



UNIVERSITY OF TARTU



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# Origin of rod and dumbbell shaped phosphate precipitates in Namibian shelf sediments

Kaarel Mänd, Jake Bailey, Aivo Lepland, Kalle Kirsimäe



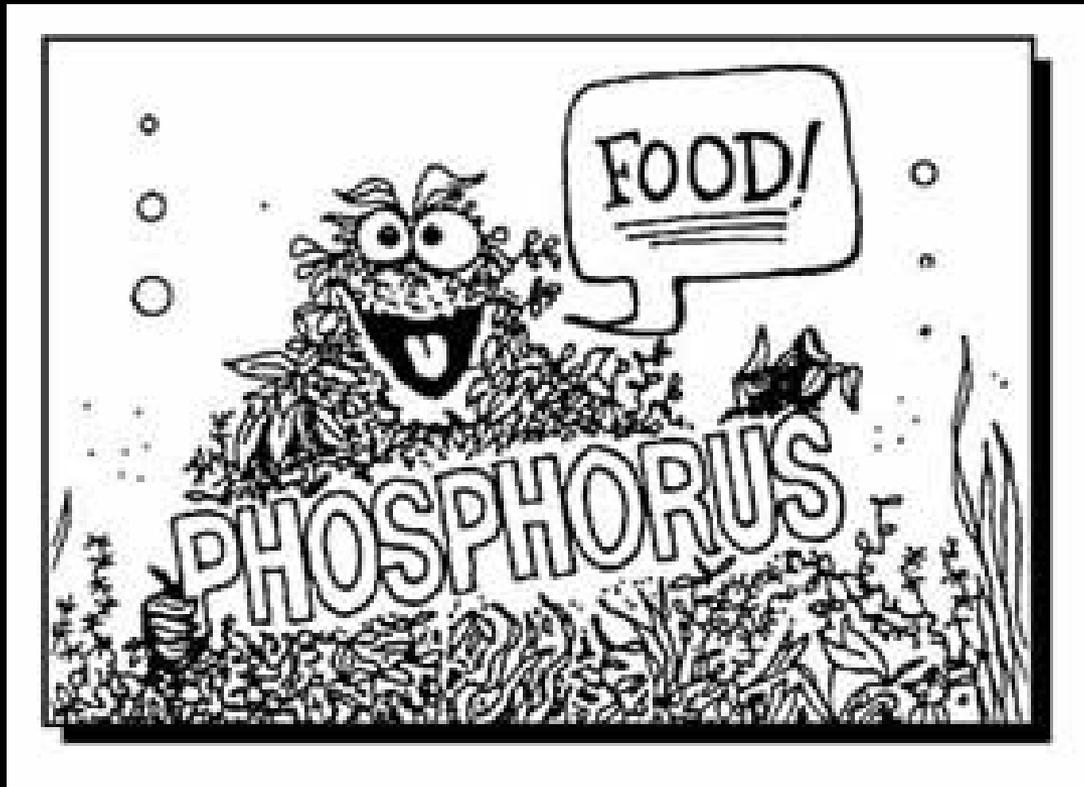
GEOLOGICAL  
SURVEY OF  
NORWAY

- NGU -



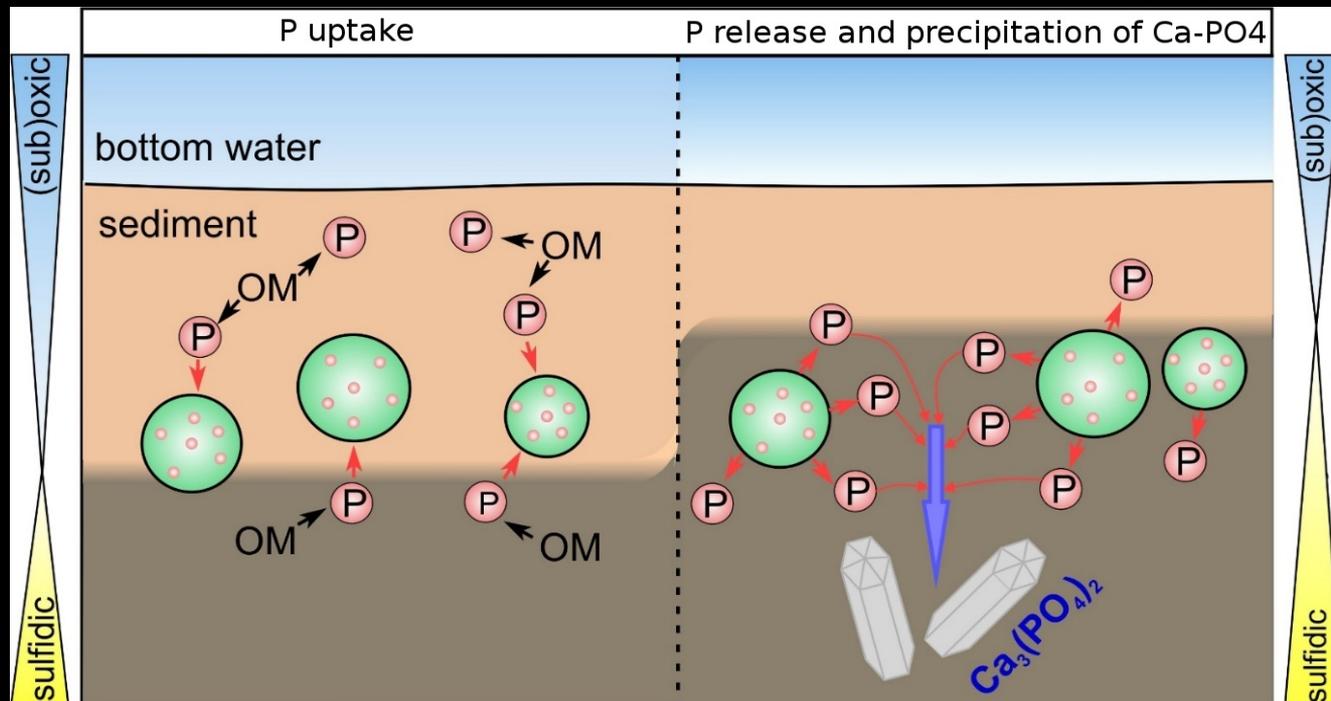
# Introduction

- Phosphorous can be the limiting nutrient in a variety of marine and terrestrial ecosystems.
- As a component of fertilizers, it is important in agriculture.



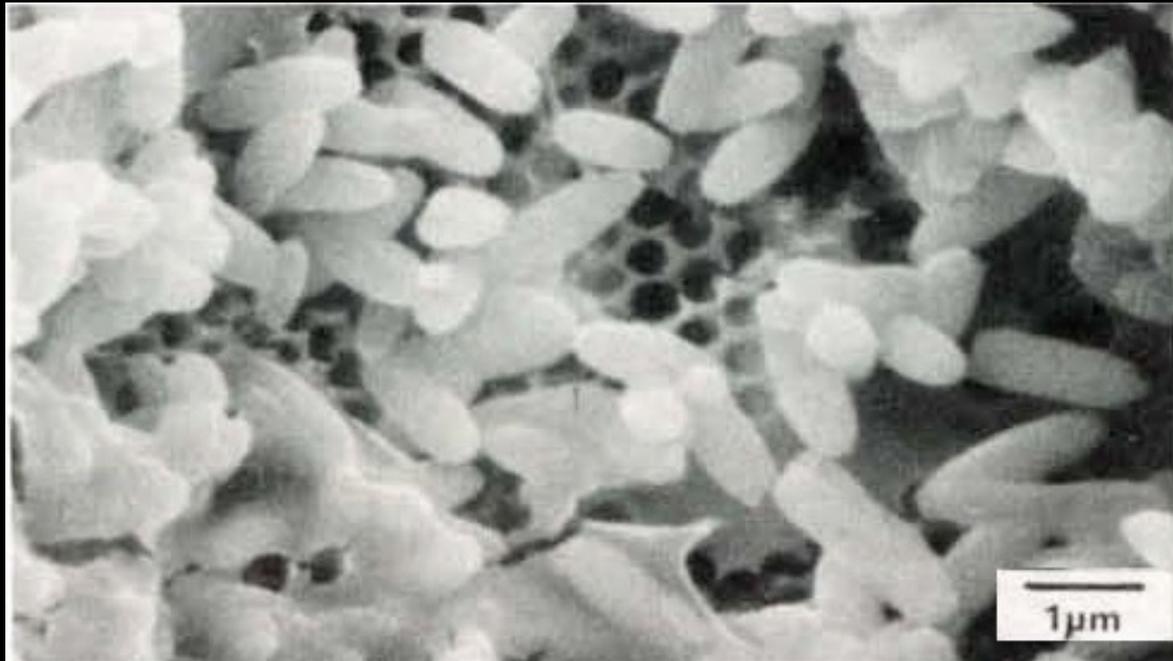
# Microbially mediated phosphogenesis

- The origins of phosphorites are still poorly understood.
- One of the proposed formation mechanisms emphasizes the role of polyphosphate-metabolizing bacteria that are capable of storing and releasing phosphate.



Modified, Brock and Schulz-Vogt (2011)

# Phosphatization is well-known as a fossilization mechanism



- Apatitic microstructures in ancient and recent phosphorites have been (controversially) interpreted as fossilized microbes (e.g. Lamboy, 1990), therefore providing evidence for the important role of microbial processes on phosphogenesis.

# Goals

- Initiation of phosphorite precipitation is still poorly understood.

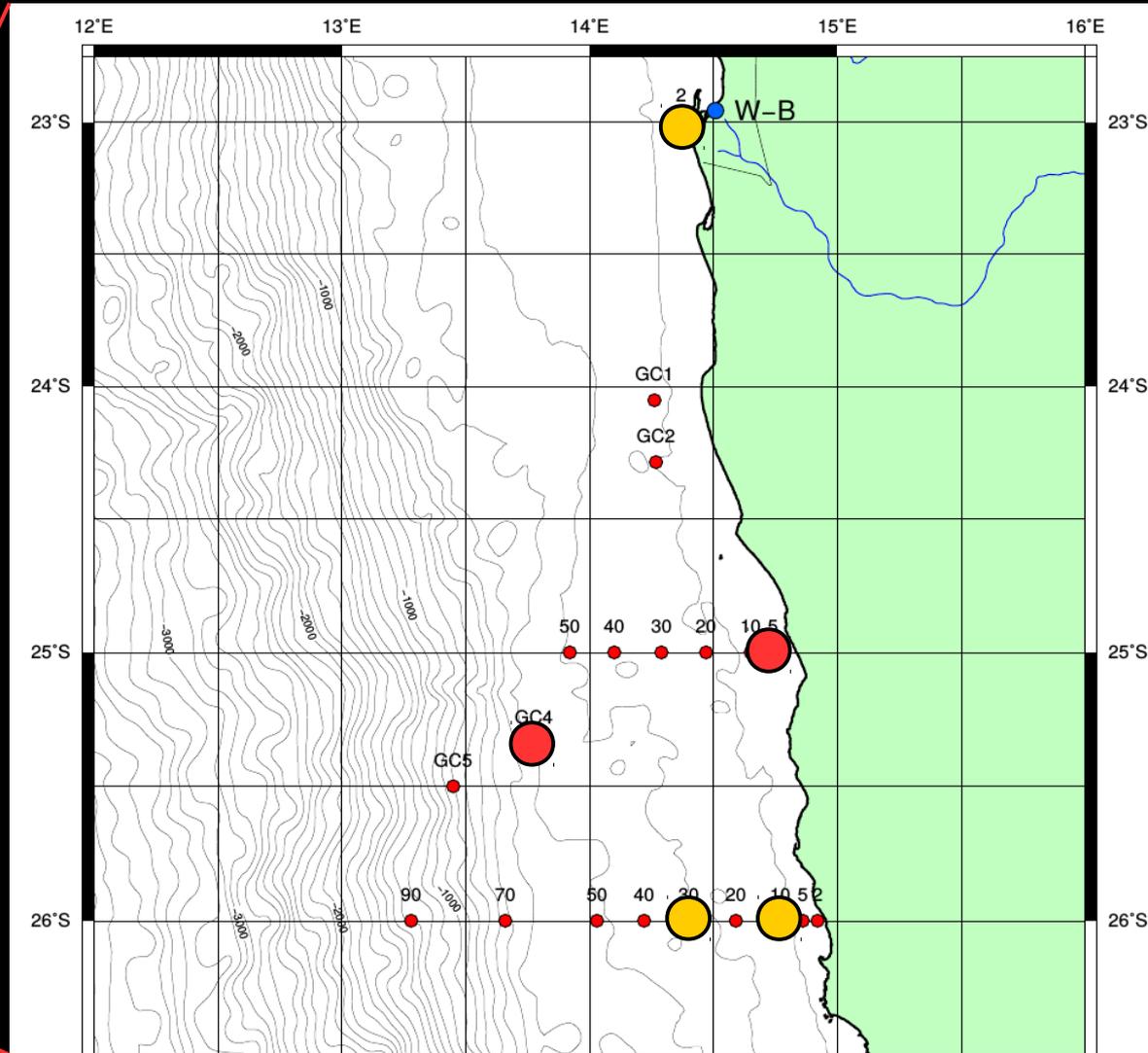
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- The goals of this study are:
  - to study microbial structures present and preserved in modern phosphorites;
  - to understand if and how phosphate precipitation is controlled/influenced by microbial/biological structures.

