

Morphological transitions in mineral dendrites

Dawid Woś*, Piotr Szymczak, Zhaoliang Hou

*Email: dd.wos@uw.edu.pl



What are mineral dendrites?

- **Branched structures** that resemble tree-like or fern-like patterns.
- Commonly composed of **manganese** oxides or **iron** oxides.
- Often found on **rock surfaces**, **fossils**, or between **sedimentary layers**.
- Not actual fossils or plant remains – **inorganic growth**.



Manganese and ferric dendrites on limestone



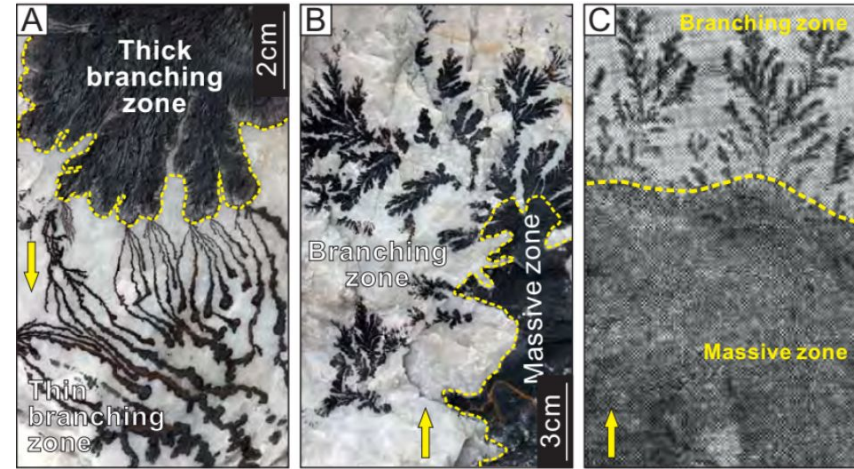
Manganese dendrites on quartz



Mineral dendrites in Agate

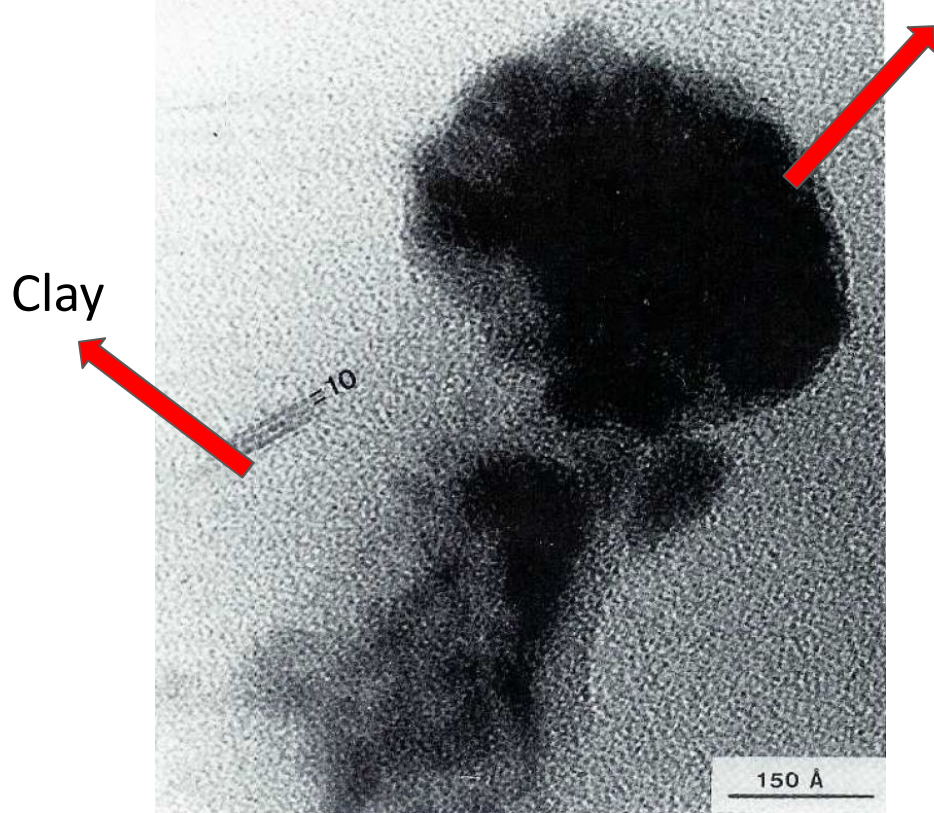
Morphological transitions

Changes in shape within a single growing dendritic structure.



