

# Modeling the Influence of Microorganisms on the Formation of Banded Manganese Dendrites

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# Mineral dendrites



Manganese and ferric dendrites on a limestone



Manganese dendrites



Mineral dendrites in Agate



Manganese dendrites on quartz basis

What causes such diversity of shapes?

What the shapes of dendrites can tell us about the physical conditions in which they grew?

# Mineral dendrites



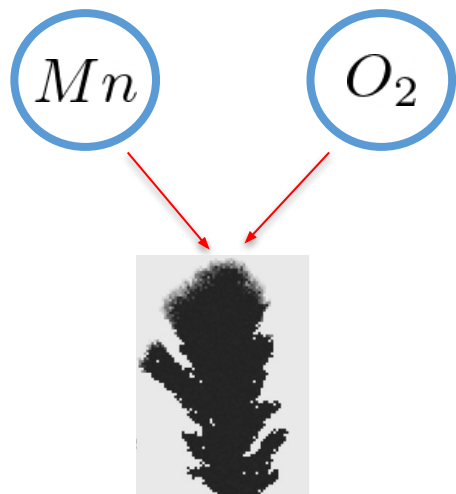
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What the shapes of dendrites can tell us about the physical conditions in which they grew?

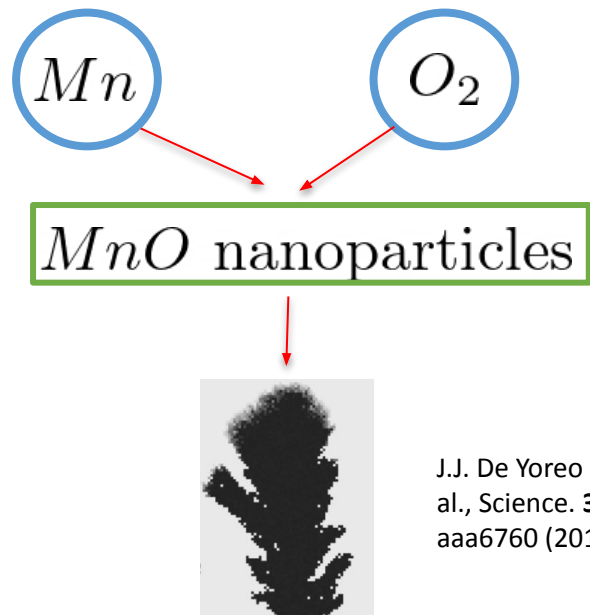
# Crystallization pathways

Mineral dendrite growth is a **reaction-diffusion system**. Includes transport of reactants as well as chemical reactions. Two reaction mechanisms:

- Directly on the surface



- By particle attachment

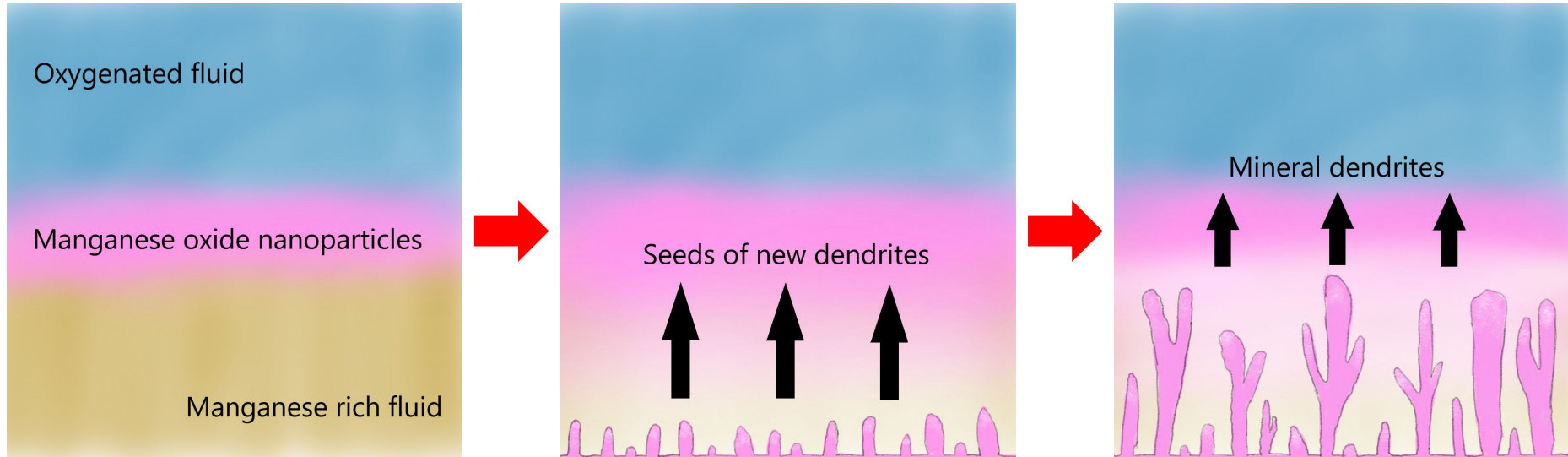


J.J. De Yoreo et al., Science. **349**: aaa6760 (2015)



# Particle attachment model

The model assumes an initial growth of small nanoparticles which then aggregate into branched structures.