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- Initiation of phosphorite precipitation is still poorly understood.
- The goals of this study are:
  - to study microbial structures present and preserved in modern phosphorites;
  - to understand if and how phosphate precipitation is controlled/influenced by microbial/biological structures.
- Recrystallization of ancient phosphorites makes it difficult to recognize primary structures, but comparison with modern phosphorites can help assess controls of past phosphogenesis.

# Materials

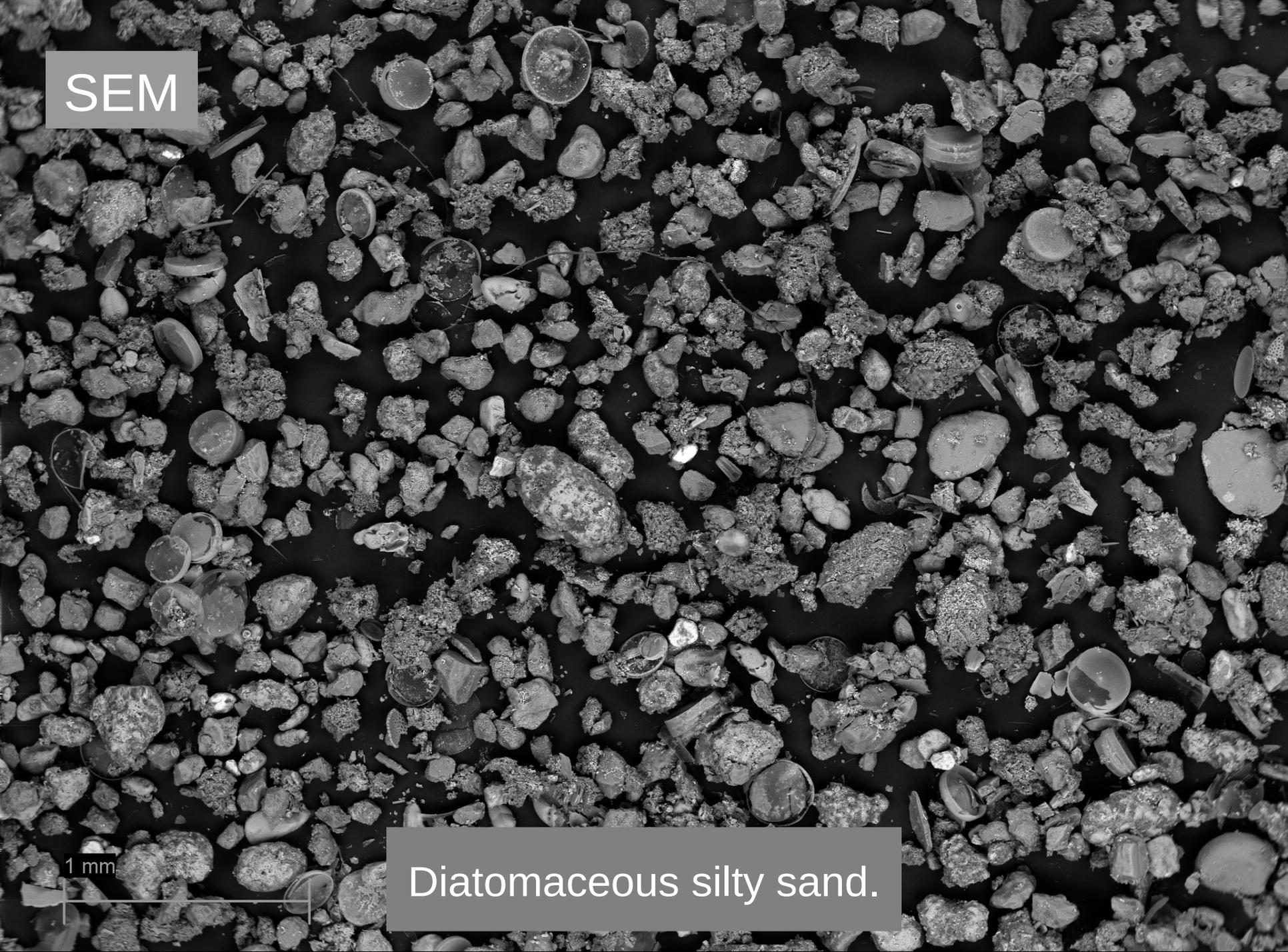


- Samples were collected from the Benguela Upwelling System off of Namibia, a site of modern phosphogenesis.

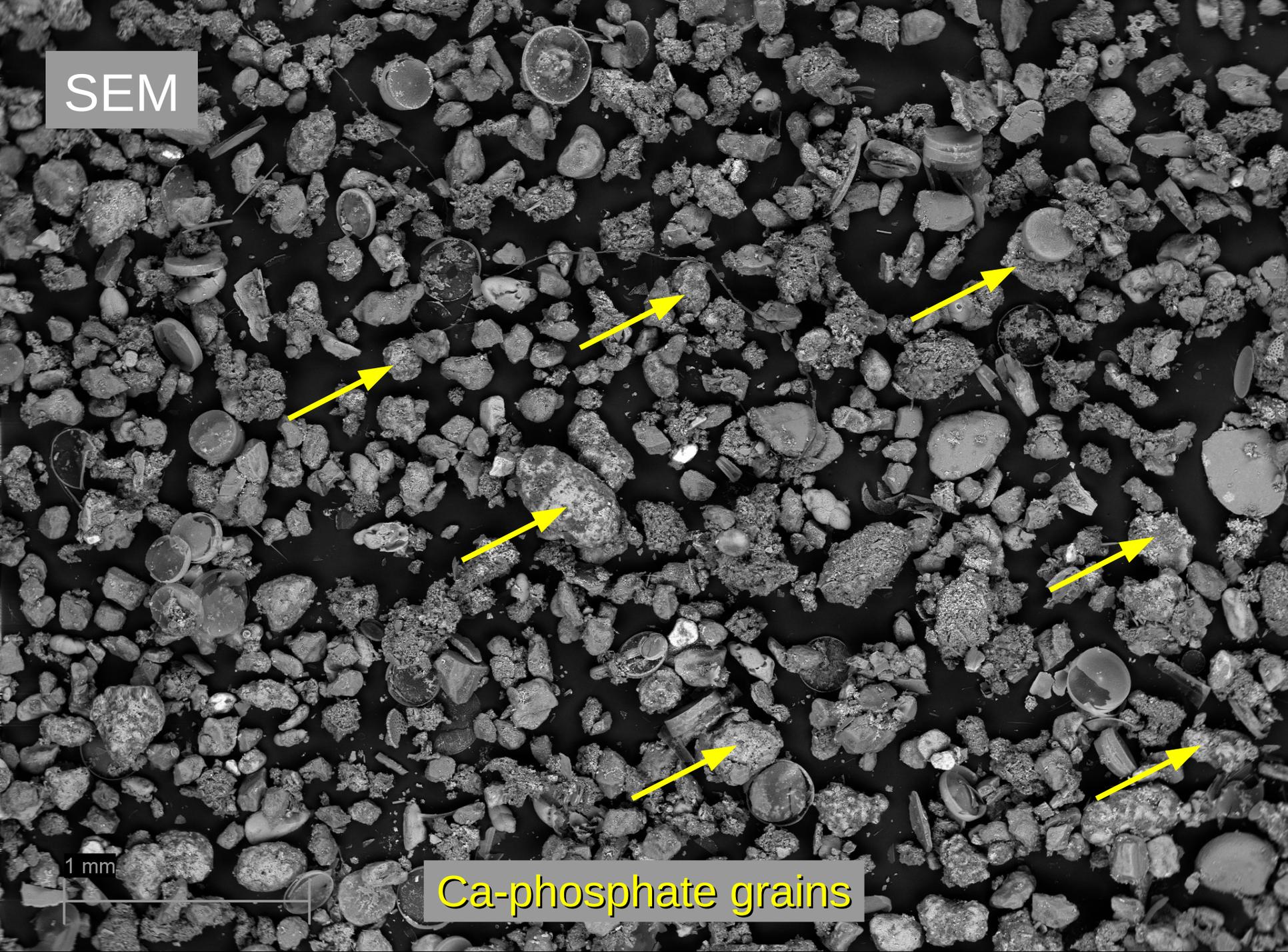
SEM

1 mm

Diatomaceous silty sand.



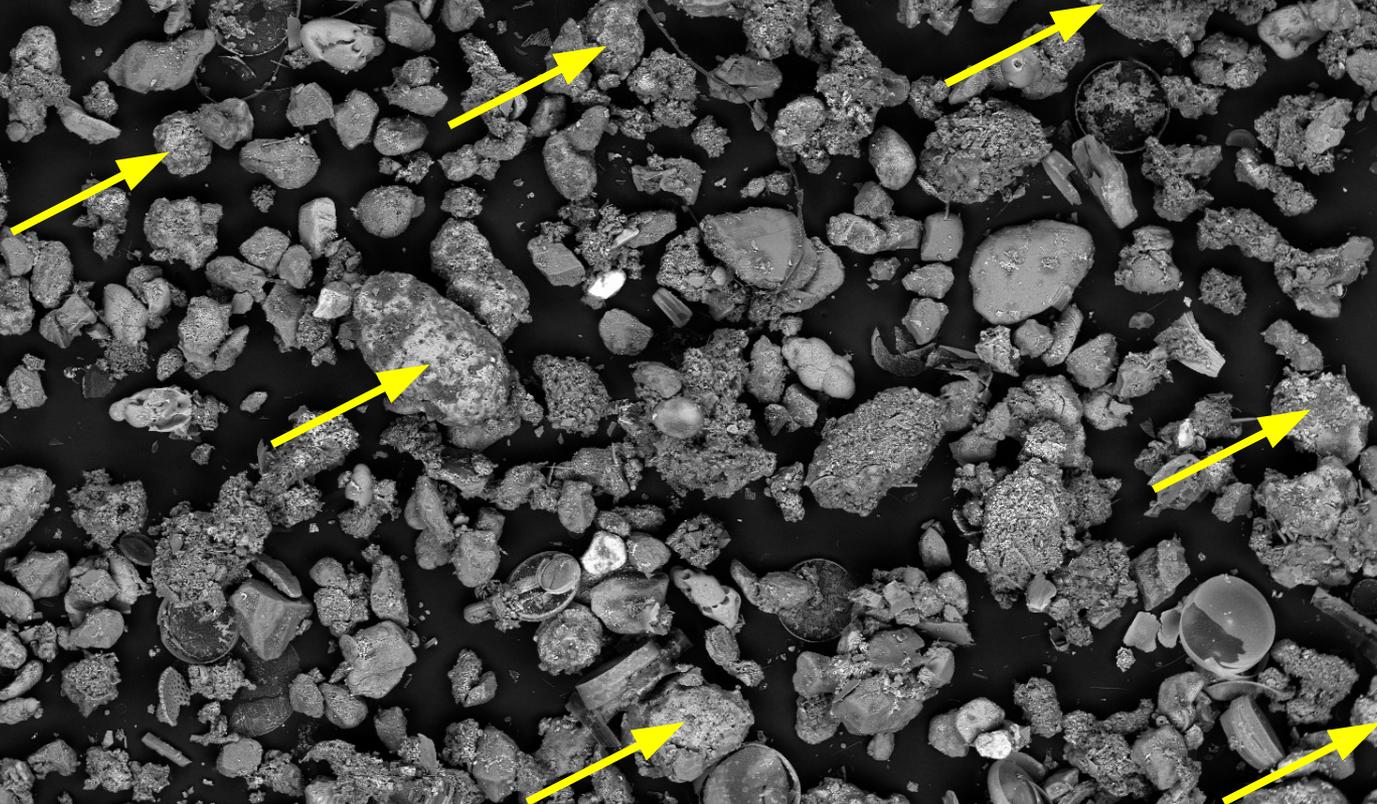
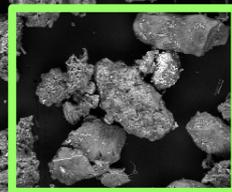
SEM