What is the physical mechanism underlying these morphological transitions?

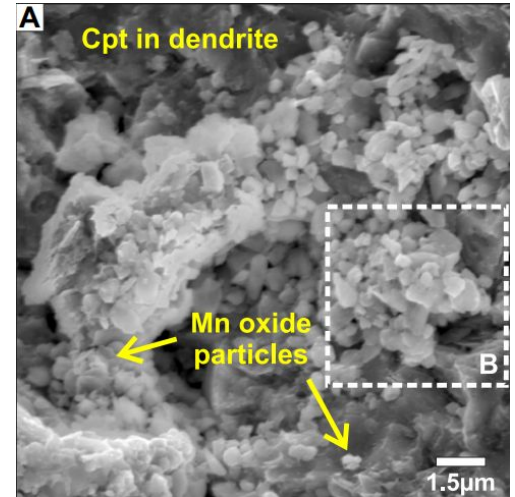
Low crystallinity



Electron microscopy view of Mn oxide particles showing the lack of long-range order.

Dendrite

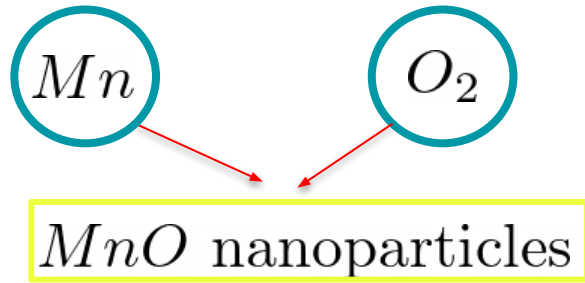
Electron microscopy reveals that Mn dendrites lack long-range order in their structure, highlighting their colloidal nature.



SEM
data

Crystallization by particle attachment

Mineral dendrite growth results from a **reaction-diffusion system**. It includes transport of reactants as well as chemical reactions.



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



Atoms, ions
molecules



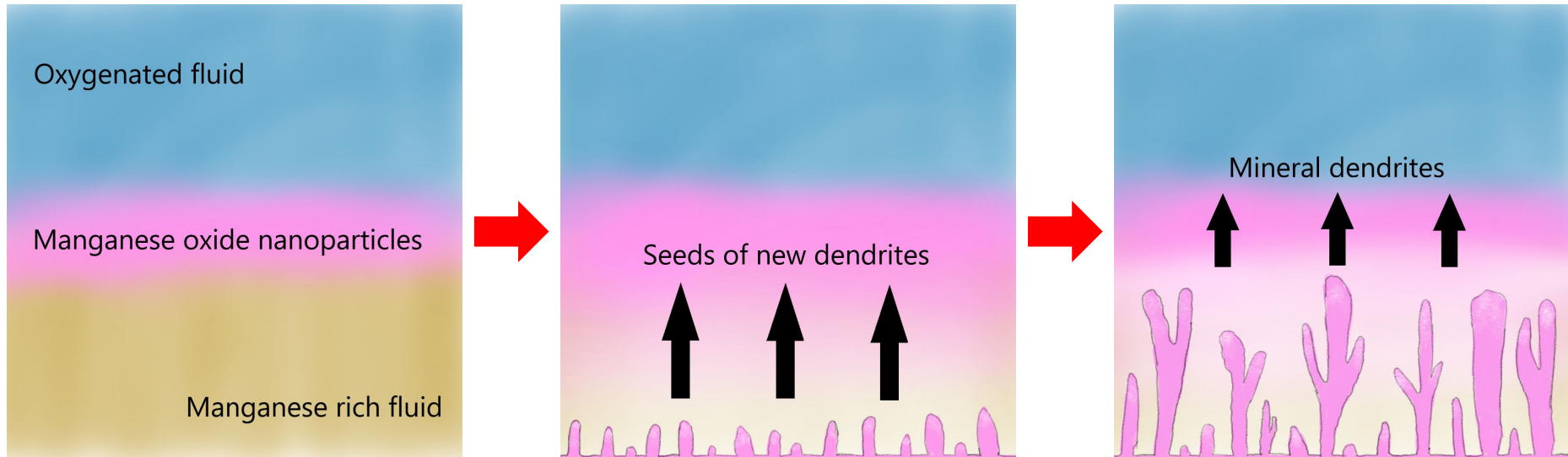
Nanoparticles



Bulk crystal

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

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

- Mn ions

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

- manganese oxide particles

$$\frac{\partial}{\partial t} c_{\text{MnO}} = D_{\text{MnO}} \nabla^2 c_{\text{MnO}} + \nu k c_{\text{O}_2} c_{\text{Mn}} - \lambda^* c_{\text{MnO}}$$