# Numerical model

Reaction-diffusion equations for concentrations:

- oxygen

$$\frac{\partial}{\partial t} c_{O_2} = D_{O_2} \nabla^2 c_{O_2} - k c_{O_2} c_{Mn}$$

- Mn ions

$$\frac{\partial}{\partial t} c_{Mn} = D_{Mn} \nabla^2 c_{Mn} - k c_{O_2} c_{Mn}$$

- manganese oxide particles

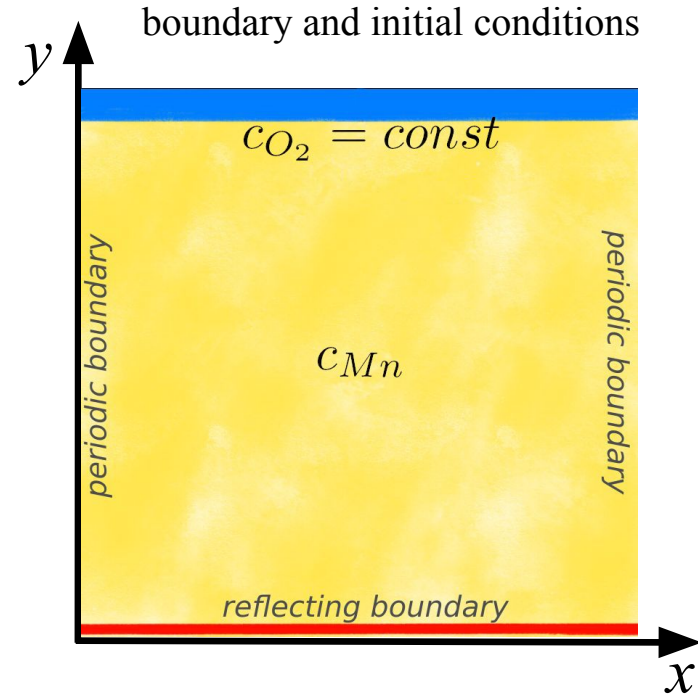
$$\frac{\partial}{\partial t} c_{MnO} = D_{MnO} \nabla^2 c_{MnO} + v k c_{O_2} c_{Mn} - \lambda^* c_{MnO}$$

- dendrite growth  
(on the dendrite surface)

$$\frac{\partial}{\partial t} v_p = \lambda^* V_m c_{MnO} \quad + \text{noise}$$

volume fraction

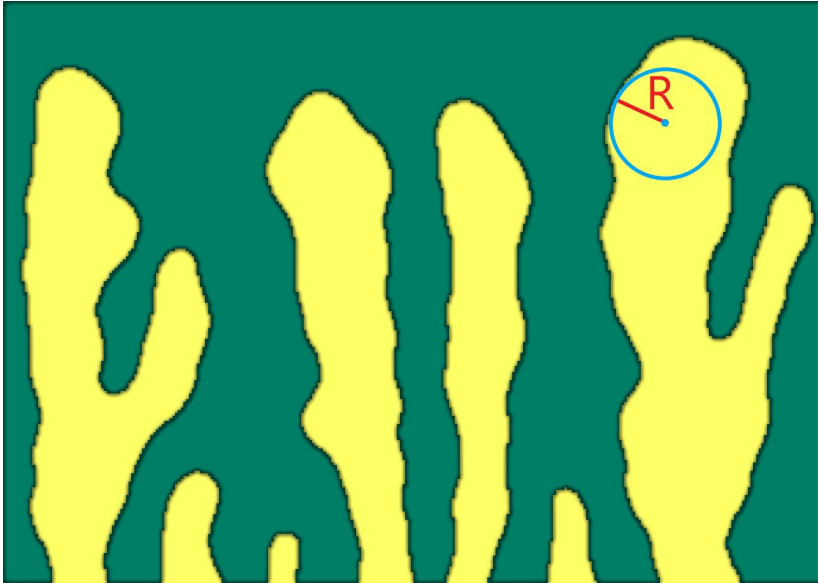
molar volume



modeled by the lattice-Boltzmann method

# Surface Energy

- Nucleation along the perimeter, when a fixed concentration threshold is exceeded
- The growth rate depends on the local curvature:



Change of saturation concentration:

$$\delta c_{sat} \propto \frac{l_c}{R}$$

Diffusive length

$$l_d = D/U$$



Ratio of  
diffusion  
constant and  
average growth  
velocity

Capillary length

$$l_c = \nu \frac{\sigma v_m}{kT}$$

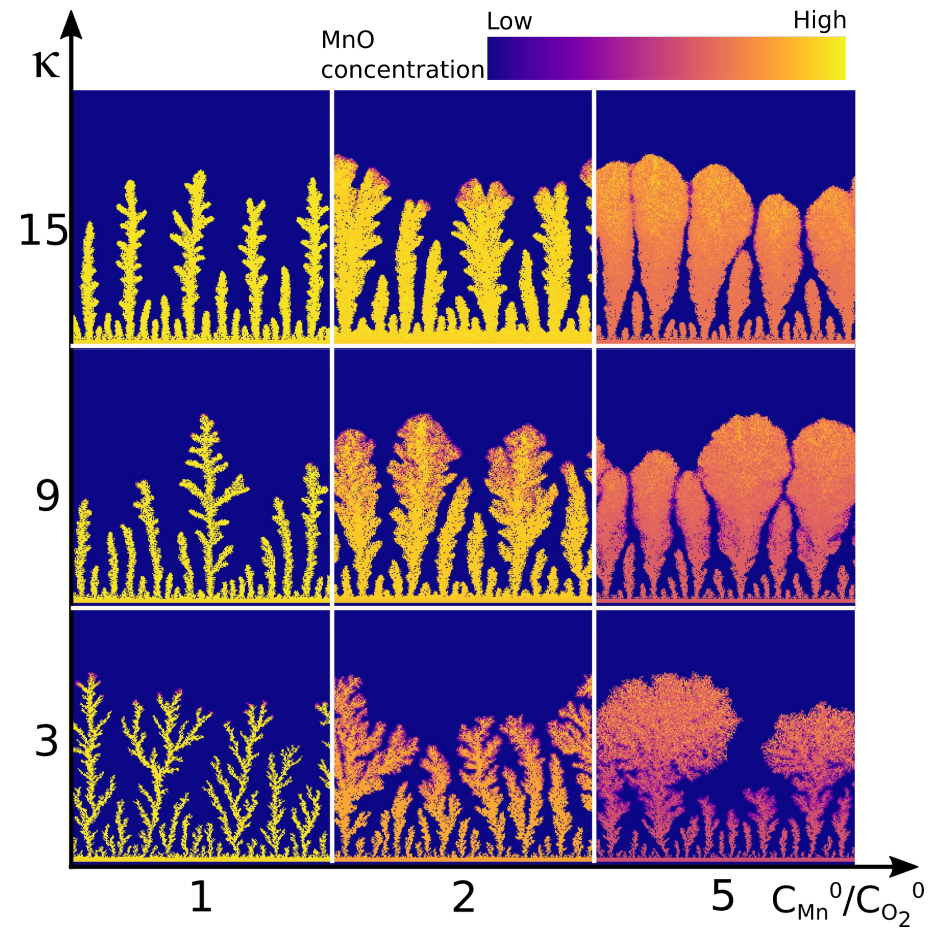


$\sigma$  - surface energy  
density  
 $\nu$  - acid capacity  
number

$$\kappa = l_c/l_d$$

Reactive rate is  $\kappa$  dependent

# Phase diagram



- The shape of the dendrites helps to find the physico-chemical conditions prevailing during growth
- With increasing surface energy, dendrites are more compact and have fewer branches
- Increasing the ratio of initial concentrations of manganese to oxygen makes the dendrites thicker and more packed
- Increasing this ratio increases porosity of the dendrites

$\kappa$  – surface energy parameter,  
 $C_{O_2}^0$ ,  $C_{Mn}^0$  - initial concentrations

# Direct crystallization model

Assumes formation of manganese oxides directly on the surface of the dendrites, which then elongate