1 mm

Ca-phosphate grains

SEM



1 mm

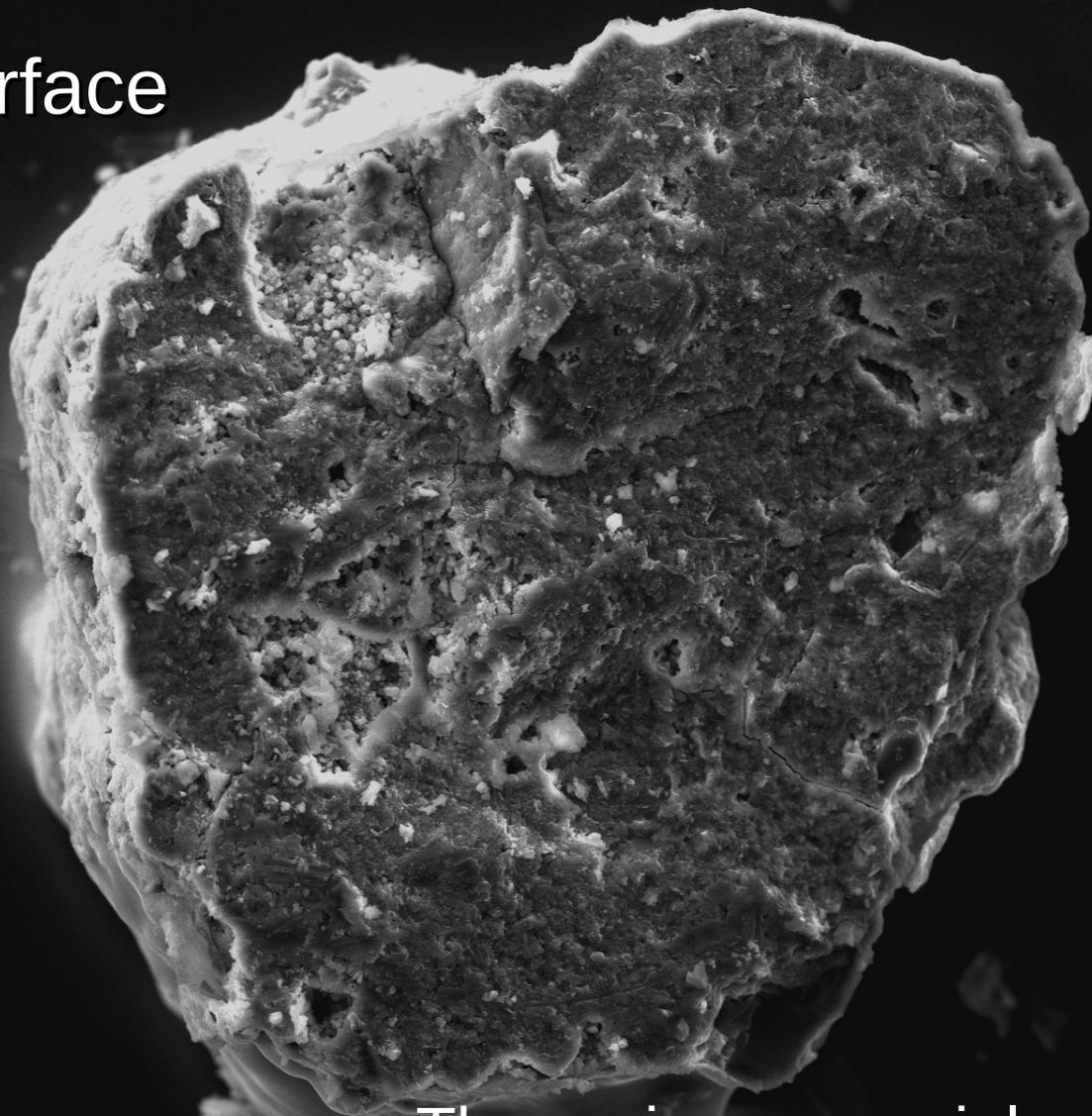
Ca-phosphate grains



100  $\mu\text{m}$

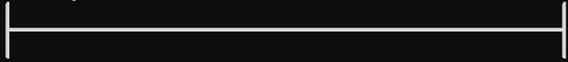
The grains are rounded and a few hundred  $\mu\text{m}$  in diameter.

SEM -  
broken surface

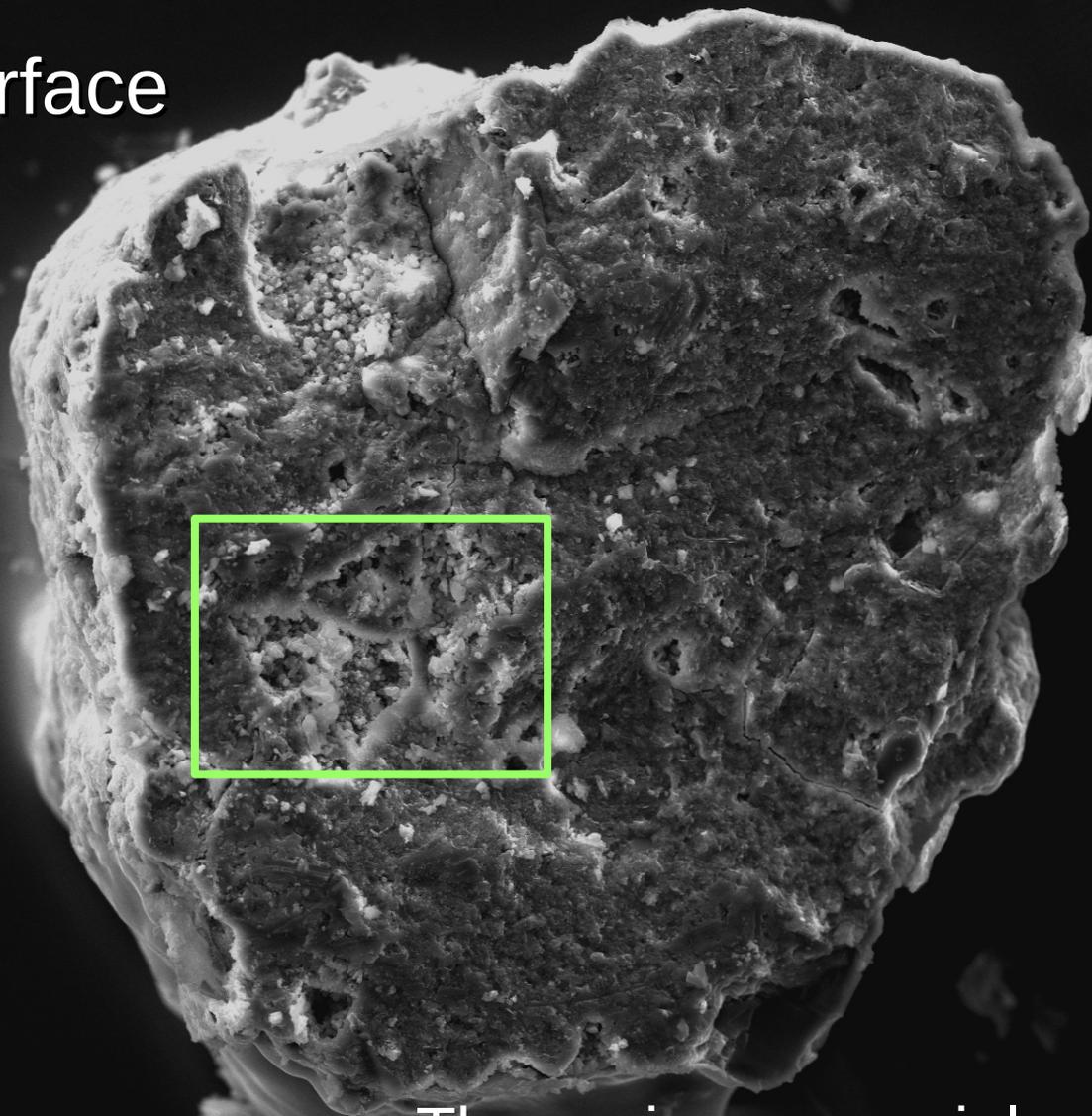


The grains are mainly composed of almost pure Ca-phosphate mineral apatite and are typically porous.

