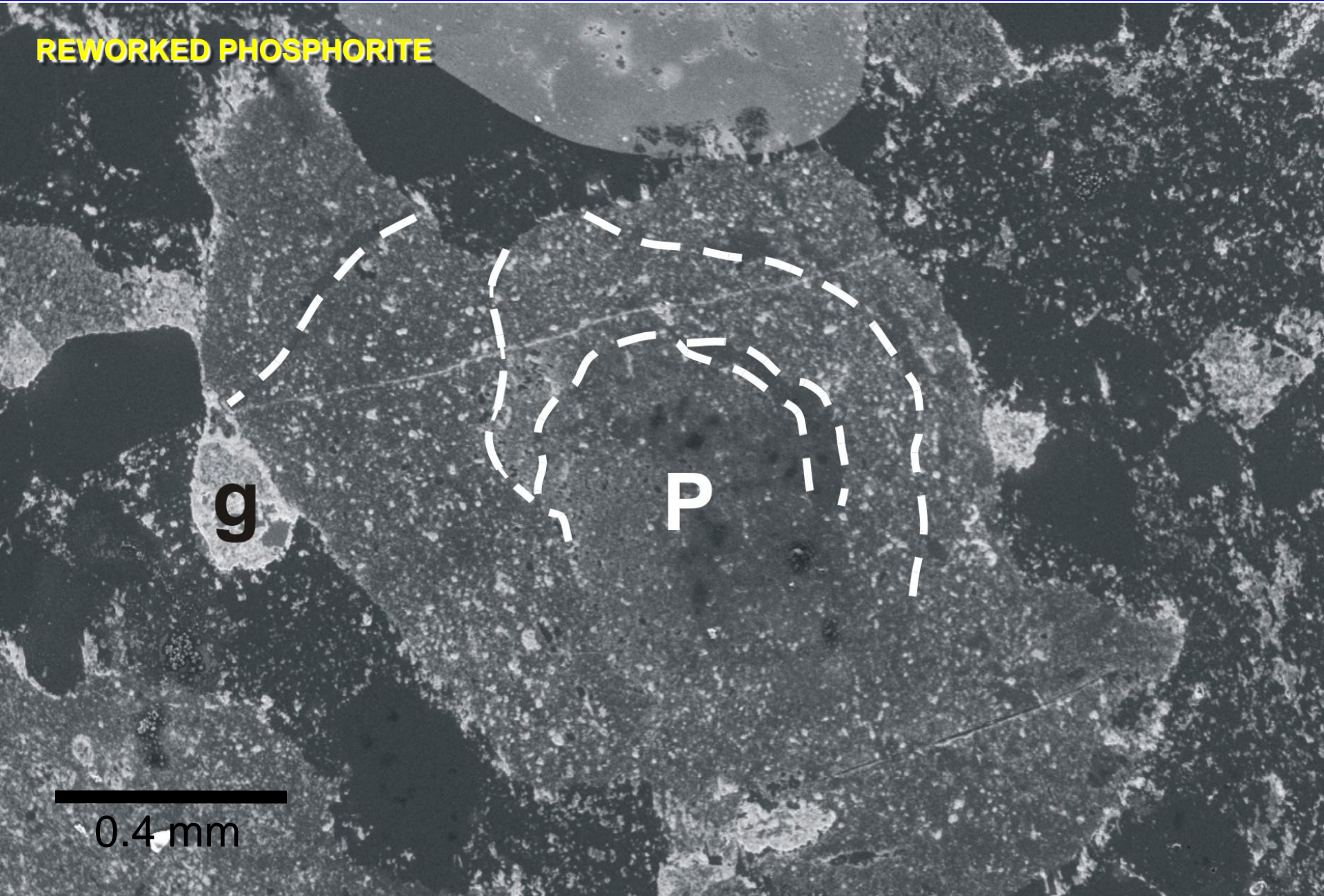
Precambrian

REWORKED PHOSPHORITE

g

P

0.4 mm



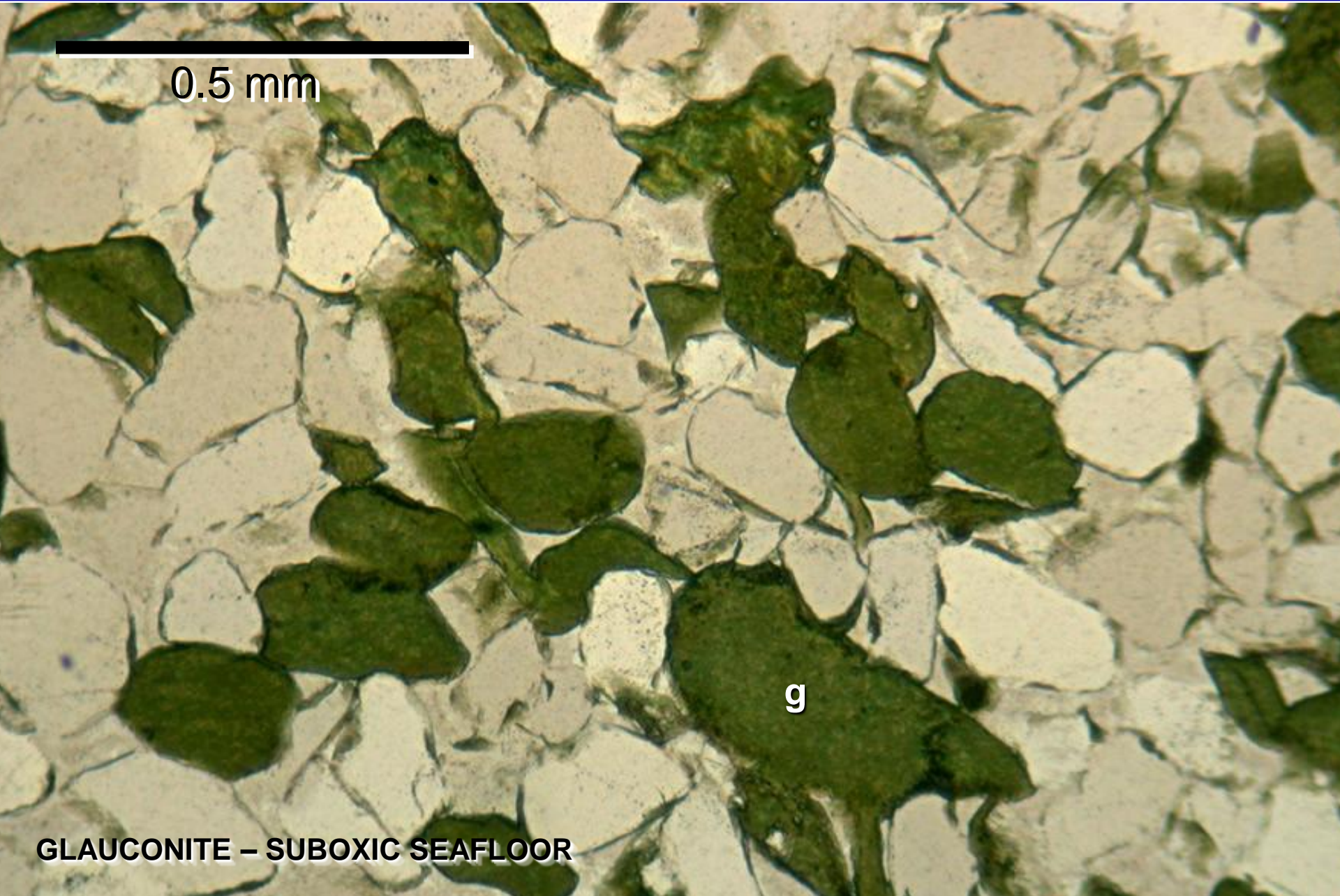
# Phosphorite

Precambrian