- oxygen

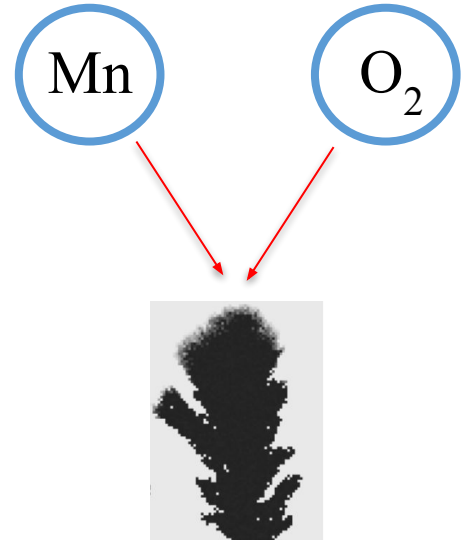
$$\frac{\partial}{\partial t} c_{\text{O}_2} = D_{\text{O}_2} \nabla^2 c_{\text{O}_2} - \lambda^{\text{a}} c_{\text{O}_2} c_{\text{Mn}}$$

- Mn ions

$$\frac{\partial}{\partial t} c_{\text{Mn}} = D_{\text{Mn}} \nabla^2 c_{\text{Mn}} - \lambda^{\text{a}} c_{\text{O}_2} c_{\text{Mn}}$$

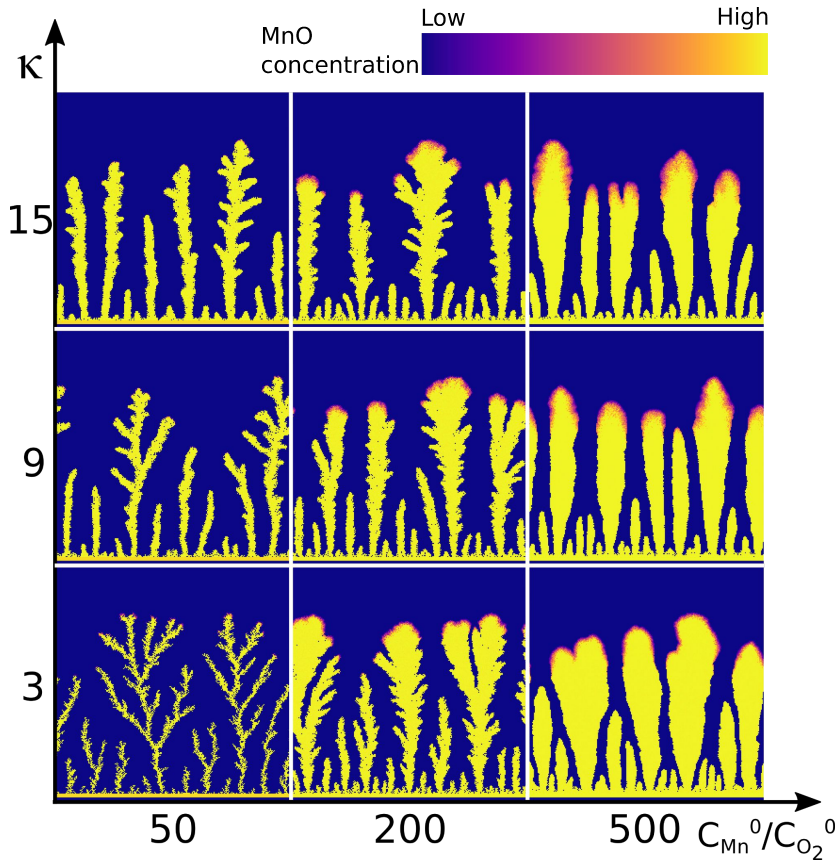
- dendrite growth  $\frac{\partial}{\partial t} v_p = \lambda^* V_m c_{\text{O}_2} c_{\text{Mn}}$