100  $\mu\text{m}$

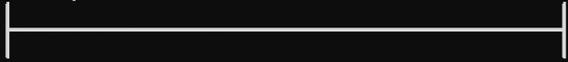


SEM -  
broken surface

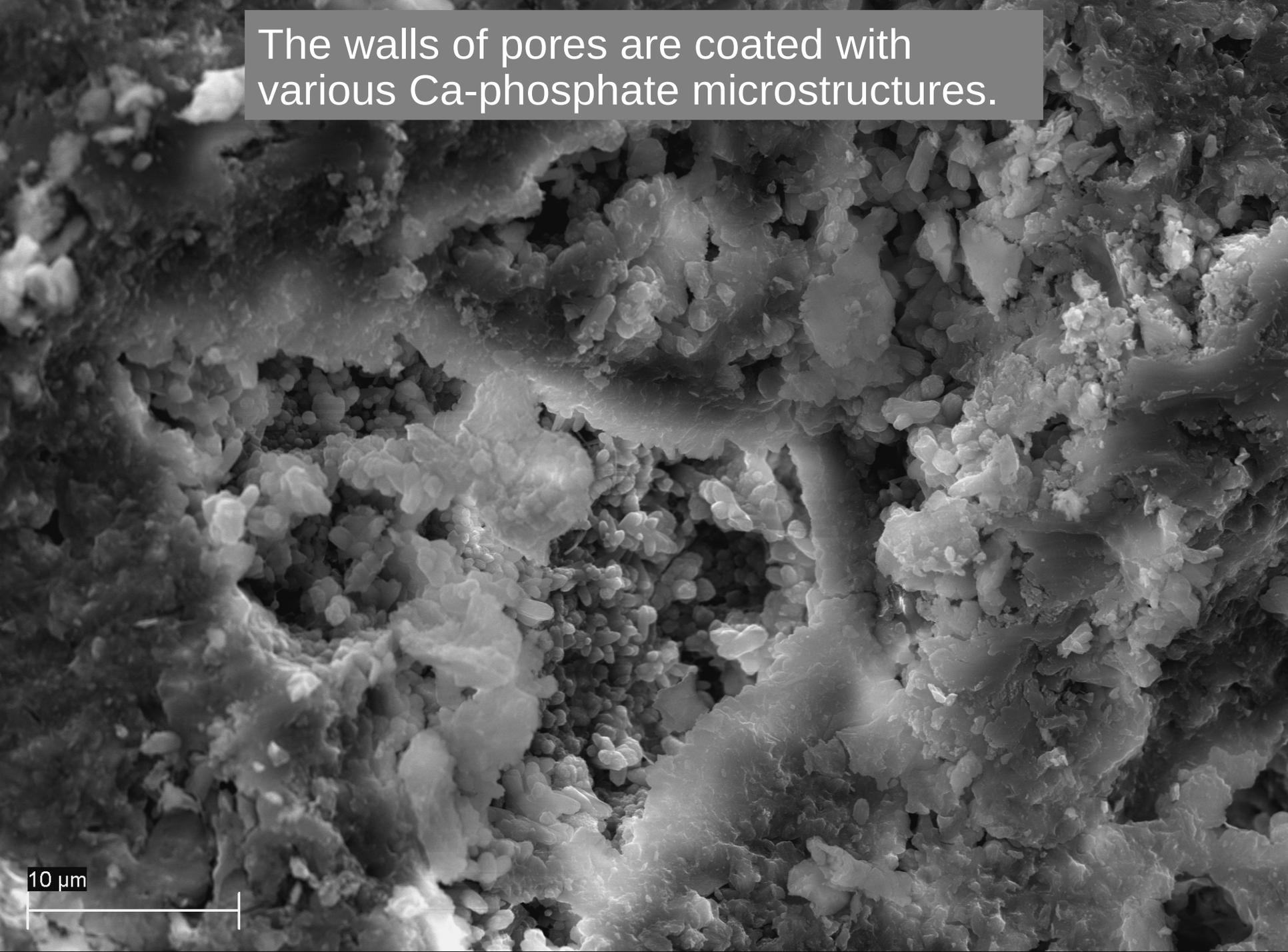


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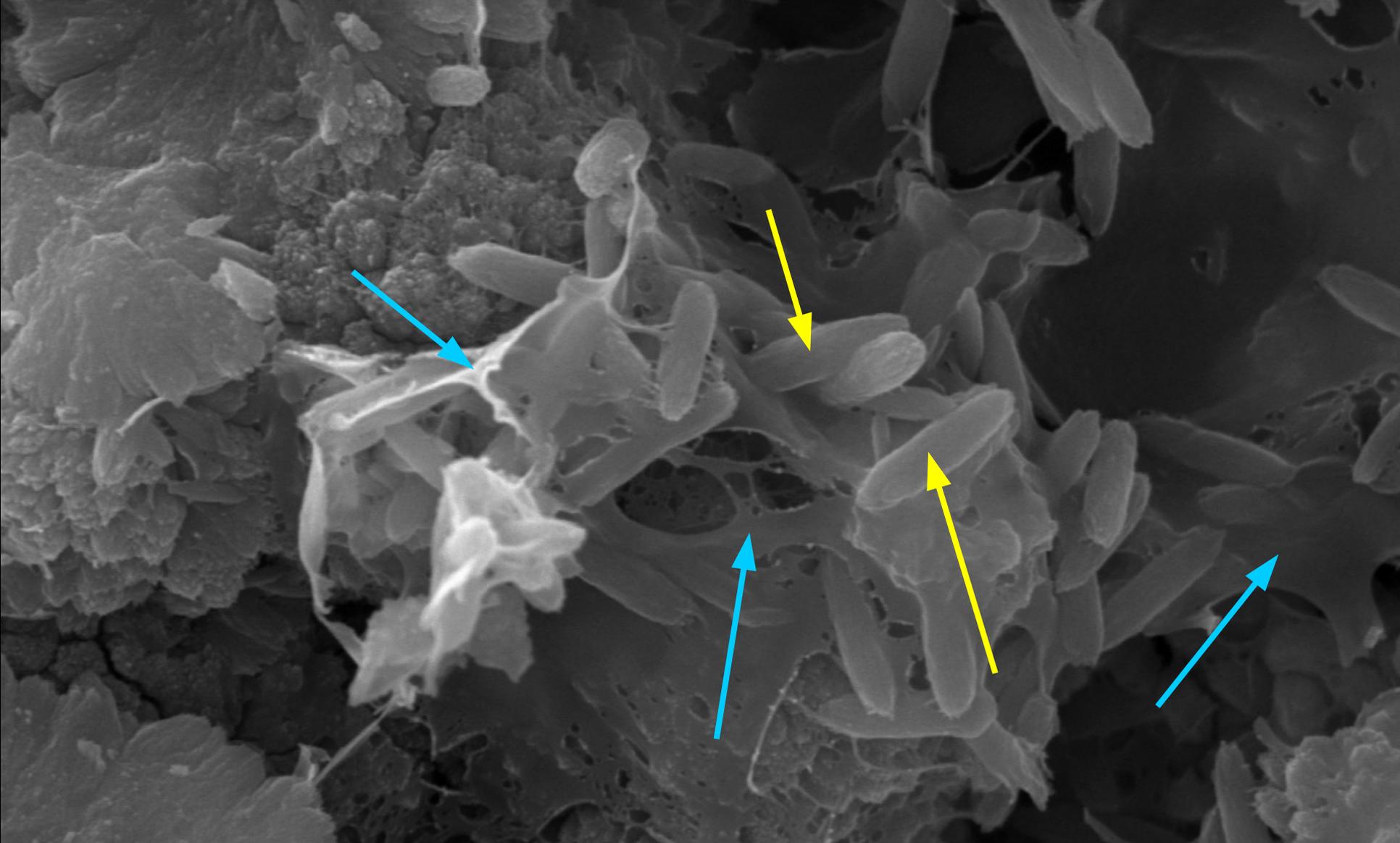
100  $\mu\text{m}$



The walls of pores are coated with various Ca-phosphate microstructures.



10  $\mu\text{m}$



2 μm

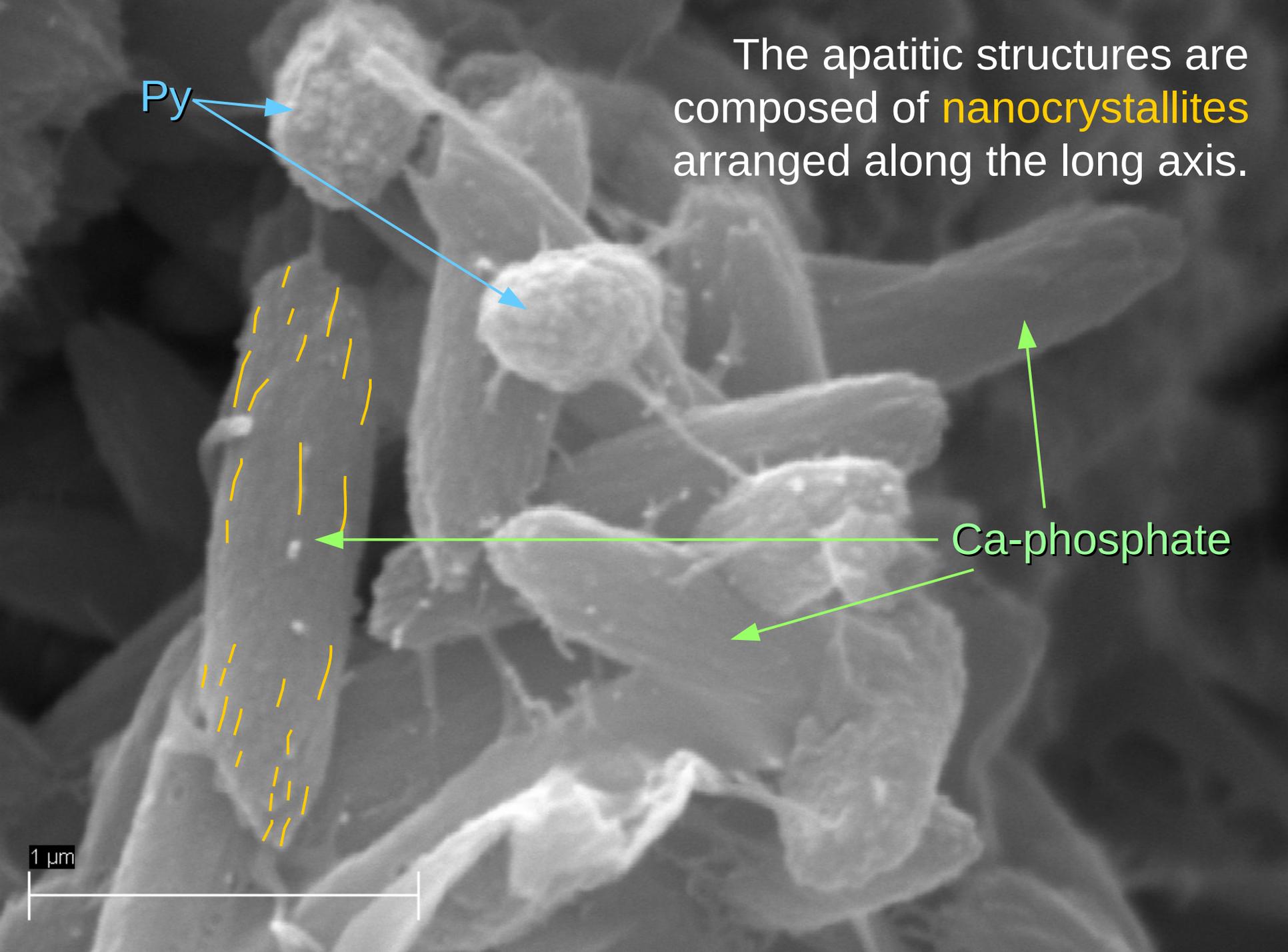
Many of the structures are **rod-shaped**. They co-occur with an **organic film-like substance**. The structures are predominantly Ca-phosphatic.

The apatitic structures are composed of **nanocrystallites** arranged along the long axis.