0.5 mm

g

GLAUCONITE – SUBOXIC SEAFLOOR



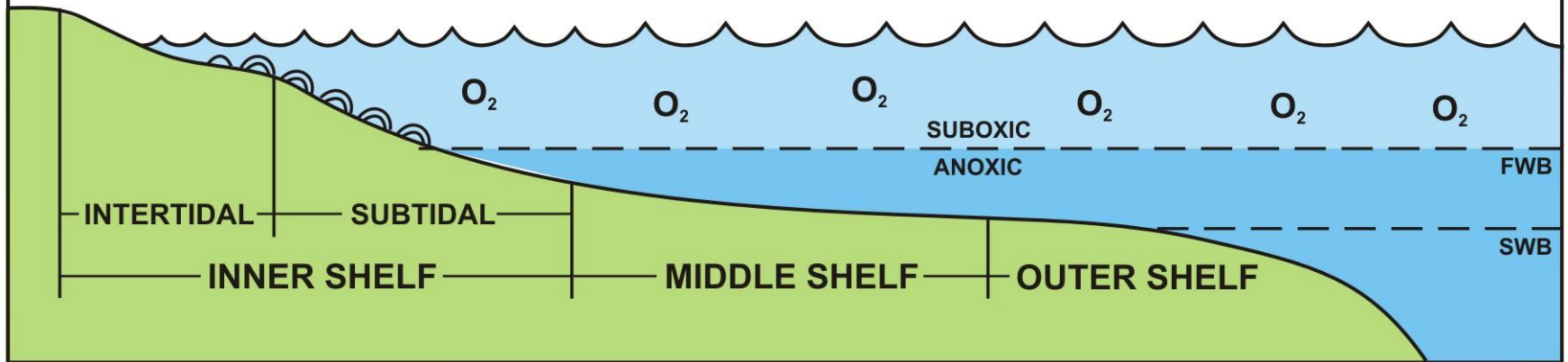
*Thin phosphatic beds in shallow  
-water paleoenvironments.*