+ noise



modeled by the lattice-Boltzmann method

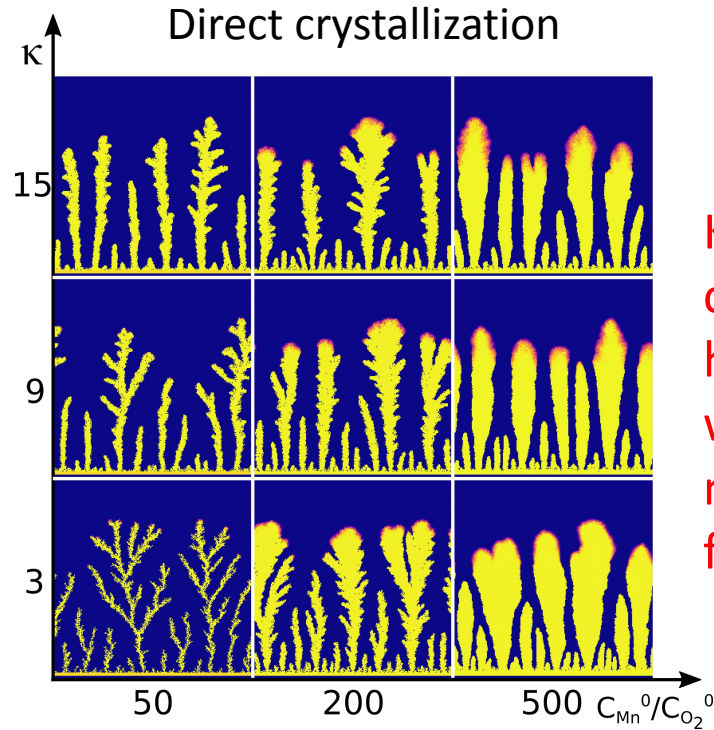
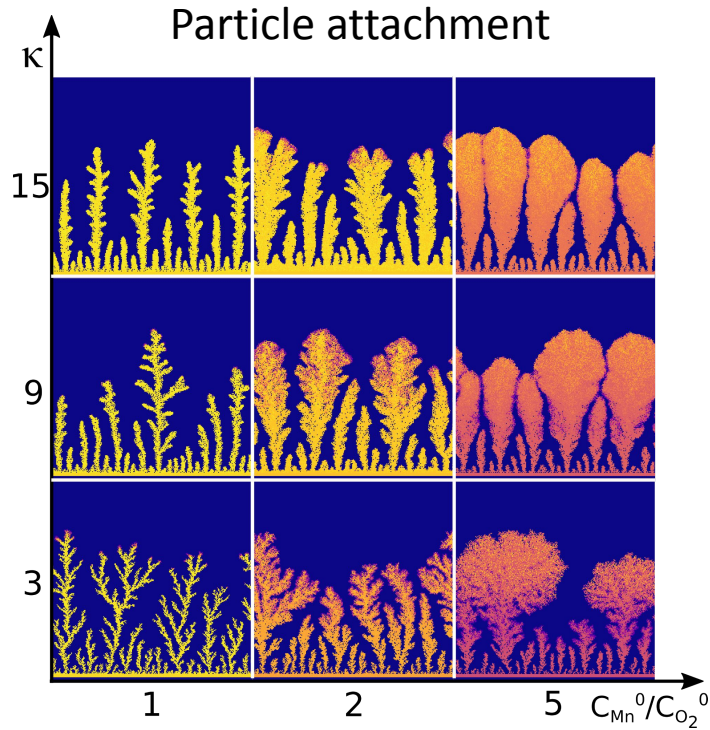
# Phase diagram



- With increasing surface energy, dendrites are more compact and have fewer branches
- Increasing the ratio of initial concentrations of manganese to oxygen makes the dendrites thicker and more packed
- Increasing this ratio does not increase porosity of the dendrites
- The ratio of concentrations is two orders of magnitude higher than in particle attachment model

$K$  – surface energy parameter  
 $C_{O_2}^0, C_{Mn}^0$  – initial concentrations

# Phase diagrams



Knowledge of the concentration ratio helps to determine which mechanism may be responsible for dendrite growth



$K$  – surface energy parameter,  
 $C_{O_2}^0, C_{Mn}^0$  – initial concentrations

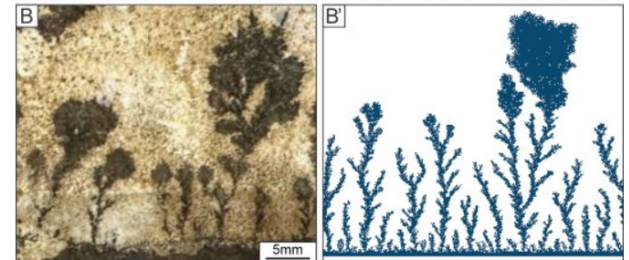
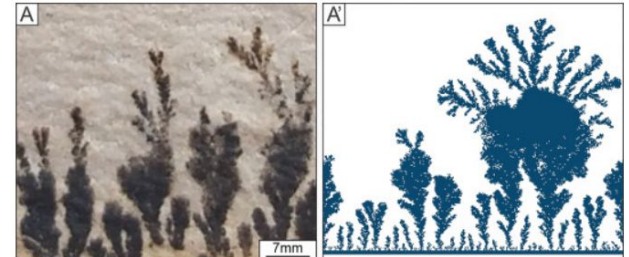
# Morphological transitions