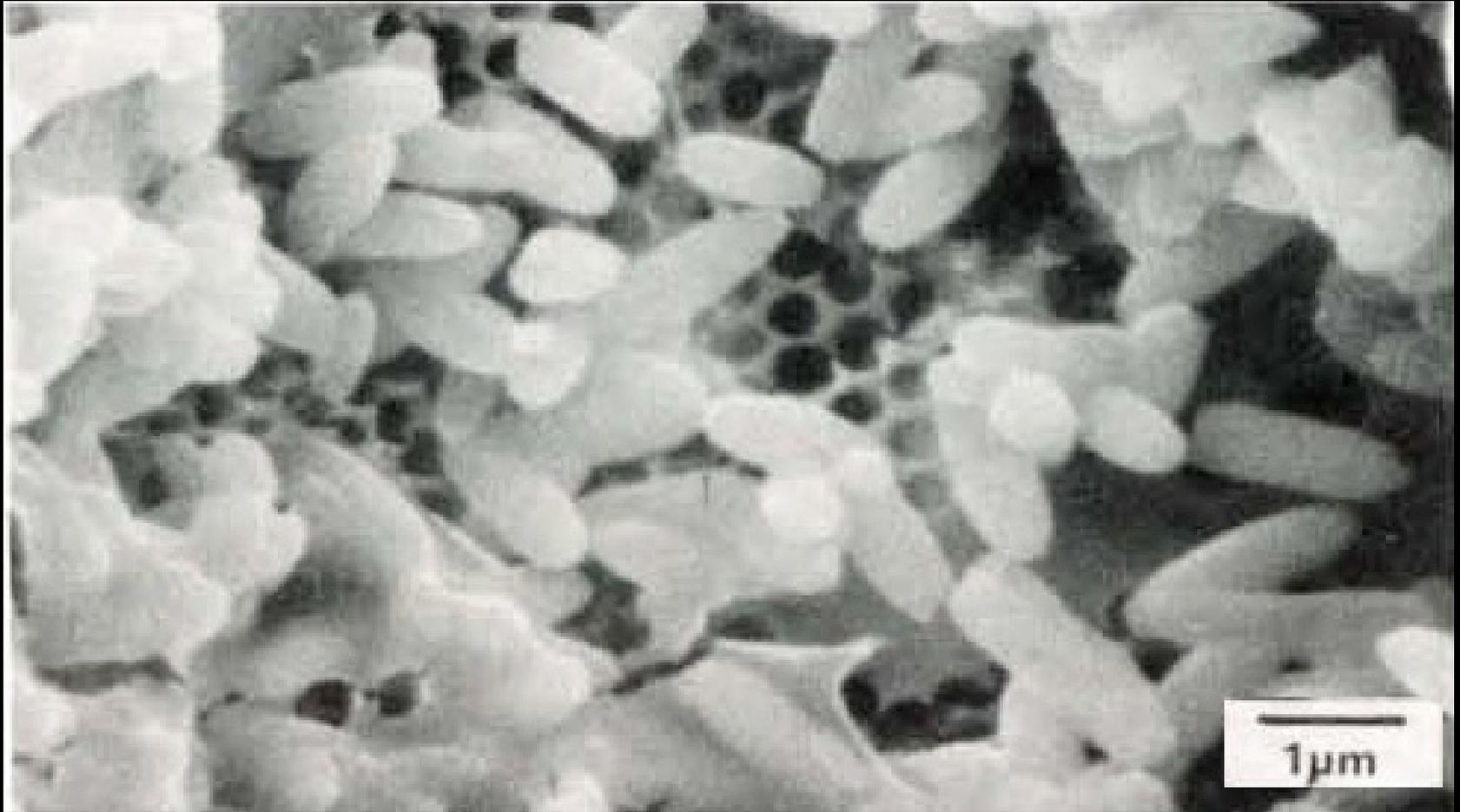
Py

Ca-phosphate

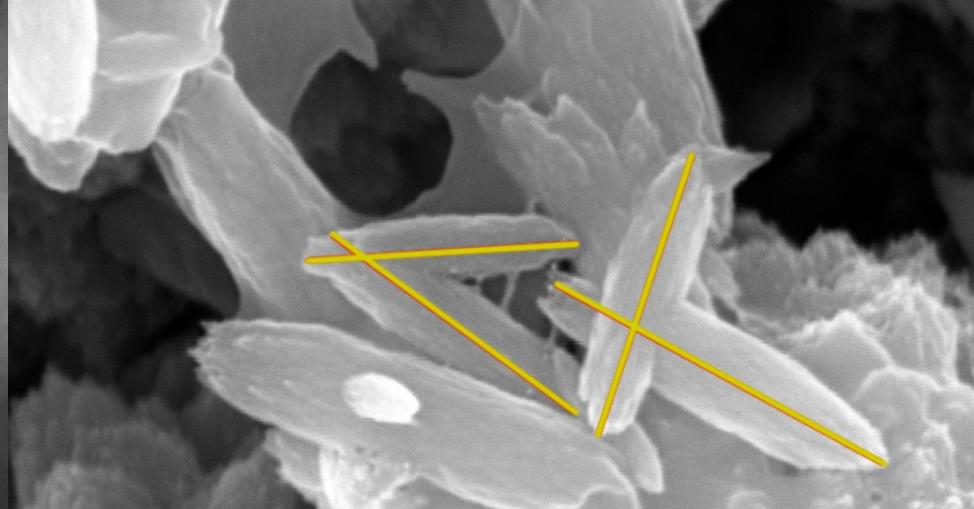
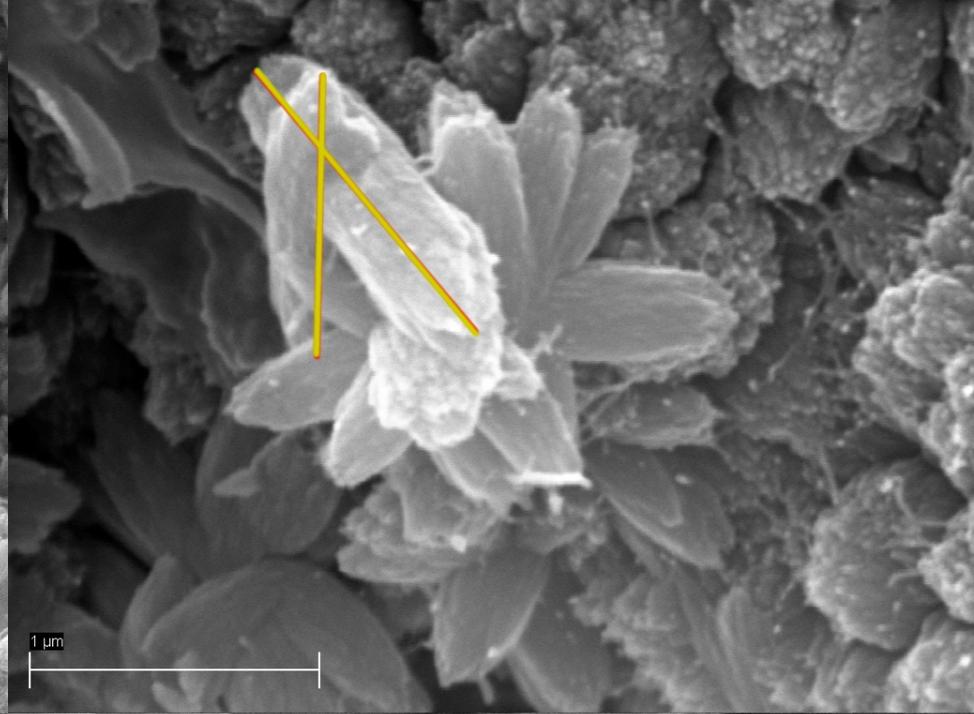
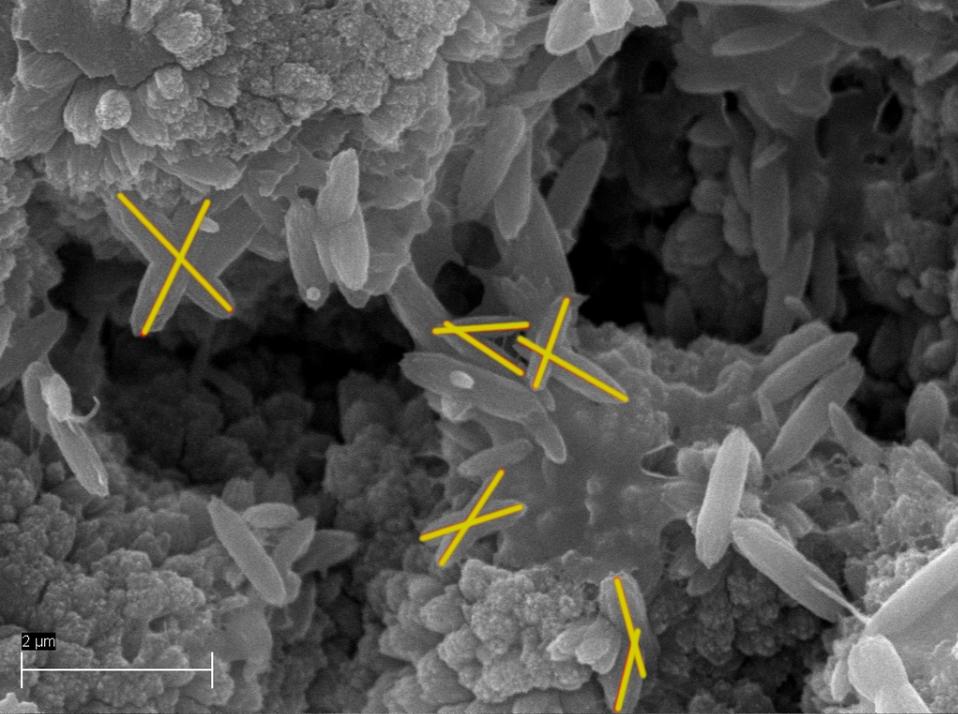
1  $\mu\text{m}$



# Interpretation: what are these structures?

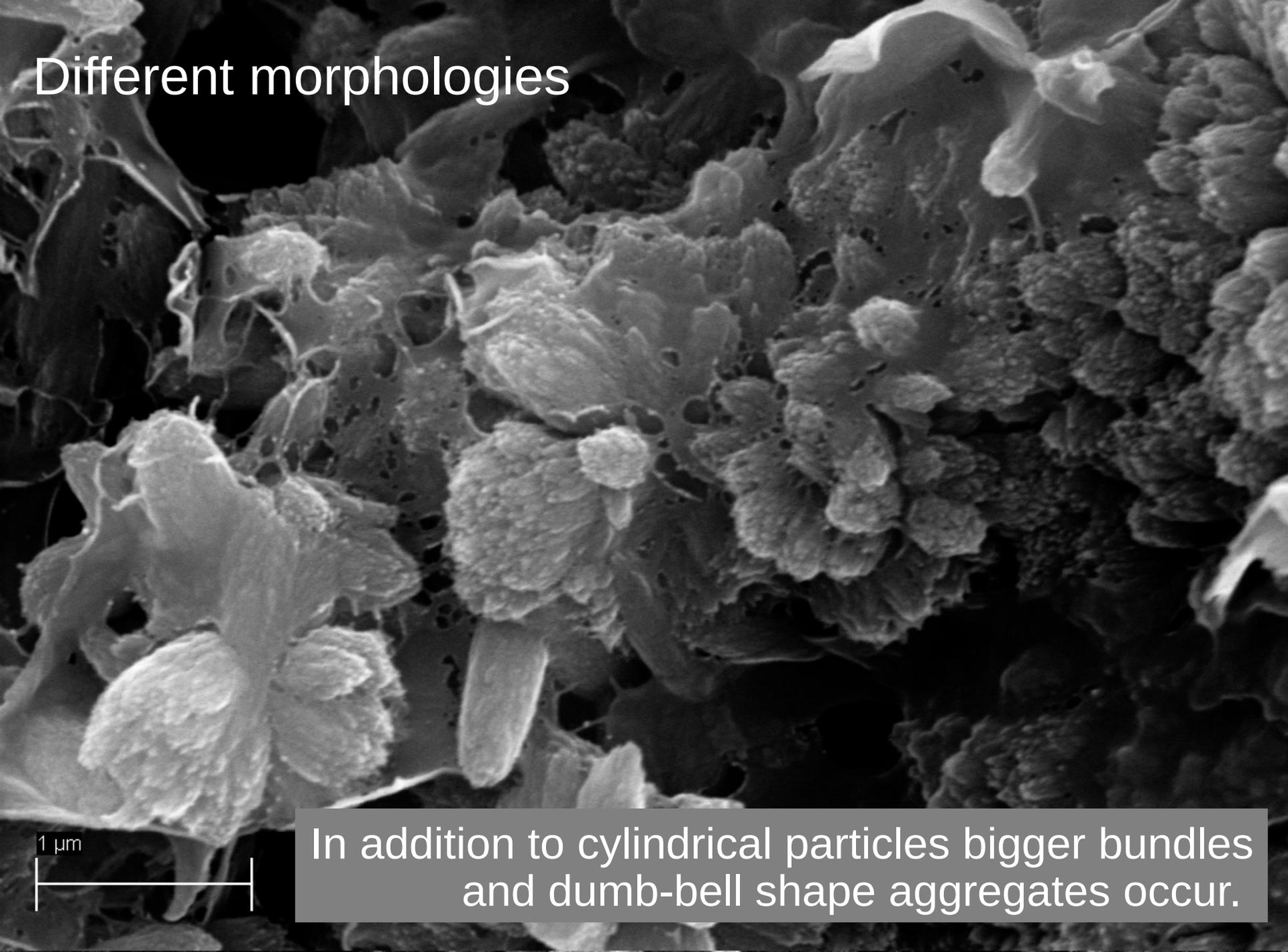


Similar apatite microstructures in phosphorites have been previously interpreted as fossilized microbes (e.g. Lamboy, 1990).



Many particles are intersecting and typically form intertwined aggregates at angles close to  $60^\circ$  and  $90^\circ$ .

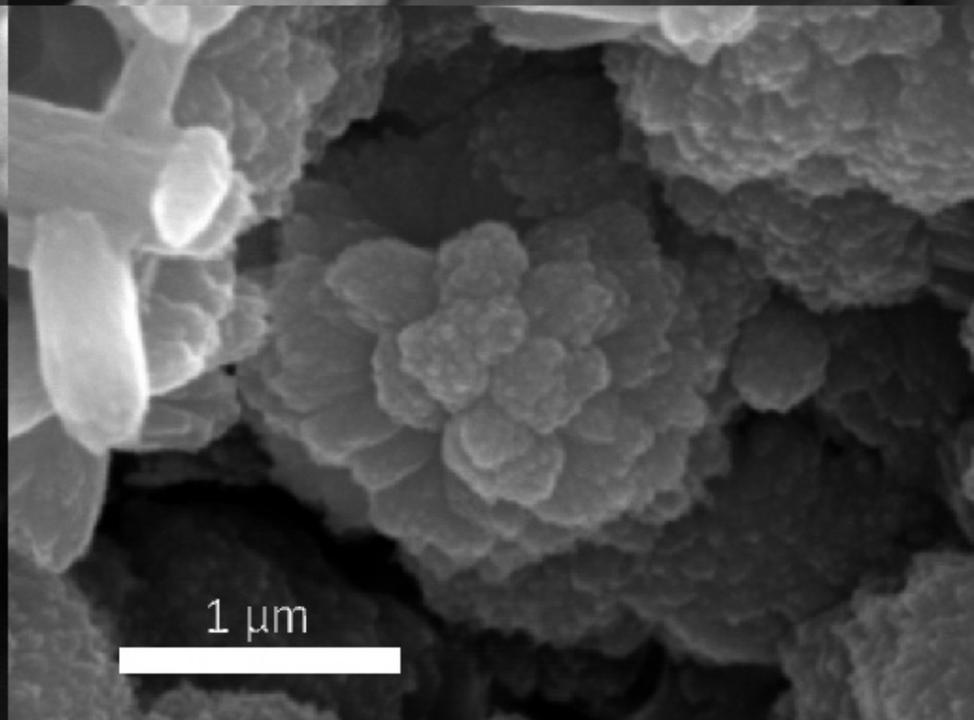
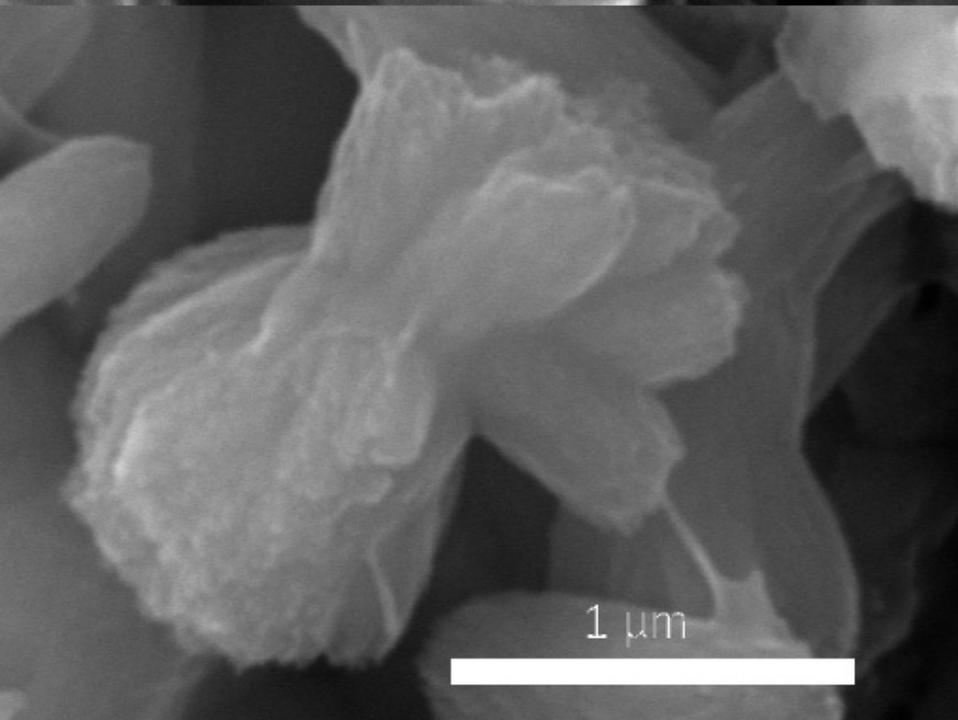
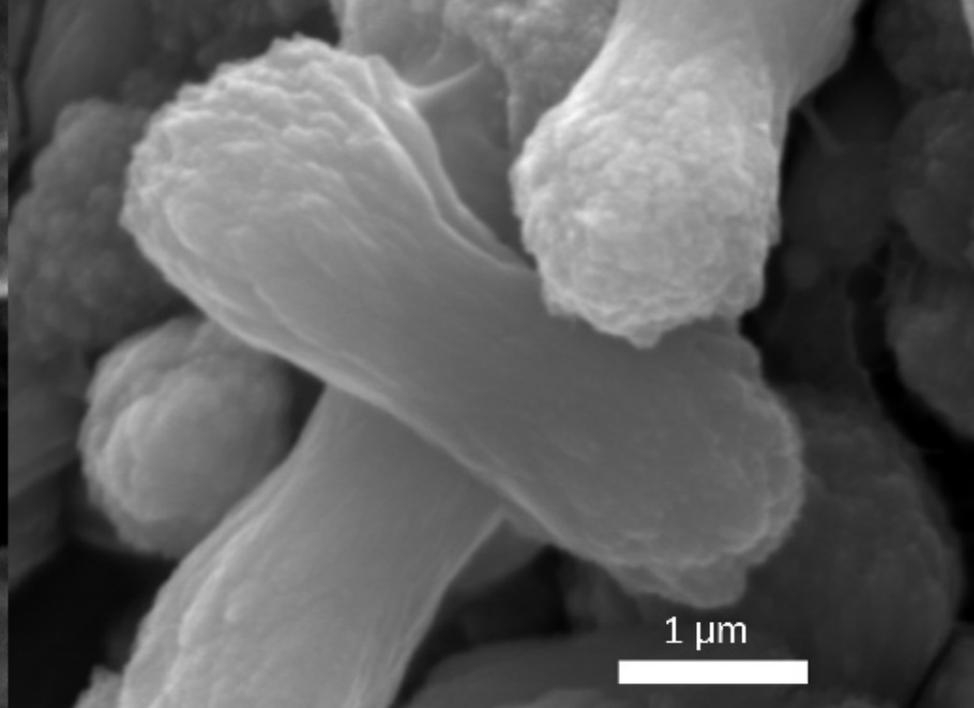
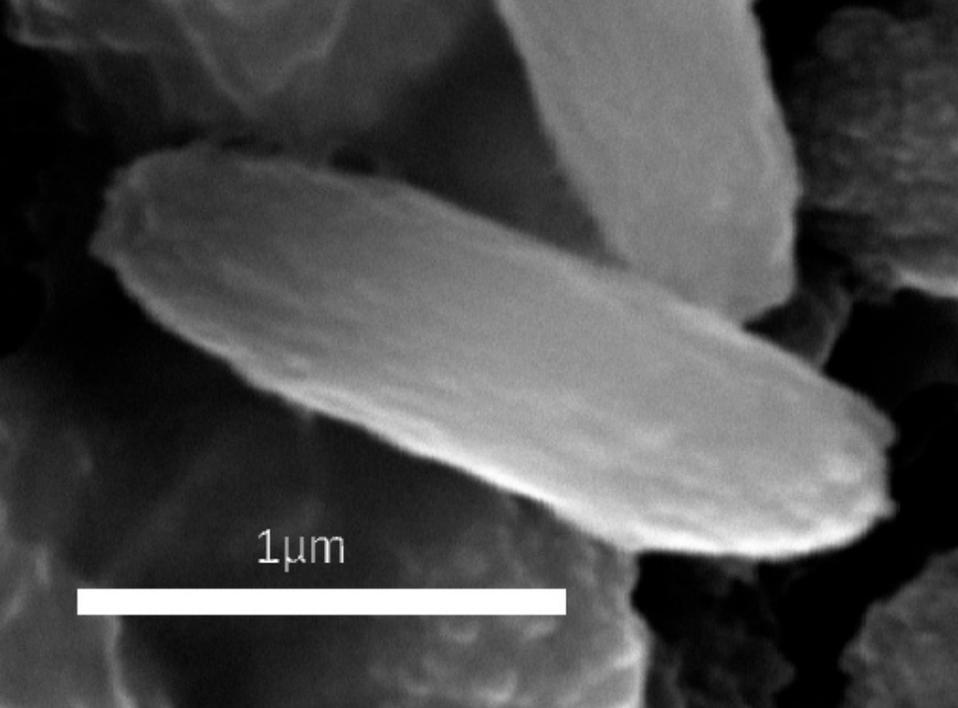
# Different morphologies