*Reworked by tides and storms.*

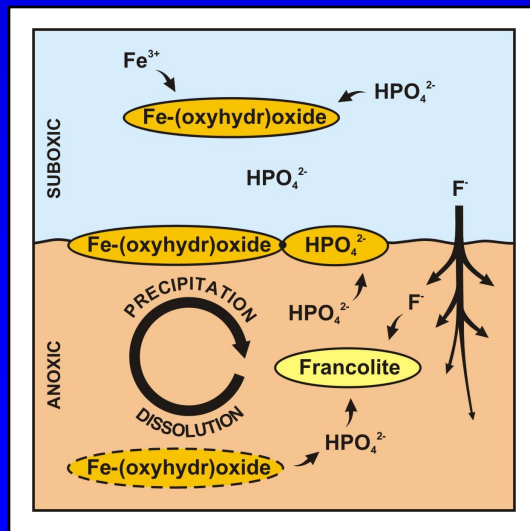
*Upwelling not important.*

# Fe-redox Pumping

## PRECAMBRIAN PHOSPHORITE



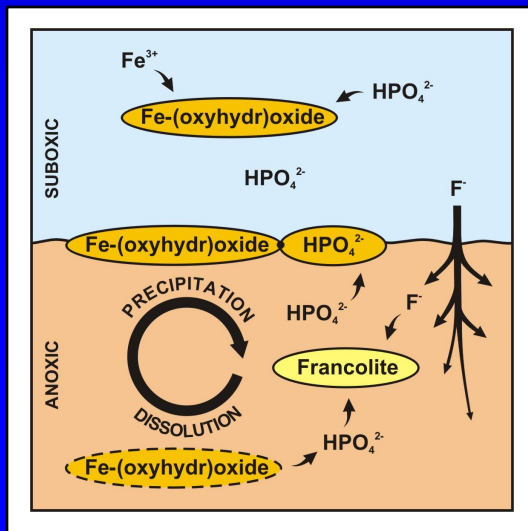
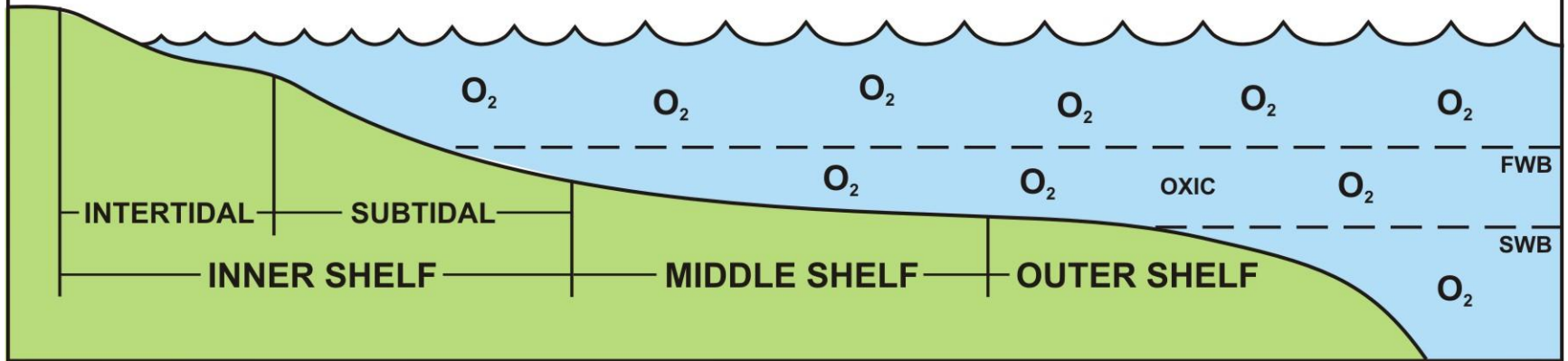
Nelson et al. (2010)