Ng & Teh, *Geol. Soc. Mal. Bull* 55,73, 2009



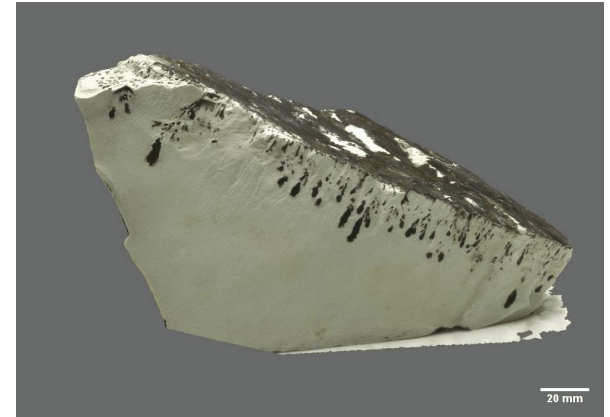
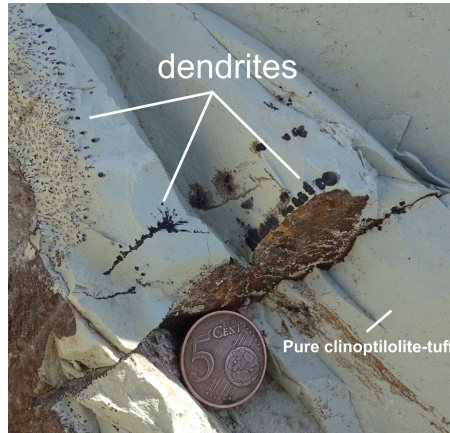
- change in the pattern of manganese dendrites during growth can be linked to the change of the Mn concentration in the infiltrating fluid



# Three-dimensional dendrites in clinoptilolites

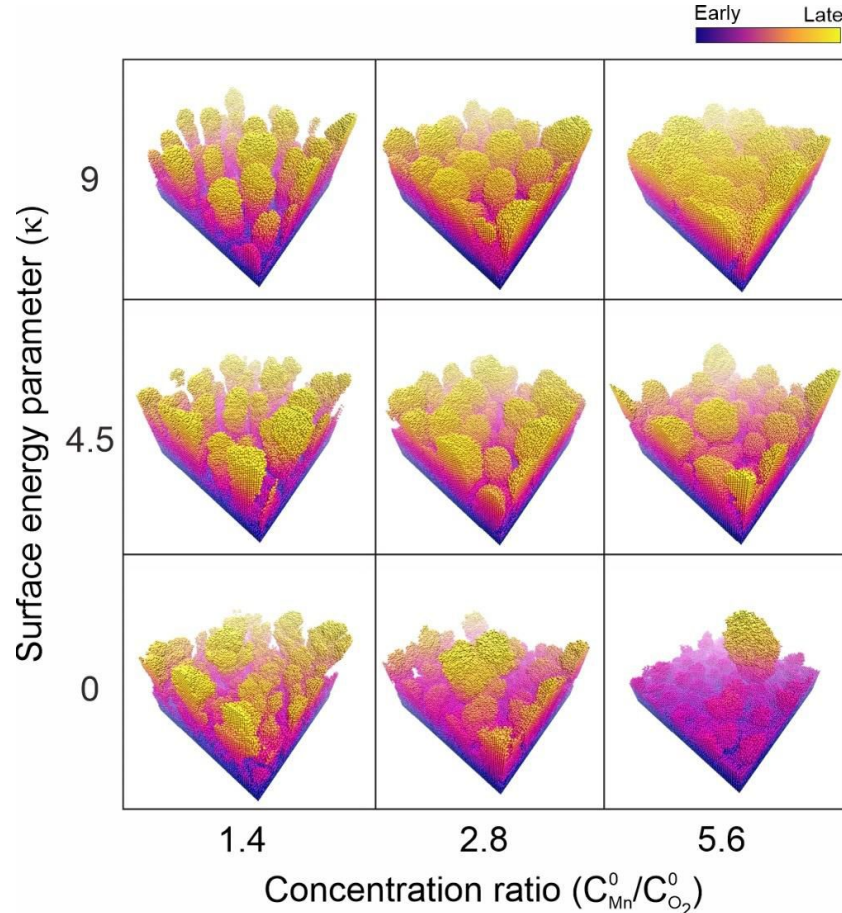


zeolite quarry, Nižný Hrabovec,  
Slovakia



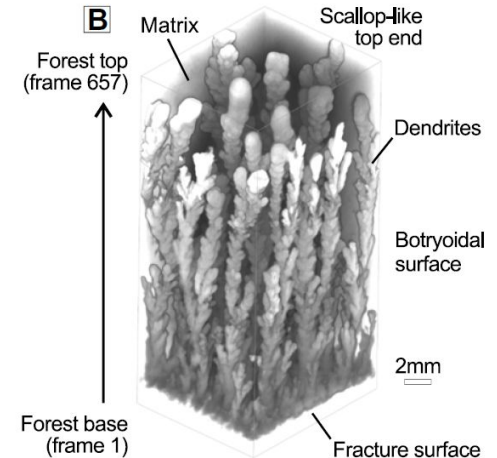
- Three-dimensional dendrite forest, comprising amorphous Mn-oxides grew adjacent and perpendicular to Mn-coated fractures in the tuffs