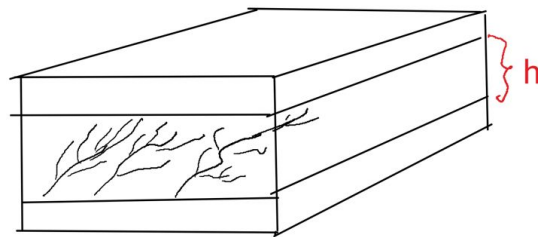
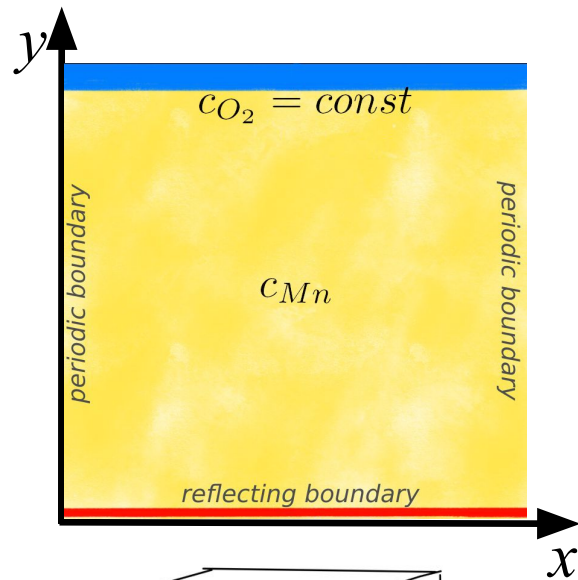
- dendrite growth
(on the dendrite surface)

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

volume fraction

molar volume

boundary and initial conditions



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
- Diffusive and capillary lengths:

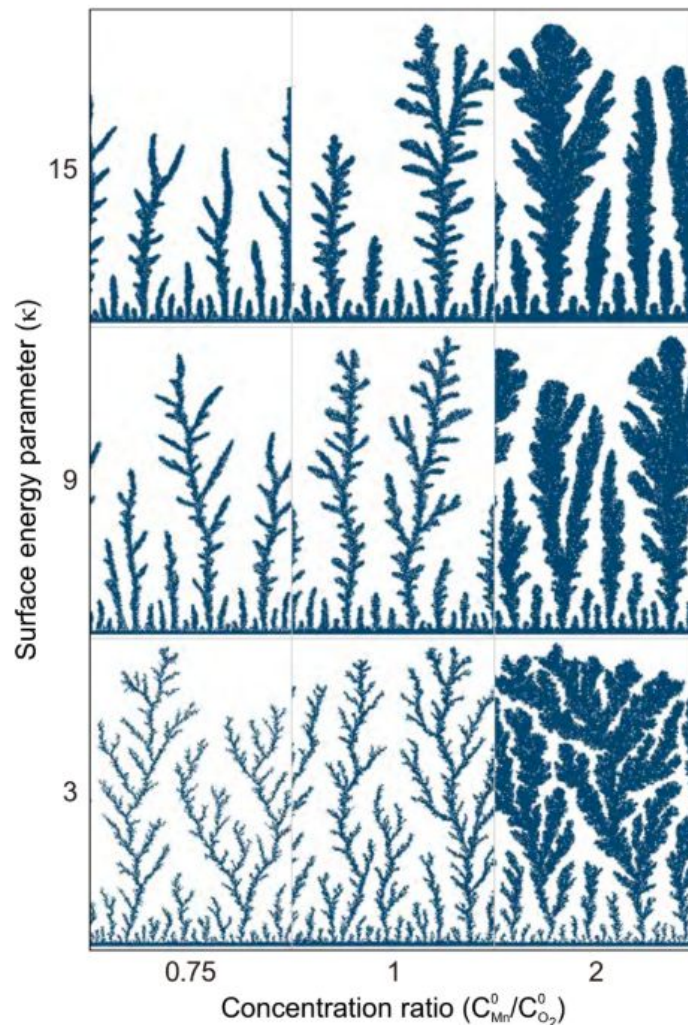
$$l_d = D/U \quad l_c = \nu \frac{\sigma v_m}{kT} \quad \kappa = l_c/l_d$$