- Fe-redox pumping in nearshore environments

# Fe-redox Pumping

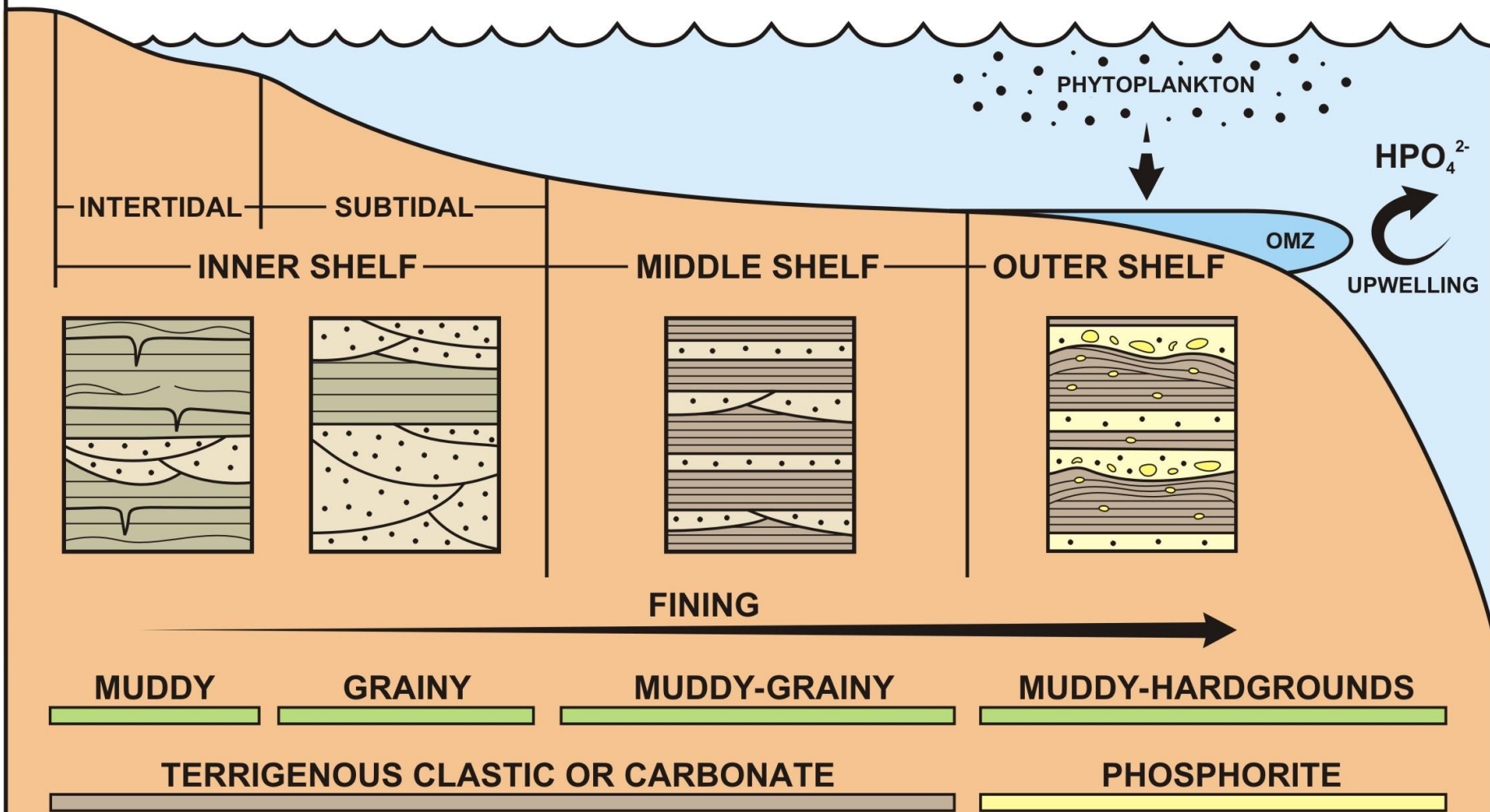
## PHANEROZOIC PHOSPHORITE



- Fe-redox pumping across entire shelf

# CONTINENTAL MARGIN PHOSPHORITE

← 100-200 kms →