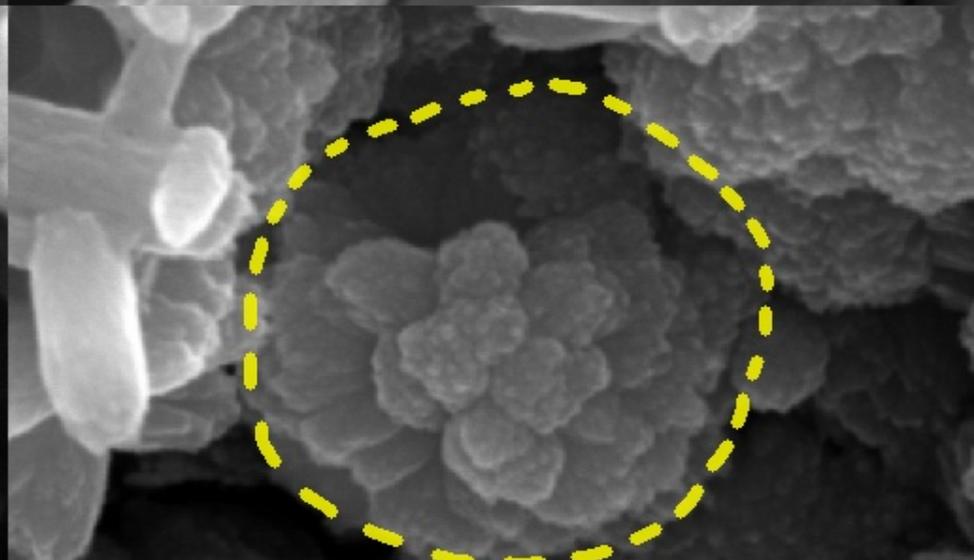
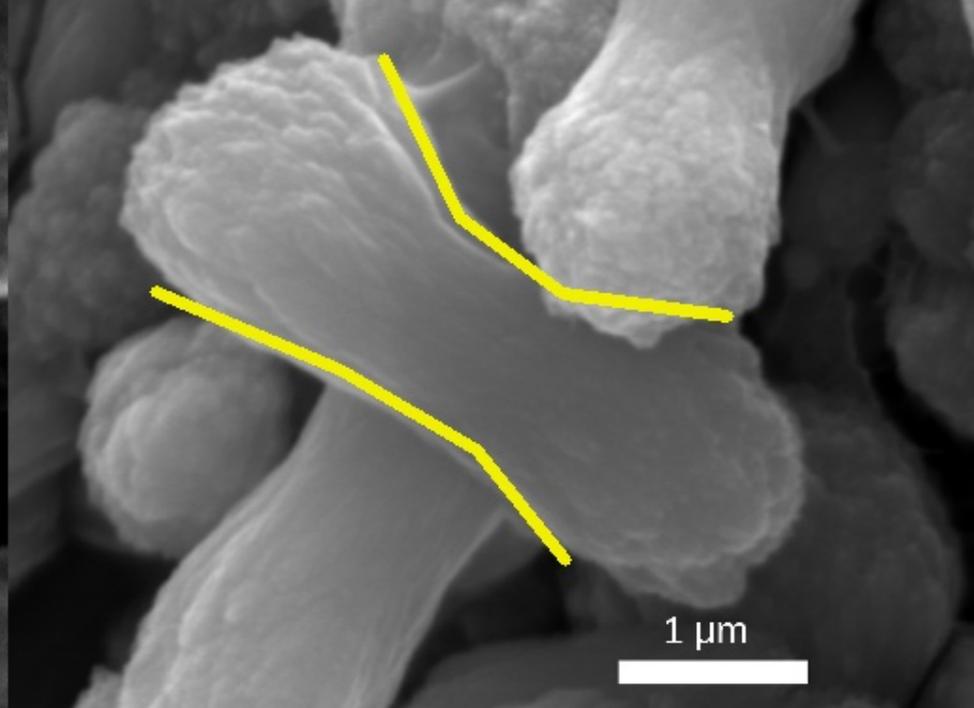
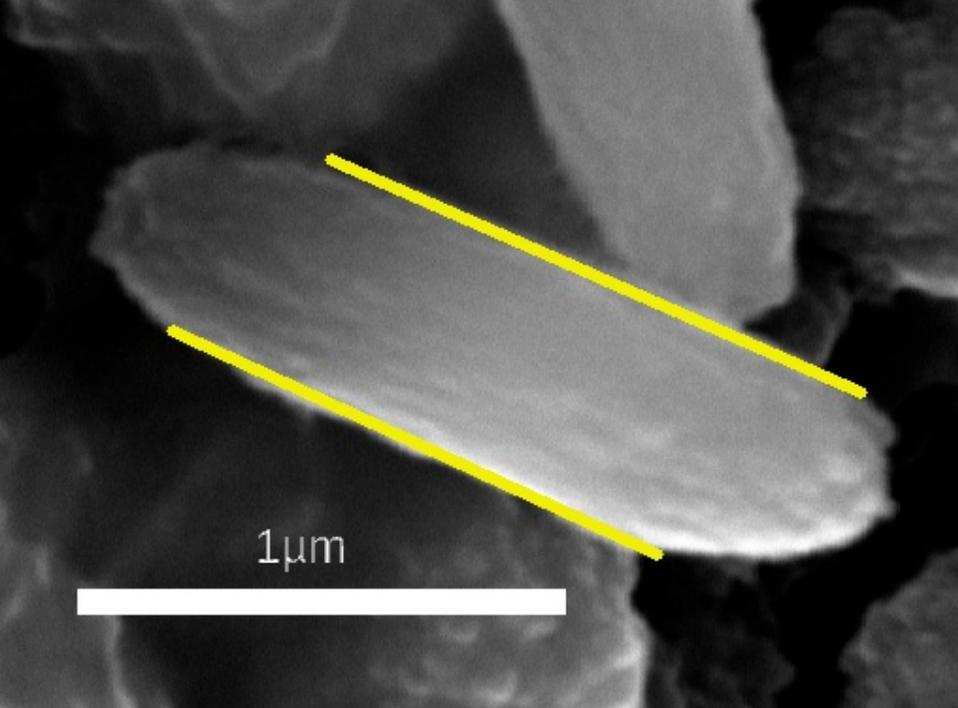


1  $\mu\text{m}$



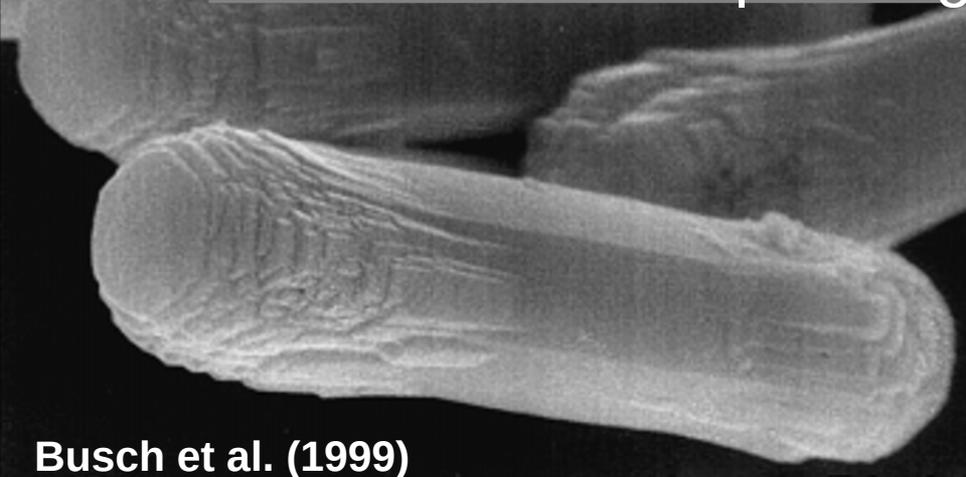
In addition to cylindrical particles bigger bundles and dumb-bell shape aggregates occur.





Cylindrical particles show a progression from rods to dumb-bells with widened ends to finally spherical forms.

Similar apatitic aggregates are found in artificial biomimetic fluorapatite–gelatine nanocomposites.