Ratio of diffusion
constant and average
growth velocity

σ - surface energy density
 ν - acid capacity number

κ – surface energy parameter

$c_{\text{Mn}}^0, c_{\text{O}_2}^0$ initial concentrations

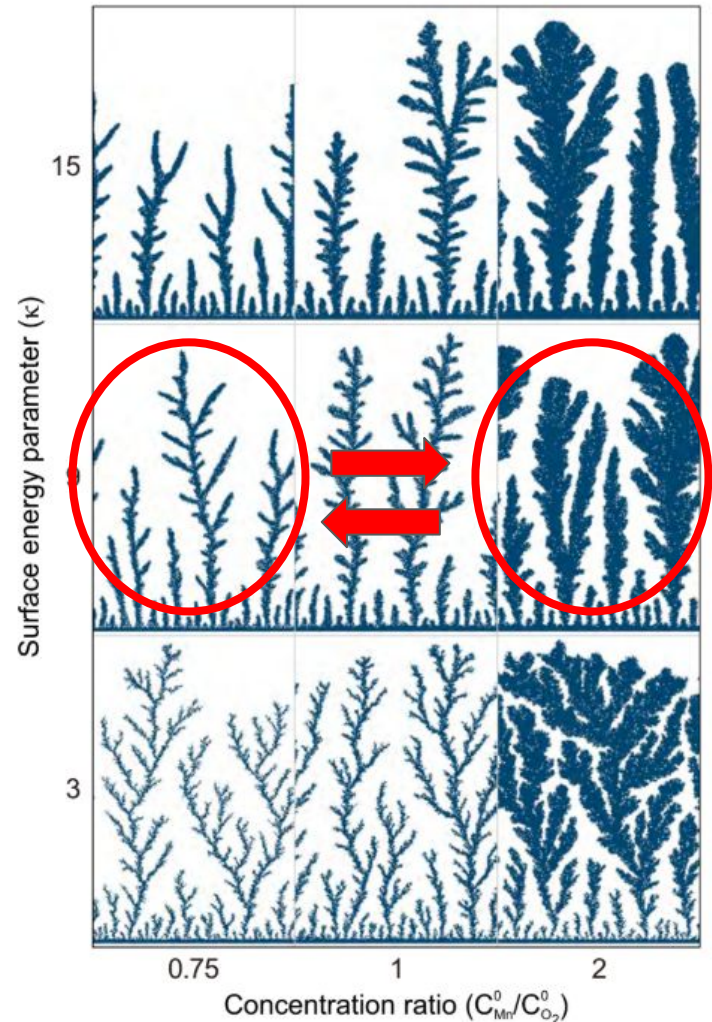


Multiple infiltrations

- Multiple **infiltrations** of **manganese-bearing** fluids with varying concentrations can occur during growth.
- Since dendritic shape depends on **Mn to O₂ initial concentration ratio**, such variations may induce morphological transitions.