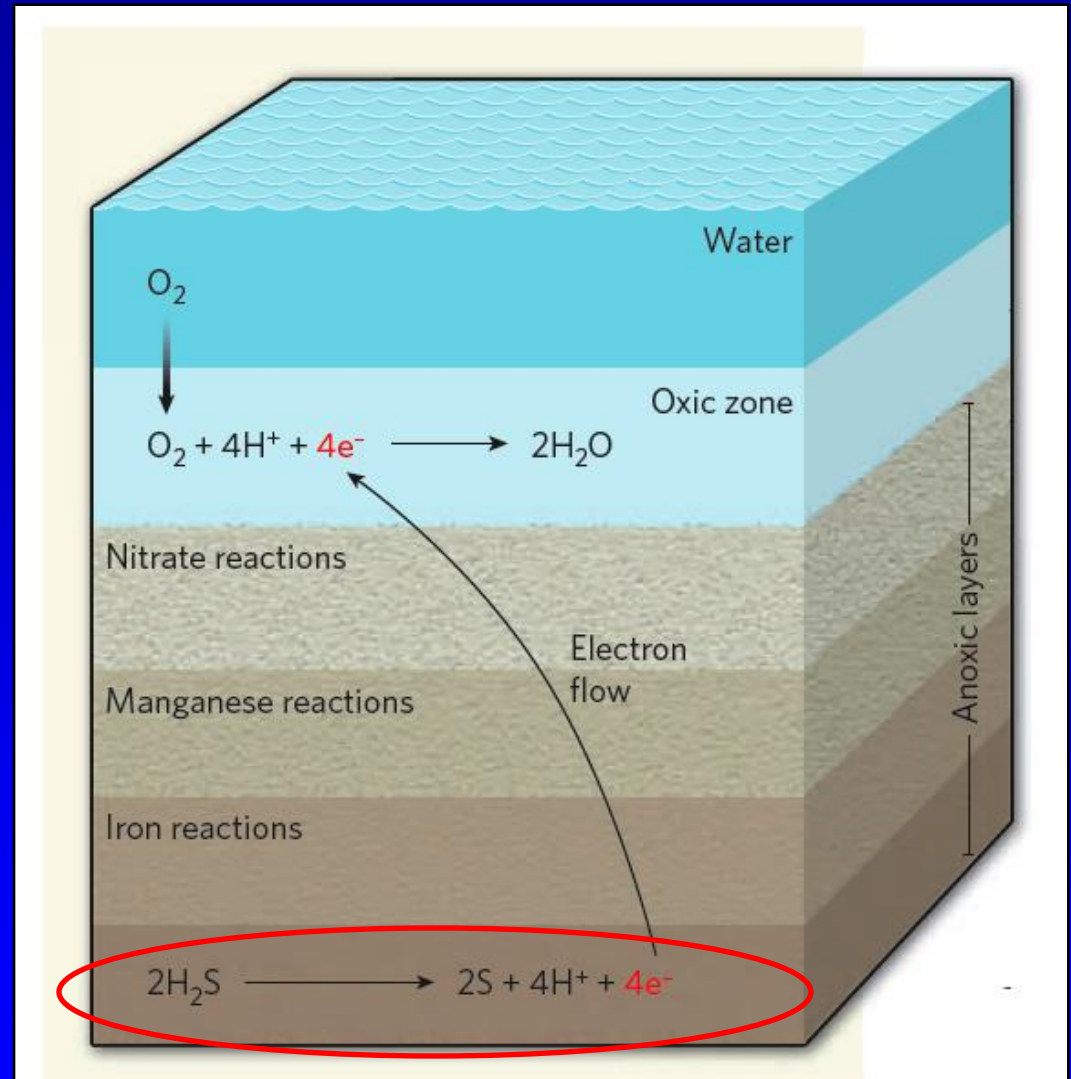


Pufahl (2010)

# Microbes

- tiered microbial communities
- bacterial sulfate reduction most important

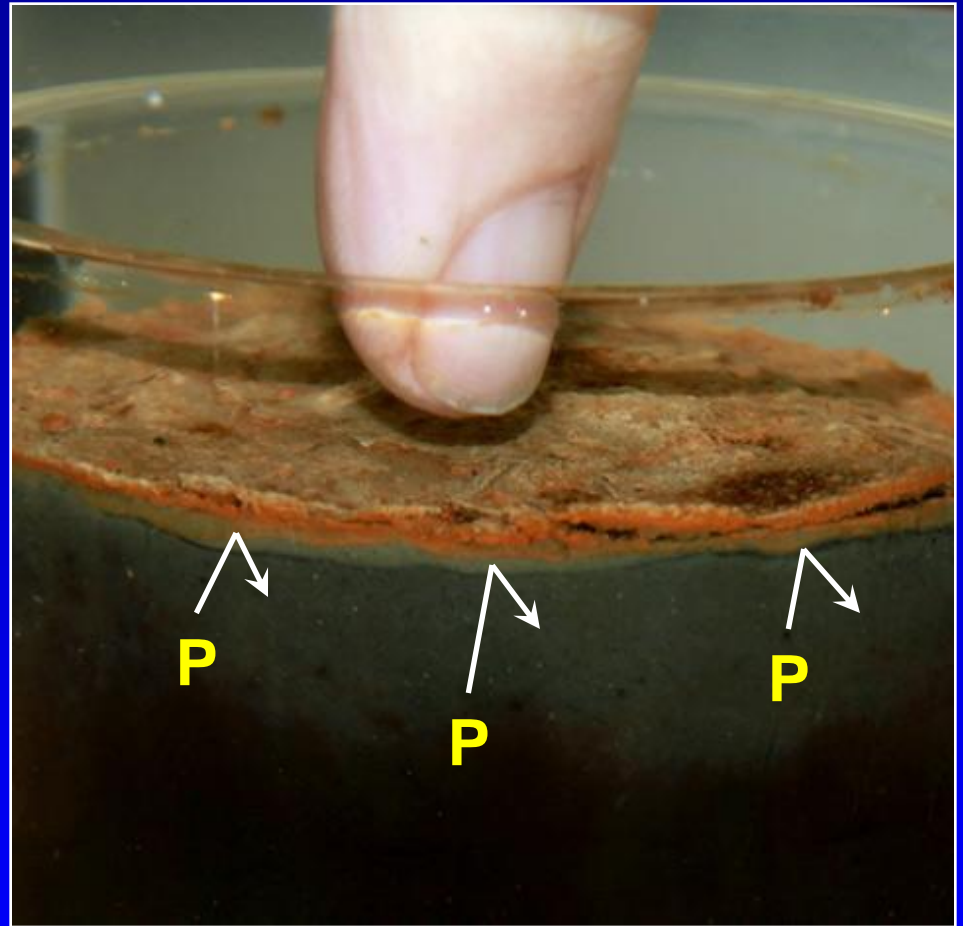
(Arning et al., 2009)



(Nealson, 2010)