Busch et al. (1999)

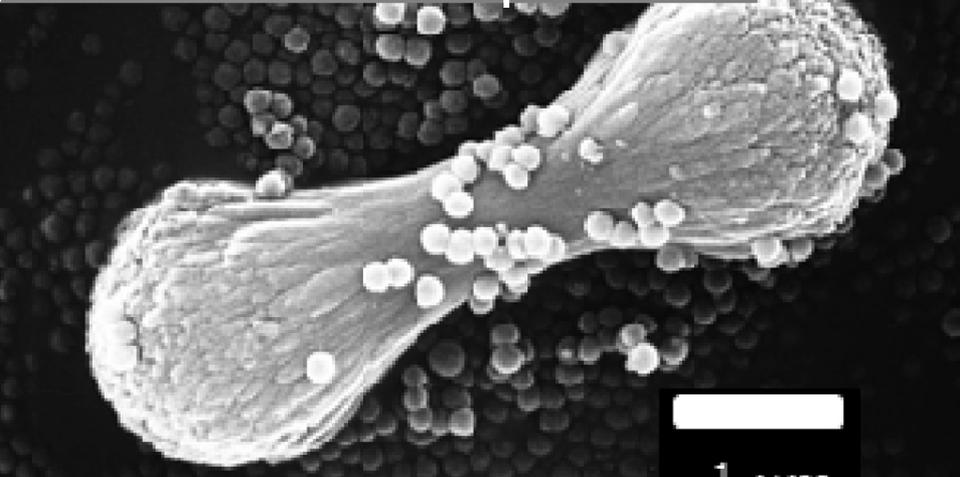
268496

20KV

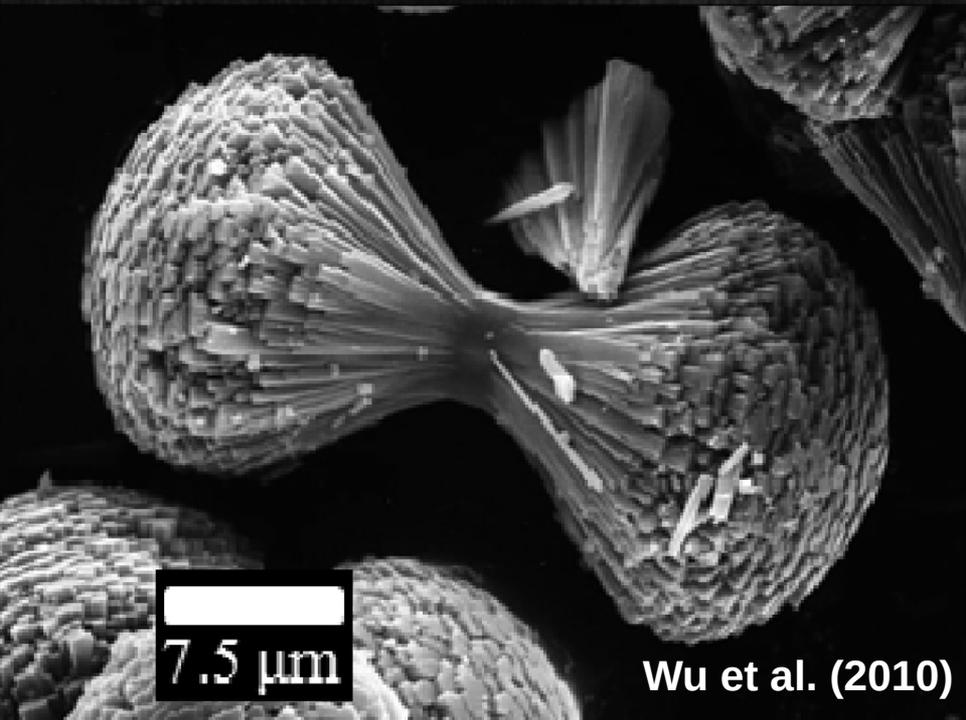
1  $\mu$ m F1 L

X7,500

14mm

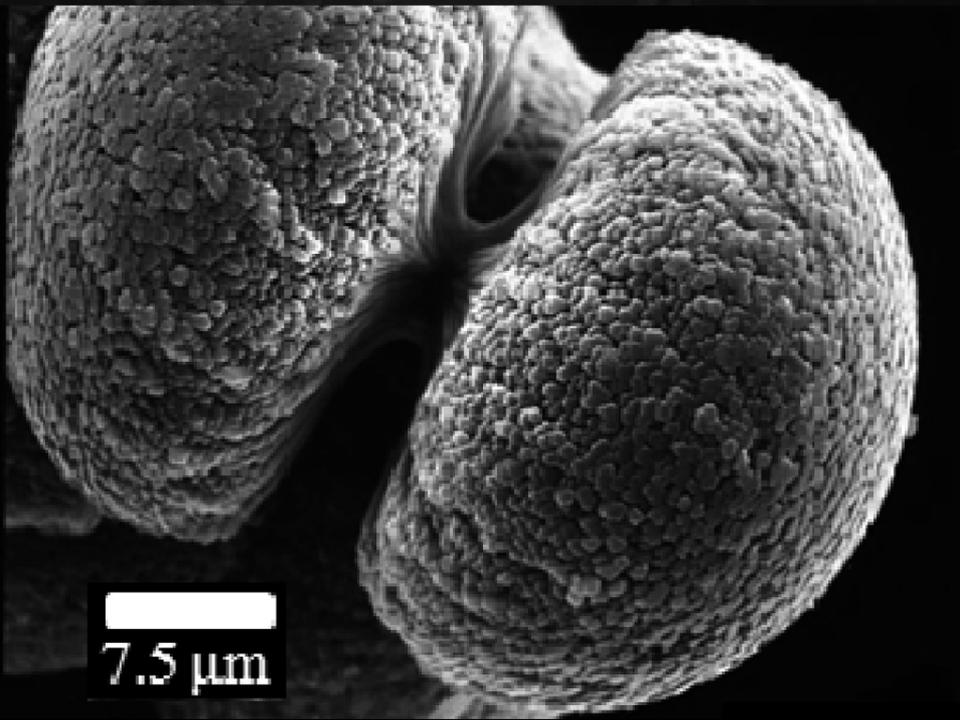


1  $\mu$ m



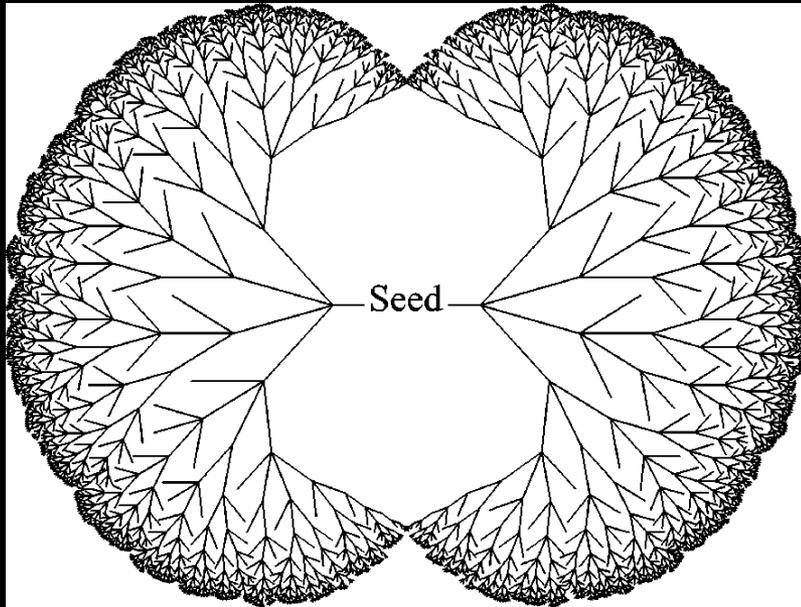
7.5  $\mu$ m

Wu et al. (2010)

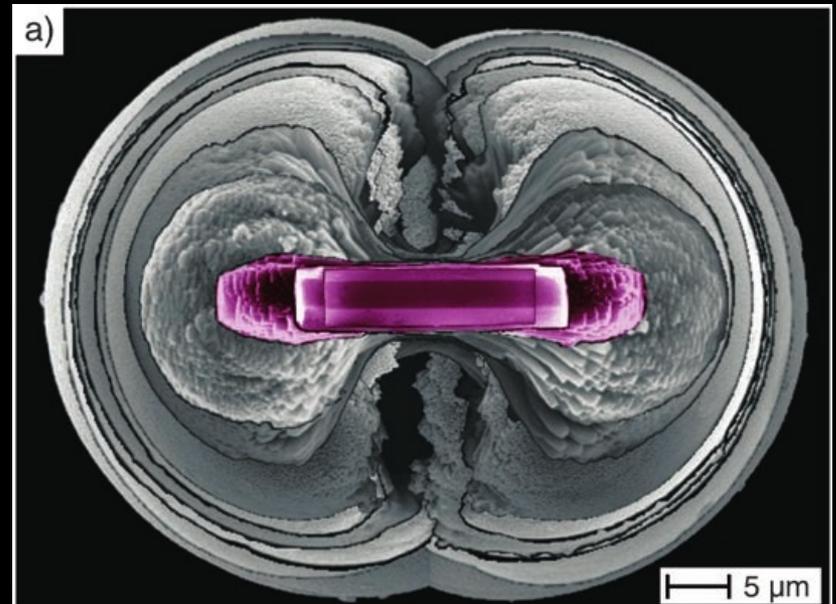


7.5  $\mu$ m

# Formation mechanism of biomimetic fluorapatite–gelatine nanocomposites



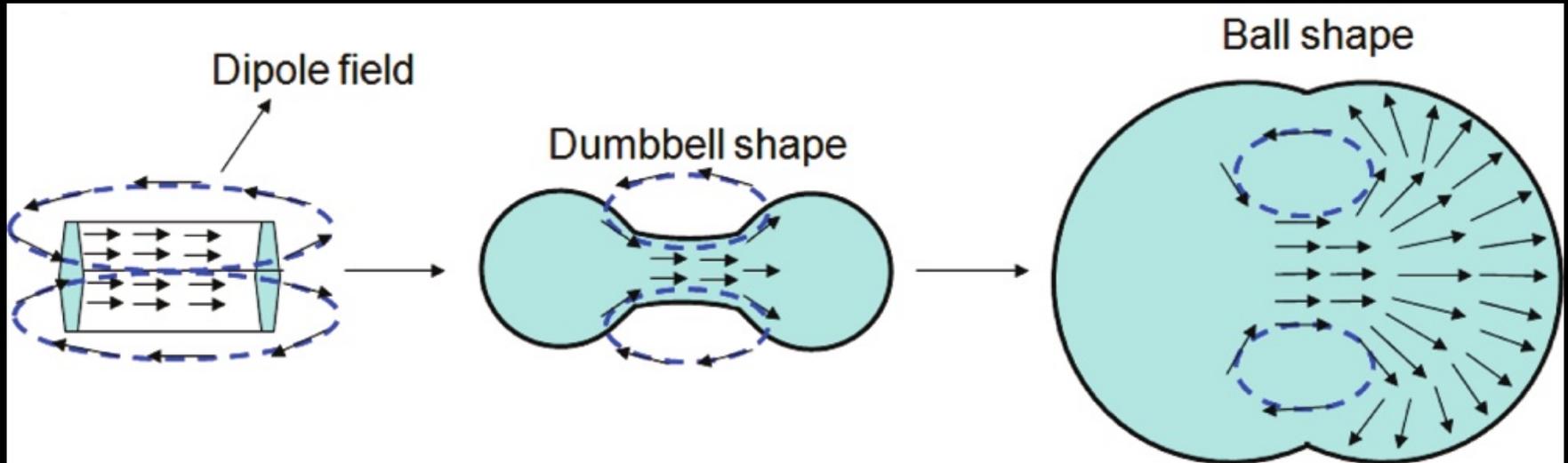
Busch et al. (1999)



Simon et al. (2006)

- Fractal growth of an initial seed crystal results in formation of a dumbbell-shape and eventually a closed sphere.

# Formation mechanism of biomimetic fluorapatite–gelatine nanocomposites: link to biomatrices



Modified, Wu et al. (2010)

- The growth is related to the arrangement and charge of organic molecules in the matrix of the structures.

# Conclusions

- The Namibian phosphatic grains contain conspicuous rod-shaped Ca-phosphate particles.

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- “Bacteriomorphic” apatitic microstructures thus need not be fossils.
- However, these structures are still formed in presence of biological matrices.
- It is still unclear what triggered Ca-phosphate nucleation. Do the microorganisms serve as nucleation templates? How do the phosphatic grains grow?