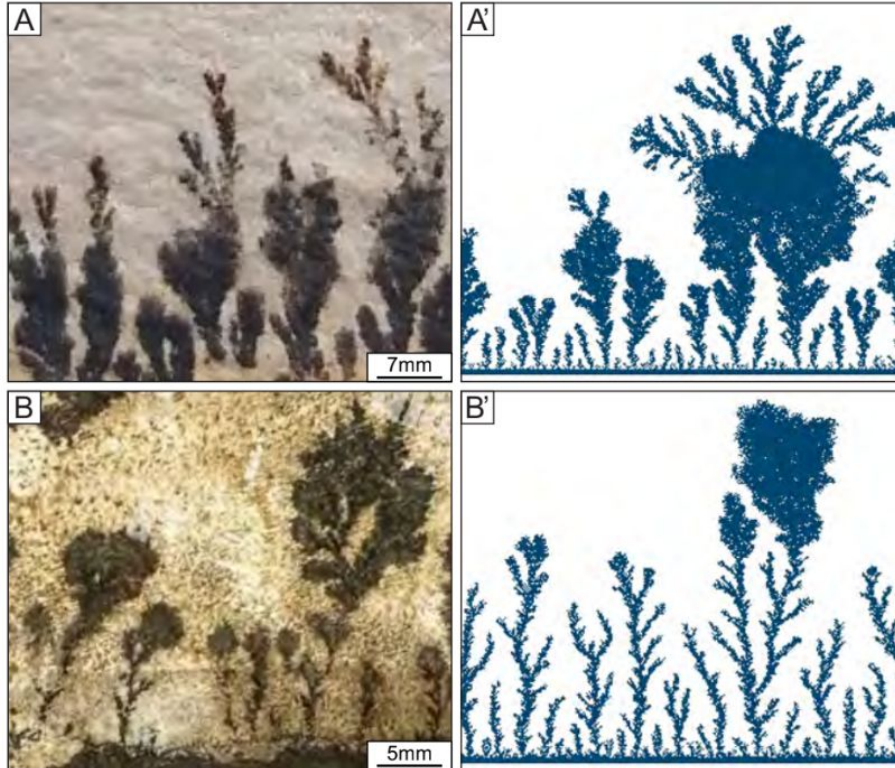
κ – surface energy parameter

$c_{\text{Mn}}^0, c_{\text{O}_2}^0$ initial concentrations



Transitions due to multiple infiltrations

Rock samples



In the simulation, the manganese to oxygen concentration ratio was **reduced from 10 to 1**

In the simulation, the manganese to oxygen concentration ratio was **increased from 1 to 10**

Fracture aperture - phase diagram

- Aperture of the fracture h influences dendrite morphology.
- Increase of aperture h results in thicker dendrites, with shorter, bulkier branches.

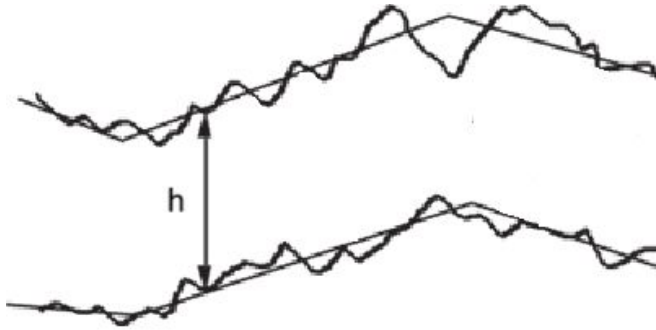
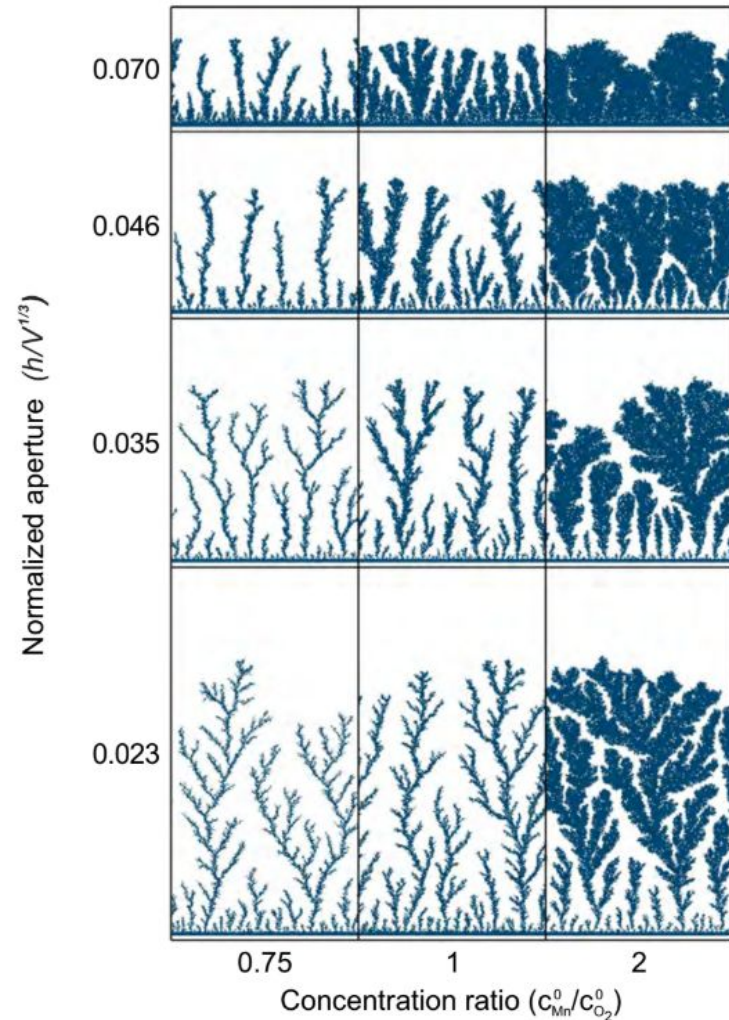