# Microbes

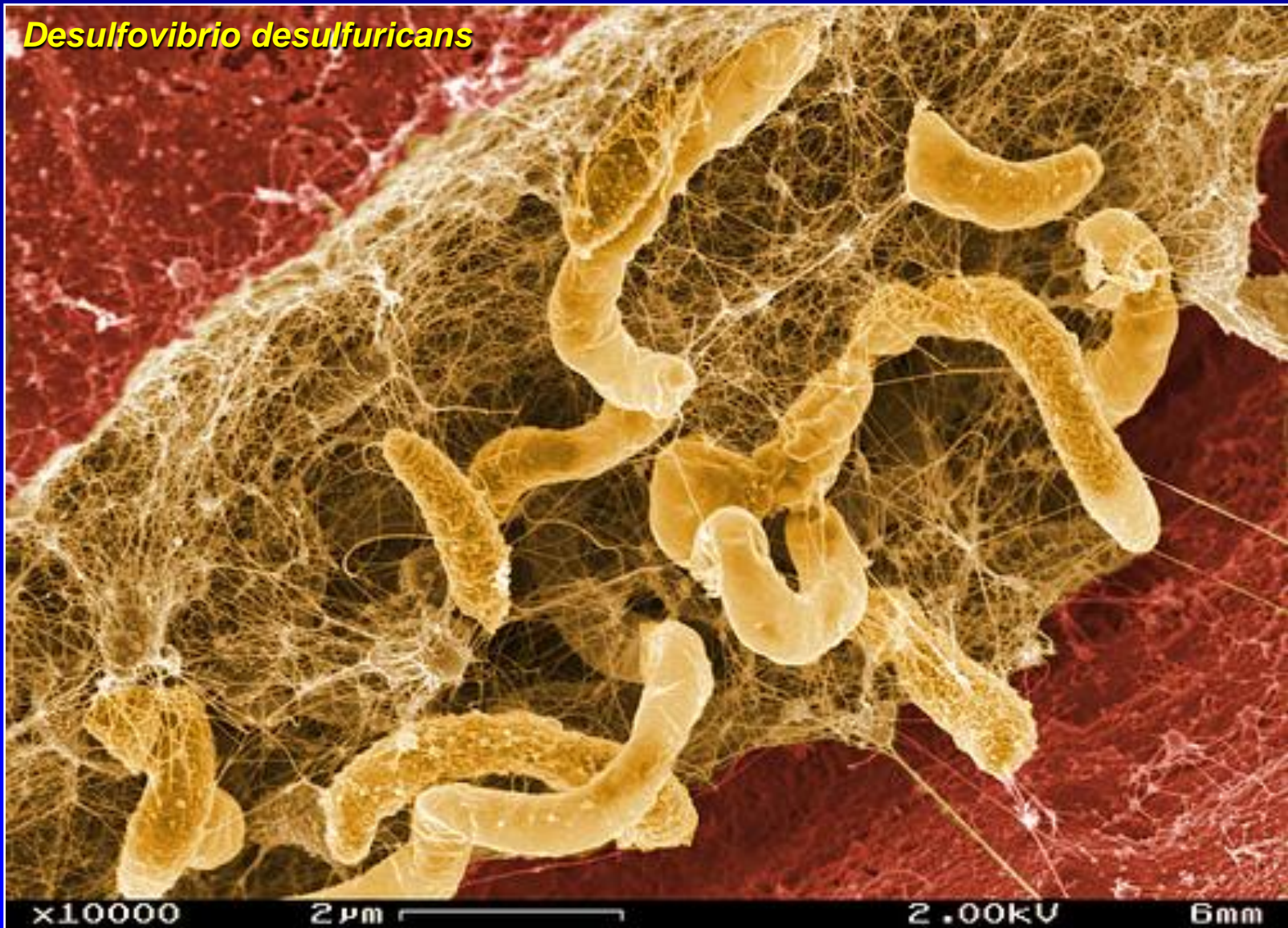
- breaks down organic matter and releases phosphate to pore water
- promotes phosphogenesis
- but Precambrian seawater low in sulfate



