Bacterial influence on the formation of manganese mineral dendrites

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Introduction

Mineral dendrites are an example of pattern formed when the rocks are infiltrated by the hydrothermal, manganese bearing fluids. As these fluids mix with the oxygenated fluid within the rock pores, manganese oxide precipitate, creating intricate patterns. Bacteria can catalyze manganese oxidation reaction and hence their presence can play a significant role in the formation and growth of manganese precipitates. We hypothesize that presence of Mn-oxidizing bacteria can also trigger band formation in the growing dendrites, which is observed in some natural structures. The aim of this research was to investigate and classify the morphology of mineral dendrites and to make comparison with structures occurring in nature.

Theoretical model – particle attachment

- The model assumes an initial growth of small nanoparticles which then aggregate into branched structures
- Reaction-diffusion equations for concentrations:

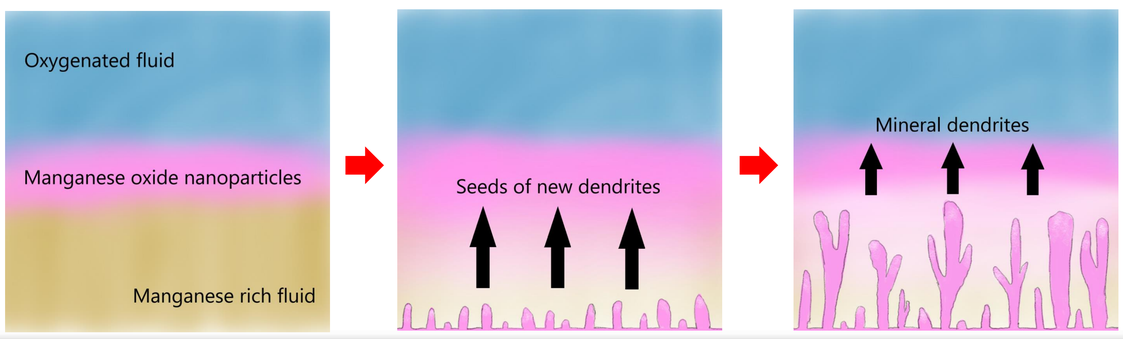
$$\frac{\partial}{\partial t}c_A = D_A\nabla^2 c_A - kc_Ac_B \longrightarrow \text{Oxygen}$$

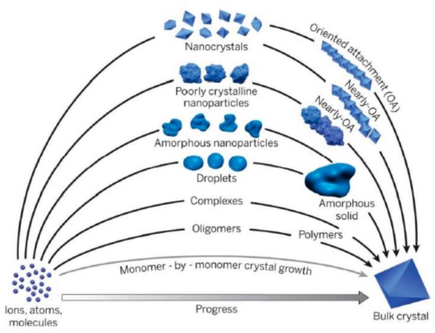
$$\frac{\partial}{\partial t}c_B = D_B\nabla^2 c_B - kc_Ac_B \longrightarrow \text{Mn ions}$$

$$\frac{\partial}{\partial t}c_C = D_C\nabla^2 c_C + kc_Ac_B - \lambda^* c_C\Theta \longrightarrow \text{Mn oxide nanoparticles}$$

$$c_{sol}\frac{\partial}{\partial t}v_p = \lambda^* c_C\Theta \qquad \Theta = \begin{cases} 1 & \text{surface or perimeter of the dendrite} \\ 0 & \text{elsewhere} \end{cases}$$

$\lambda^*(\kappa)$ ⟶ Effective reaction constant (function of dendrite curvature)





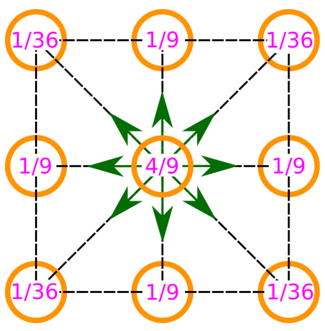
Pathways to crystallization by particle attachment, proposed by J.J De Yoreo [6]

Lattice Boltzmann method

- Used to solve the convection-reaction equations
- Two dimensions, nine particle populations, evolving according to:

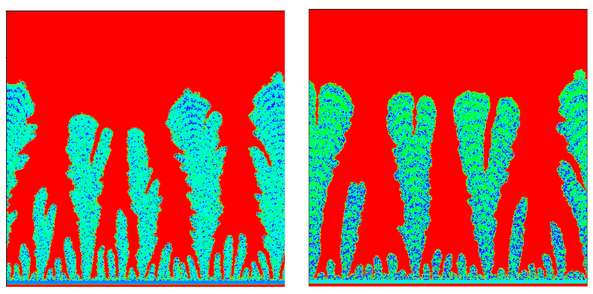
$$\underbrace{f_i(\vec{r}+\vec{dr},t+dt) = f_i(\vec{r},t)}_{\text{streaming}} - \overbrace{\frac{f_i(\vec{r},t) - f_i^{eq}(\vec{r},t)}{\tau}}^{\text{collision}}$$

$$f_i^{eq} = w_i c_i(\vec{r}) \qquad c = \sum_{i=1}^{9} f_i \longrightarrow \text{concentration}$$

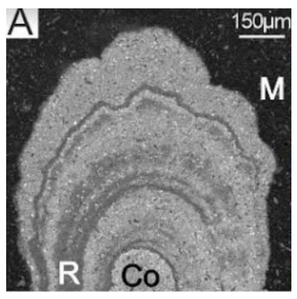


Manganese oxidizing bacteria

- Bacteria can speed up manganese oxidation by at least 2-3 orders of magnitude
- Numerical simulations involving activity of these bacteria reveal band structure on the surface of the dendrites
- Bacteria tend to reside on the surface of growing precipitates during oxidation, therefore model with bacteria activity assumes direct crystallization pathway
- Bacterial activity initiates at an oxygen concentration threshold t_1 and halts at a threshold t_2 ($t_1 > t_2$)



Simulation results for different t_1 and t_2 with q = 25



SEM data

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

Summary

- Morphology of dendrites is highly sensitive to both concentrations and surface energy
- Mn oxidizing bacteria may have significant impact on the growth of the dendrites and may trigger internal band formation

References

1. I. Lagzi, A. Volford, A. Büki, Chem. Phys. Lett. **396:** 1–3 (2004)
2. B. Chopard, H. Herrmann, T. Vicsek, Nature **353:** 409–412 (1991)
3. T. Vicsek, Phys. Rev. Lett. **53:** 2281 (1984)
4. A. Toramaru, T. Harada, T. Okamura, Phys. D: Nonlinear Phenom. **183:** 1–2 (2003)
5. P. Papp, B. Bohner, A. Tóth, D. Horv ath, J. Chem. Phys. **152**: 094906 (2020)
6. J.J. De Yoreo et al., Science. **349**: aaa6760 (2015)

Theoretical model – direct crystallization

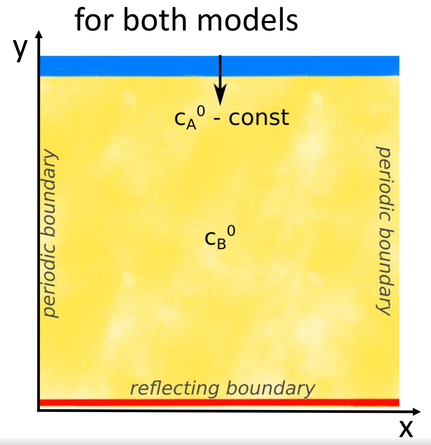
- Another model assumes precipitation of manganese oxides directly on the surface of the growing dendrite, which then elongate.
- Reaction-diffusion equations for concentrations:

$$\frac{\partial}{\partial t}c_A = D_A\nabla^2 c_A - \lambda^* c_Ac_B\Theta$$

$$\frac{\partial}{\partial t}c_B = D_B\nabla^2 c_B - \lambda^* c_Ac_B\Theta$$

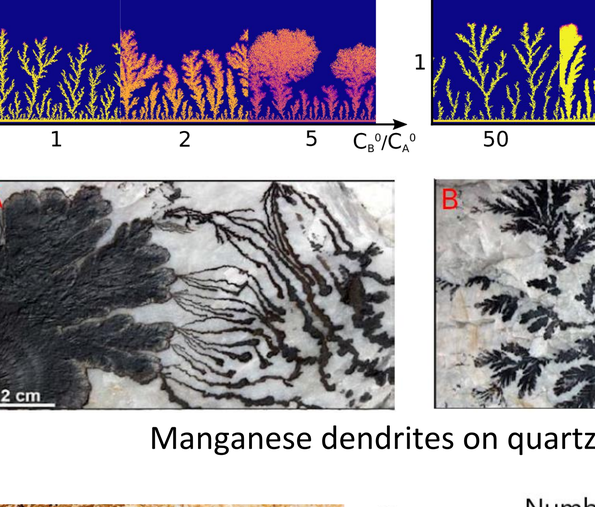
$$c_{sol}\frac{\partial}{\partial t}v_p = \lambda^* c_Ac_B\Theta$$

- Initial and boundary conditions common for both models



Surface energy

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



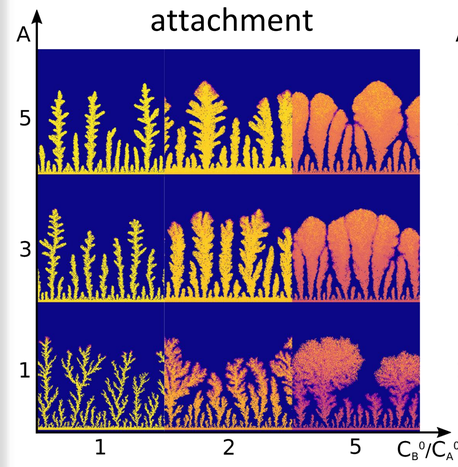
$$\lambda^* \equiv \lambda\left(A\left(\frac{N}{l^2} - \frac{l-1}{2l}\right) + \frac{1}{2}\right)$$

λ – reaction rate constant
N – number of particles belonging to aggregate within a cell of size l×l

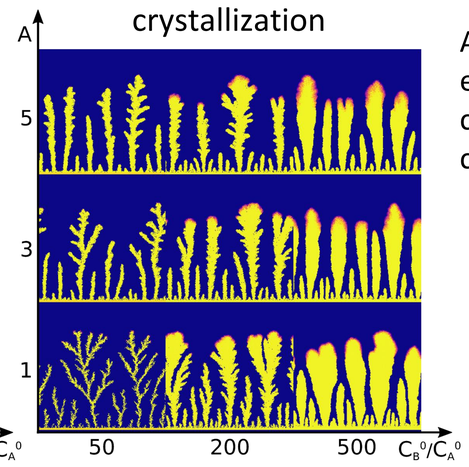
The model has been proposed by T. Vicsek [3]

Simulation results and comparison with natural examples

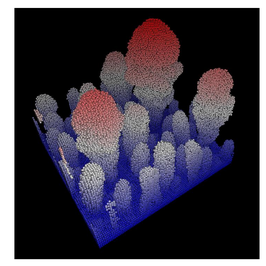
Phase diagram – particle attachment



Phase diagram – direct crystallization

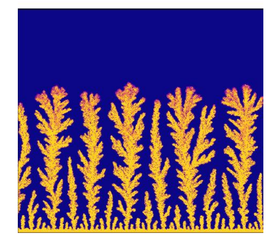


A – surface energy parameter
c_A^0, c_B^0 – initial concentrations

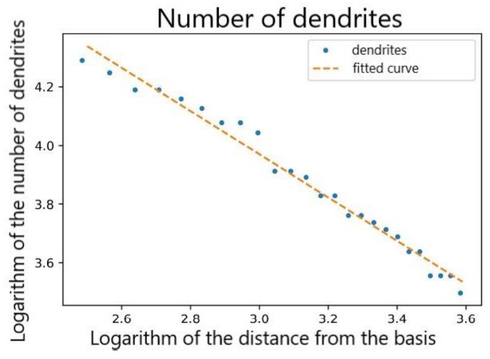


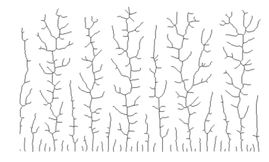
Dendrites example simulation result in 3D geometry

Manganese dendrites on quartz basis



Manganese and ferric dendrites on a limestone





Example simulation result before and after skeletonization