Illustration of aperture of the fracture



Fracture aperture - morphological transitions

- Variations in fracture aperture h within a single rock system may lead to morphological transitions in dendrites due to altered growth conditions along the fracture.

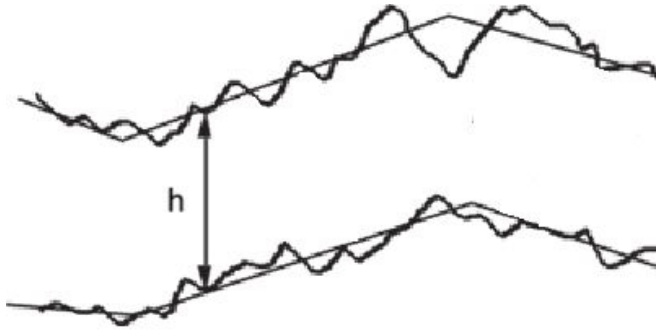
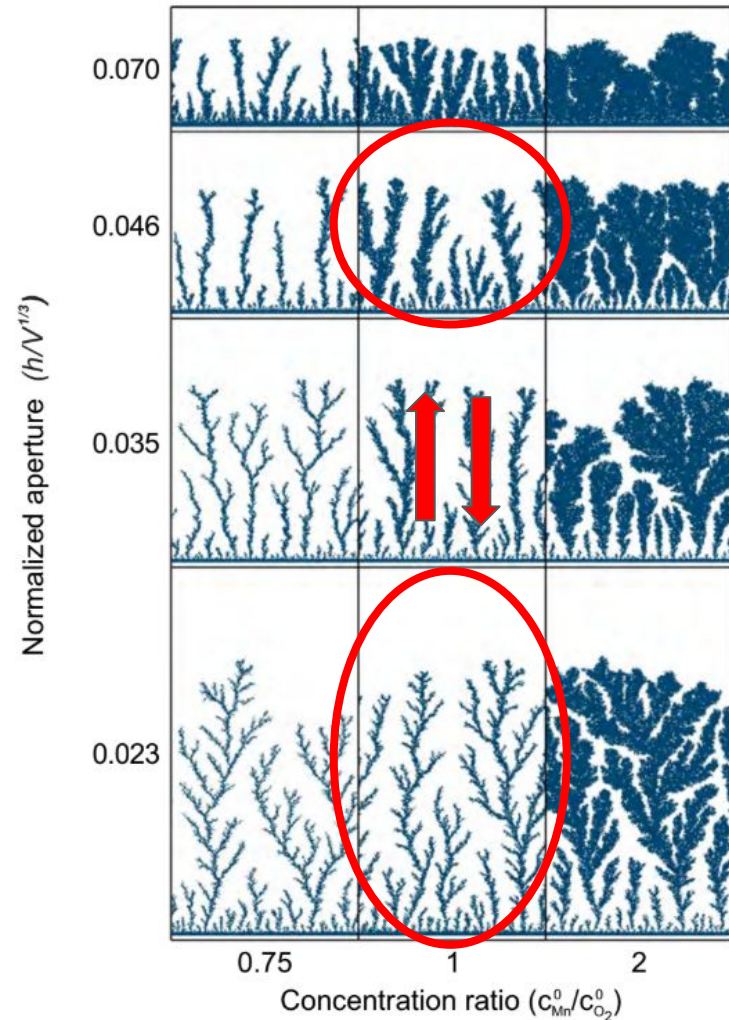
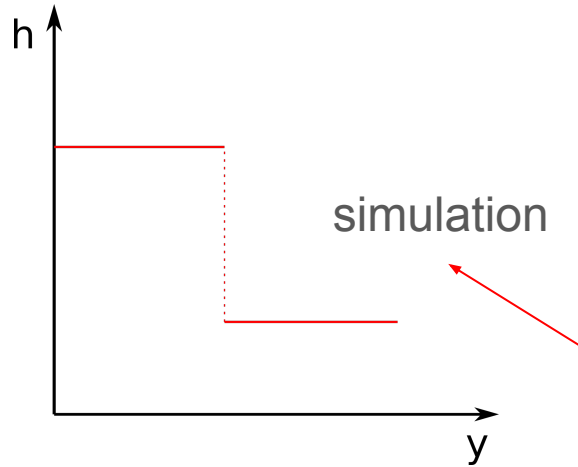