# 3D morphological diagram

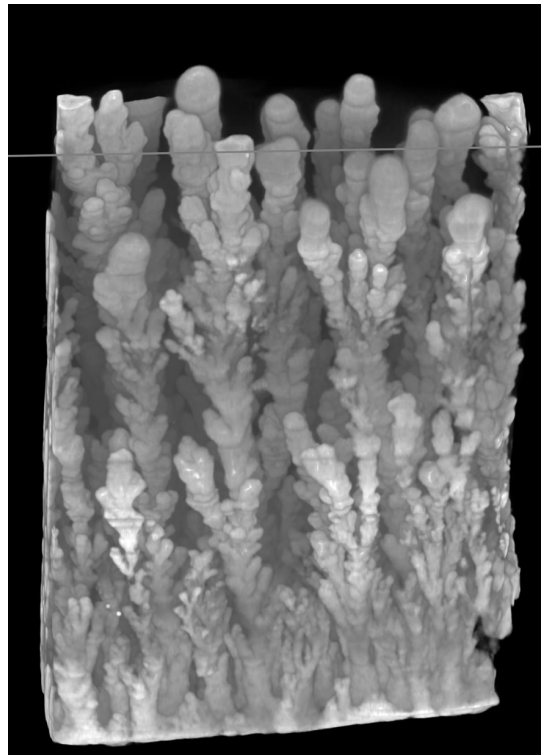


Similar conclusions to the 2D case:

- with increasing surface energy, dendrites are more compact and have fewer branches
- increasing the ratio of initial concentrations of manganese to oxygen makes the dendrites thicker and more packed