<http://news.sciencemag.org/sciencenow/2010/02/-deep-on-the-ocean.html>

# Microbes

# Sulfate Reducers

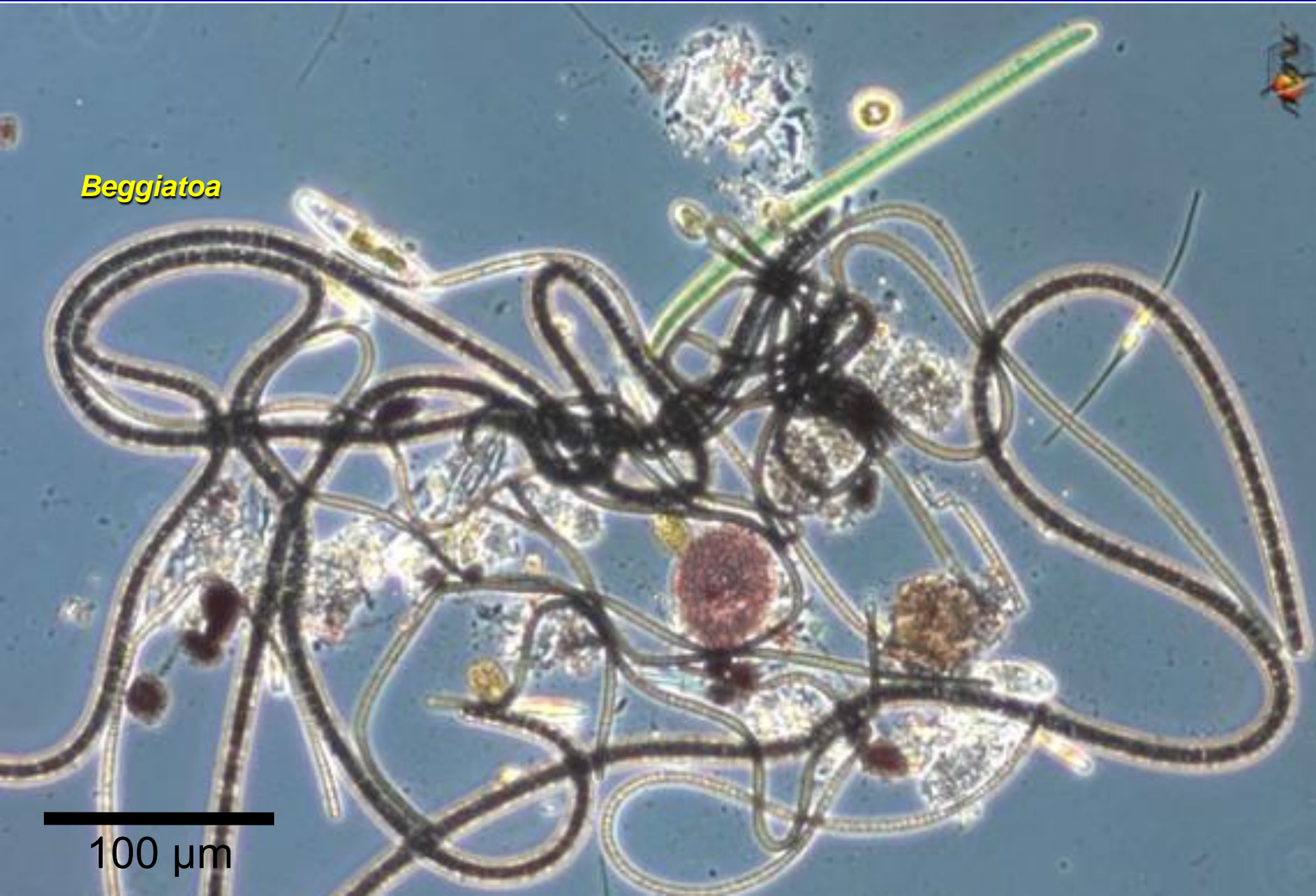


Pacific Northwest National Laboratory – US Department of Energy

# Microbes

# Sulfide Oxidizers

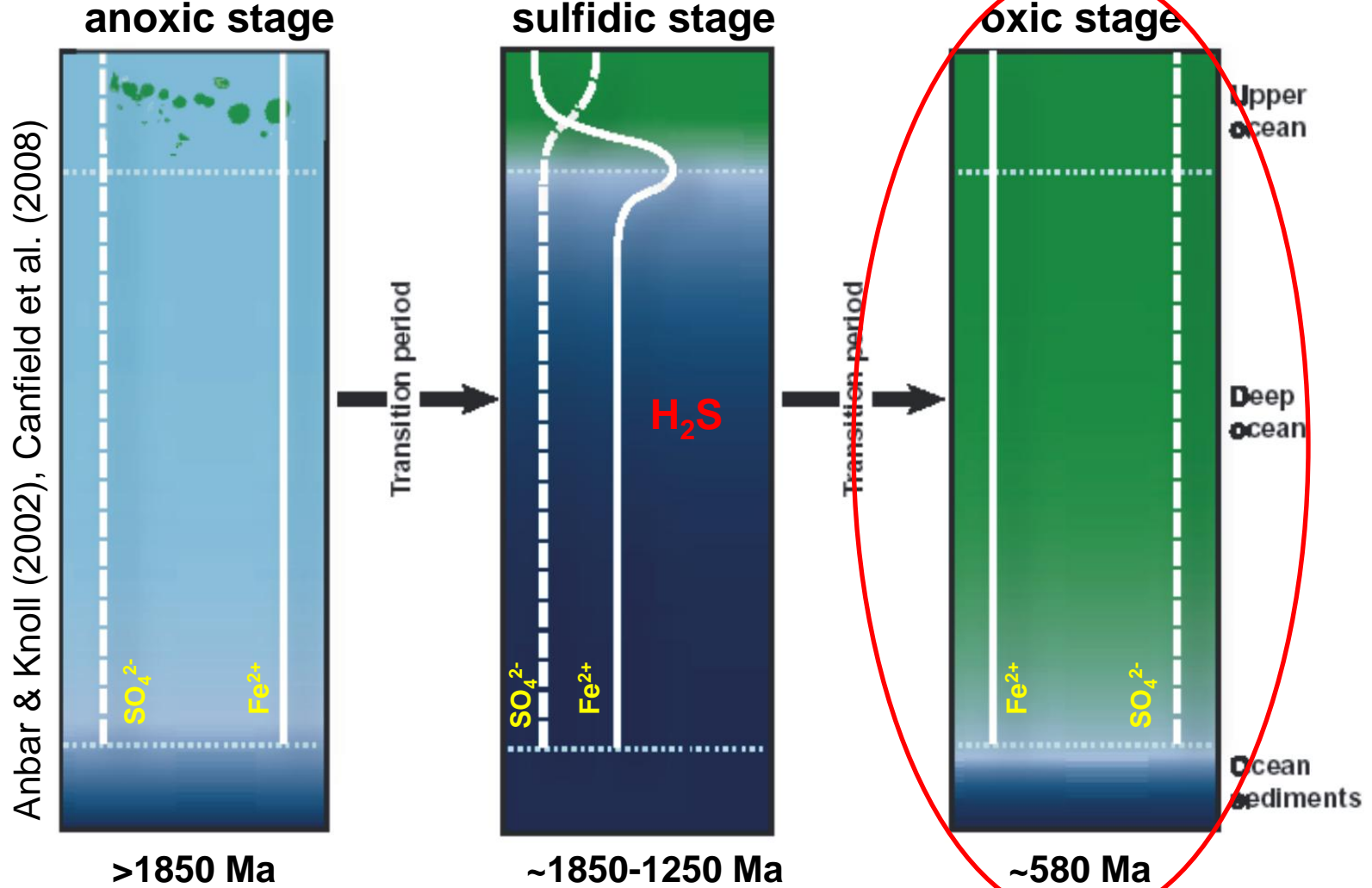
*Beggiatoa*



100  $\mu\text{m}$

# Phosphorite

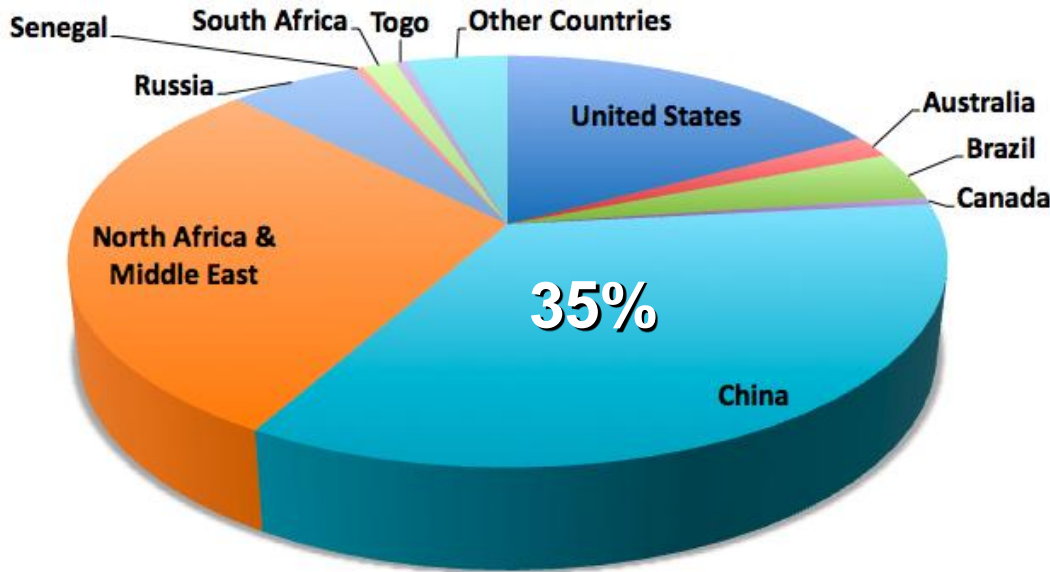
# Precambrian



**OXYGENATED SEAWATER = ECONOMIC PHOSPHORITE**

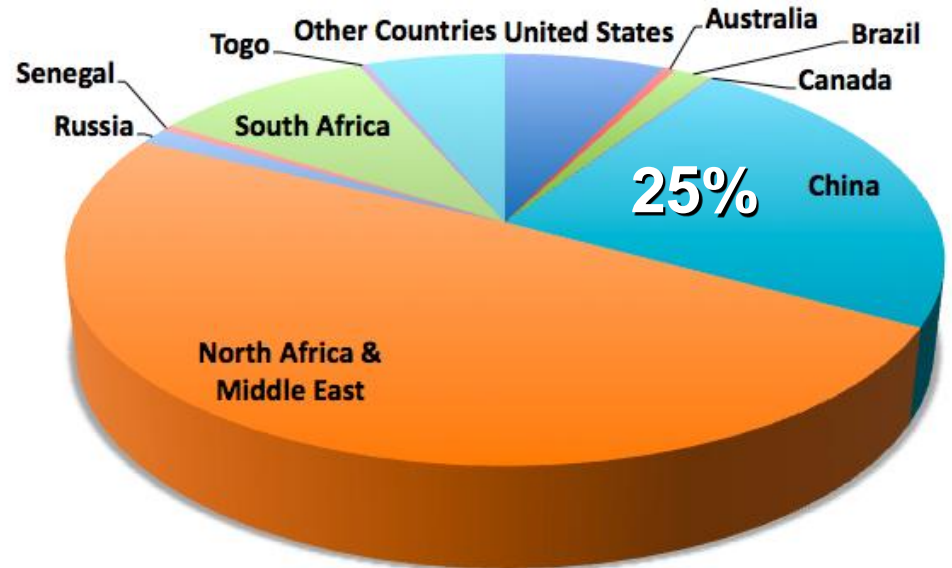
# China

# Neoproterozoic-Cambrian



## Phosphate Rock Production 2009

## Phosphate Rock Reserves 2009



# Conclusions

- different atmospheric and ocean compositions prevented the formation of Precambrian economic phosphorites
- phosphorite formed only in photosynthetically produced, nearshore oxygen oases where Fe-redox pumping concentrated P in sediment
- phosphorite giants did not accumulate until the Neoproterozoic-Cambrian when the seafloor became fully oxygenated and Fe-redox pumping and bacterial sulfate reduction worked together to precipitate sedimentary apatite