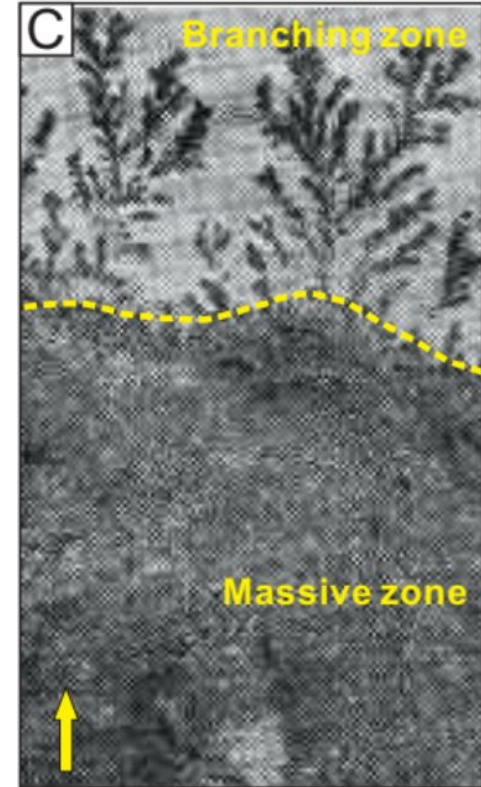
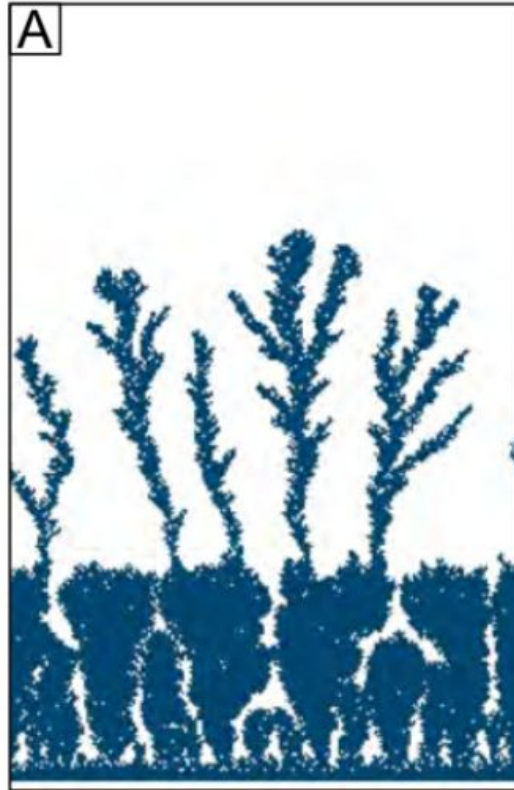
Illustration of aperture of the fracture



Transitions due to the variation of aperture



In the simulation aperture was **three times greater** at the bottom half than at the top half



rock sample

Conclusions

- Mineral dendrite morphology is influenced by factors such as **surface energy** and the **ratio of initial concentrations** of manganese to oxygen.
- Variations in **manganese** and **oxygen** concentrations during growth can induce **morphological transitions** in dendrites.
- The **aperture of the fracture** where dendrites grow affects their morphology, with larger apertures leading to thicker, bulkier branches.
- Alternation of **fracture aperture** within a rock system can also cause **morphological transitions** in dendrites.
- Mineral dendrites record the chemical and physical **history of the rock**, preserving evidence of fluid movements, fracture alteration, and environmental changes over geological time.