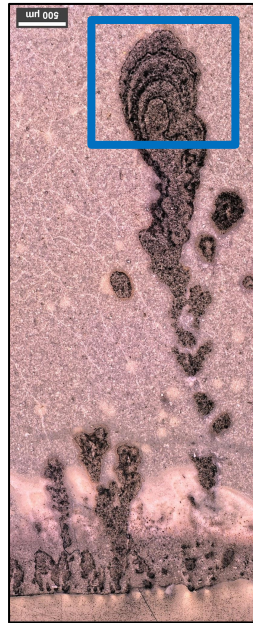


# Internal structure of the dendrites

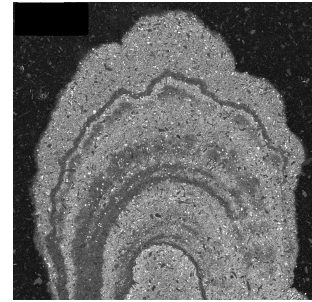


micro-CT

2mm



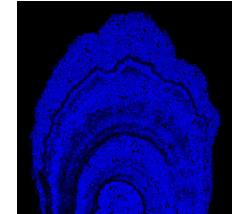
0.5mm



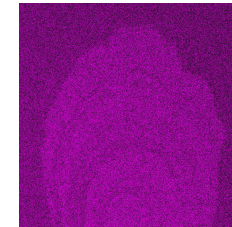
100µm

SEM

EDS elemental mapping



Mn



Ni

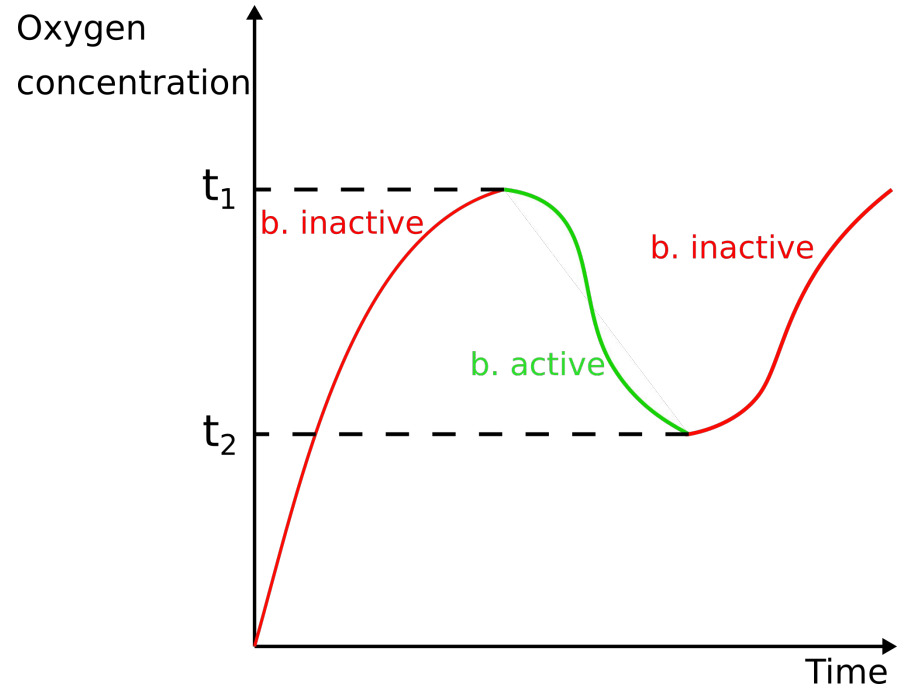
- a characteristic banded structure, with alternating layers of less and more porous material
- mostly manganese oxide in the dendrites, but also traces of nickel (a possible microbial signature?)

# Manganese oxidizing bacteria

- Bacteria can speed up Mn oxidation by **2-3 orders of magnitude**
- Numerical simulations with bacterial activity reveal **band structure** on the surface of the dendrites
- Bacterial activity **initiates** at an oxygen concentration threshold  $t_1$  and **halts** at a threshold  $t_2$  ( $t_1 > t_2$ )

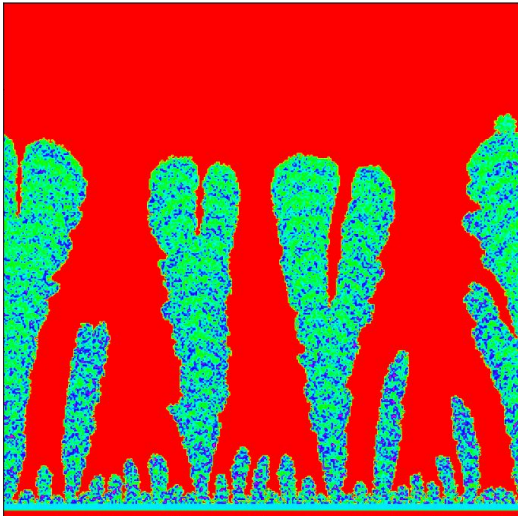
Effective reaction constant:

$$\lambda^*(\kappa) \rightarrow \begin{cases} q\lambda^*(\kappa), & \text{b. active} \\ \lambda^*(\kappa), & \text{b. inactive} \end{cases}$$

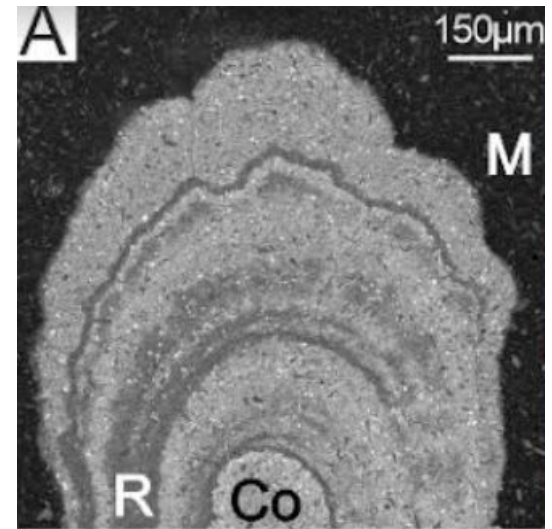


# Manganese oxidizing bacteria

$$\lambda^*(\kappa) \rightarrow \begin{cases} q\lambda^*(\kappa), & \text{b. active} \\ \lambda^*(\kappa), & \text{b. inactive} \end{cases}$$



Simulation results  $t_1$  and  $t_2$  with  $q = 25$



SEM data

# Conclusions

- morphology of dendrites is highly sensitive to both concentrations and surface energy
- with increasing surface energy, dendrites are more compact and have fewer branches
- increasing the ratio of initial concentrations of manganese to oxygen makes the dendrites thicker and more packed
- manganese-oxidizing bacterial activity offers a plausible explanation for the formation of band patterns within mineral dendrites.