# Acknowledgements:



- RGNO instructors and students
- RV Mirabilis crew and NatMIRC
- UNAM Sam Nujoma Campus
- Agouron Institute



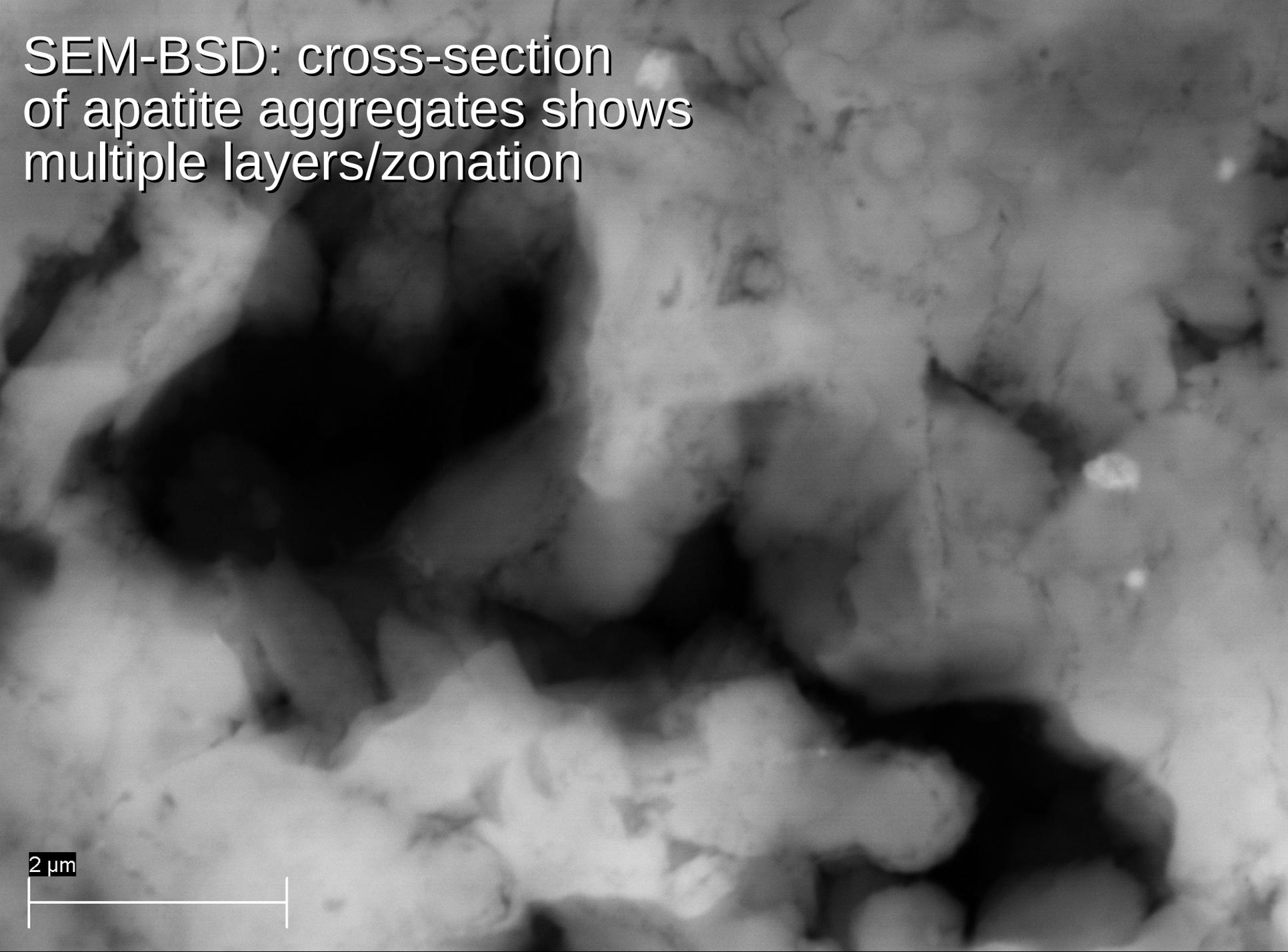
AGOURON  
INSTITUTE



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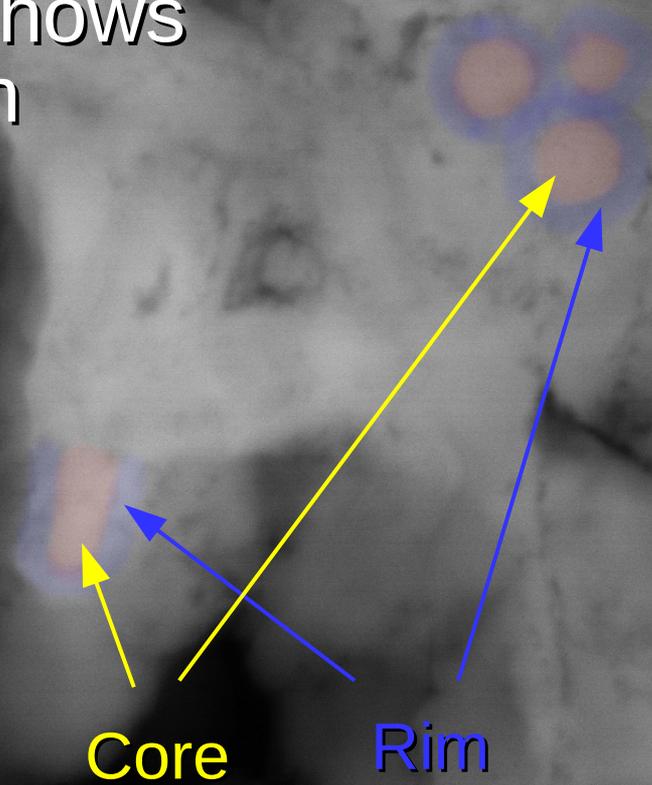
- The Namibian phosphatic grains contain conspicuous cylindrical Ca-phosphate particles.
- These occur in forms from cylindrical to bulged dumbbell-like particles representing stages of growth of apatite structures similar to biomimetic fluorapatite–gelatine nanocomposites.
- “Bacteriomorphic” apatitic microstructures thus need not be fossils.
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SEM-BSD: cross-section  
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2  $\mu\text{m}$

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2  $\mu\text{m}$



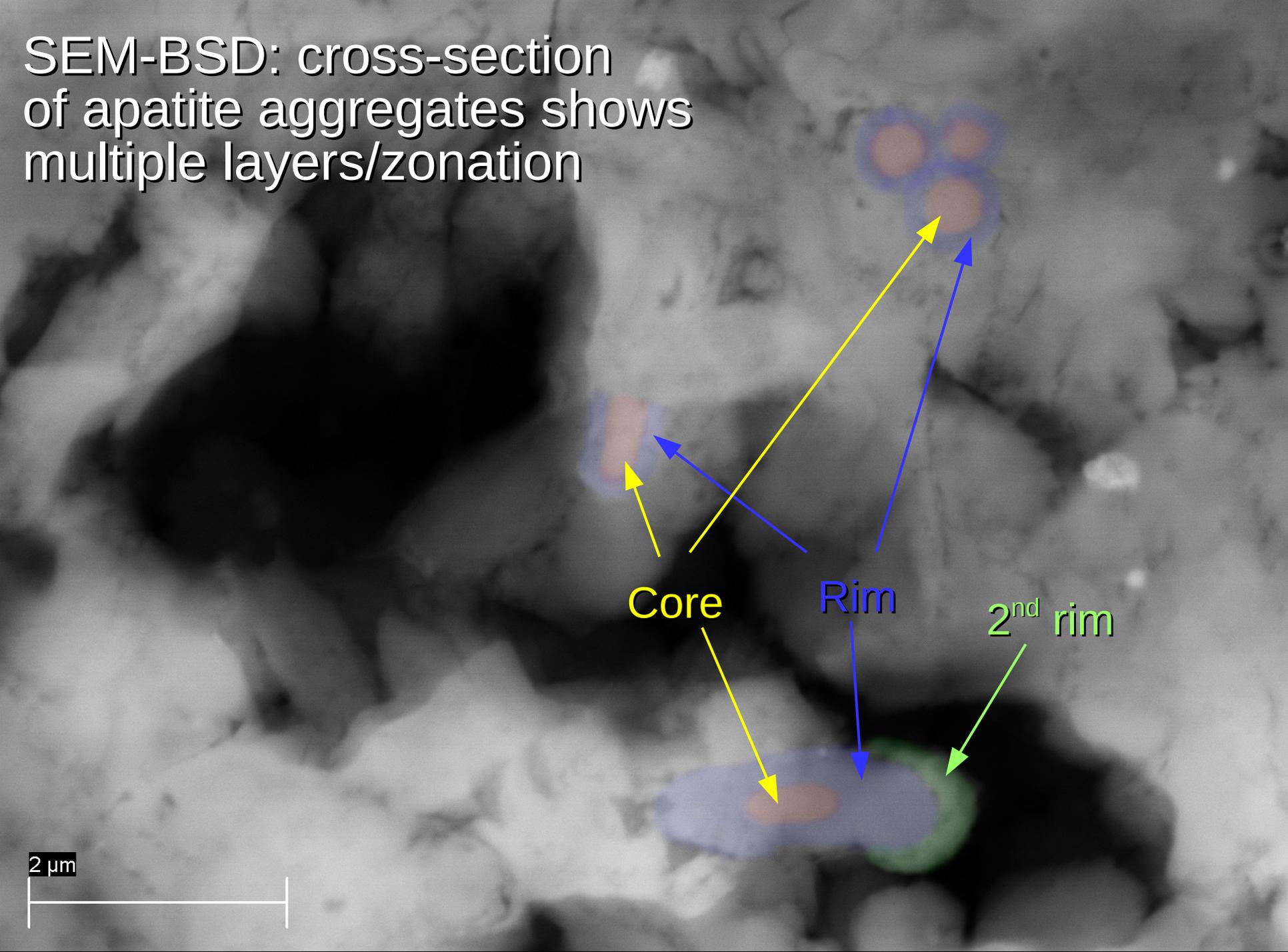
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2  $\mu\text{m}$

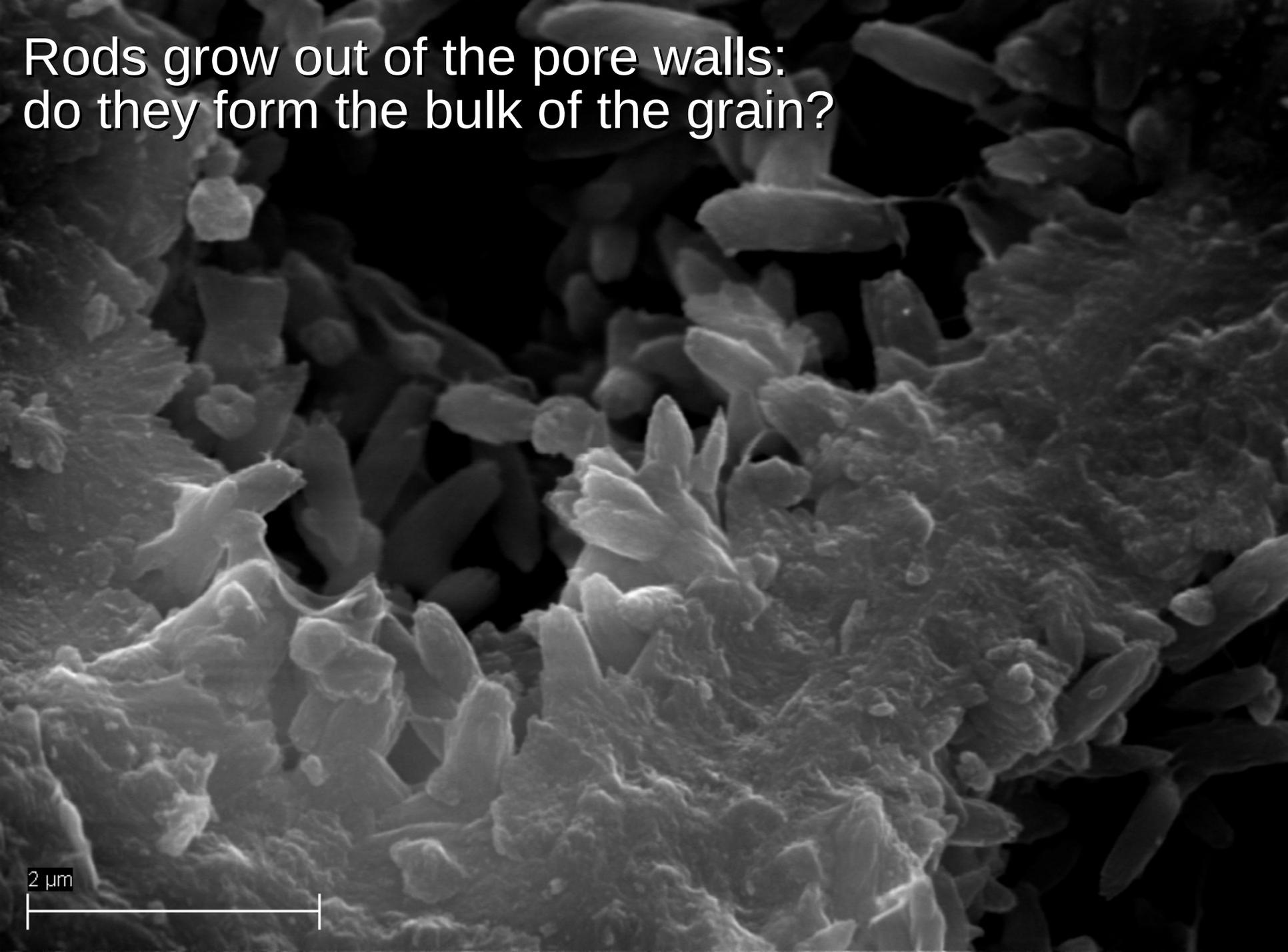
Core

Rim

2<sup>nd</sup> rim



Rods grow out of the pore walls:  
do they form the bulk of the grain?



2  $\mu\text{m}$

