Surface Energy Effects on Formation and Preservation of Microrhombic Calcite Fabrics and Porosity*

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Abstract

Surface energy affects both nucleation and growth of small crystals. This study evaluates the theory behind several proposed mechanisms for porosity preservation by surface-energy control related to crystal and pore-size variations. These theories are tested with microrhombic calcite fabrics in the Pawnee Field (Cretaceous limestone reservoir, Bee County, Texas). Ostwald ripening, crystal growth, and size-selective nucleation are evaluated. Examined microrhombic calcite fabrics do not have the size distribution expected by Ostwald ripening. Therefore, alteration of crystal and pore-size distribution by Ostwald ripening after calcite precipitation is not a major influence on microrhombic calcite and associated micropore fabrics. Emmanuel et al. (2010) proposed that surface energy selectively preserves small pores by reducing surface-area normalized growth rate into small pores. The smallest possible stable pore has a critical radius that is controlled by degree of supersaturation and the surface energy. Smaller pores enlarge to the critical radius by dissolution. Larger pores cement until they also approach the critical radius. Observed mean crystal size and size distributions could be explained by this model, but dissolution-enlarged micropores are absent and pore-size variation is too large to be consistent with this theory. This mechanism may help form microrhombic calcite, but it is not responsible for its preservation. Nucleation controls burial cementation by controlling where and how many crystals grow in pores. Burial calcite nucleation is also controlled by surface energy and supersaturation. Because surface area per pore is small for small pores, calcite crystals are less likely to nucleate in a small pore, and if they do, they occlude only the small volume of the pore. Microrhombic calcite fabrics at Pawnee field are most consistent with selective porosity preservation during burial by nucleation. These concepts can be used to predict settings where porosity between microrhombs is expected and how this porosity is preserved during early and late burial. Supersaturation controls both nucleation and growth; so supersaturation history controls formation and preservation of porosity associated with microrhombic calcite.

Selected References

Emmanuel, S., and B. Berkowitz, 2007, Effects of pore-size controlled solubility on reactive transport in heterogeneous rock. Geophysical Research Letters, v. 34/6. Website accessed September 5, 2015, http://onlinelibrary.wiley.com/doi/10.1029/2006GL028962/full.

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Kile, D.E., D.D. Eberl, A.R. Hoch, and M.M. Reddy, 2000, An assessment of calcite crystal growth mechanisms based on crystal size distributions: Geochimica et Cosmochimica Acta, v. 67/17, p. 2937-2950.

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Problem

- Some deep carbonate reservoirs have predominantly micropore systems with larger pores occluded by cement.
- If micropores form early, micropores must be selectively preserved over large pores during burial.
- What mechanisms can explain selective micropore preservation?
- How can we use this understanding to predict the occurrence of micropore-dominated reservoirs and limestone porosity evolution with burial?

Objectives

- Evaluate mechanisms for selective preservation of micropores in microrhombic limestones.
- Test theories using fabrics from Pawnee Field (middle Cretaceous limestone, Bee Co., TX)
- Develop a conceptual model for prediction of porosity preservation and burial cementation in limestones.

Four Effects To Be Considered

- Equal cementation on all pore surfaces
- Ostwald ripening
- Surface-energy effects on cement growth in pores of different sizes.
- Nucleation effects on cementation in pores of different sizes.

Equal Cementation Rate

- Sizes of all pores decrease due to cementation on pore surfaces.
- Where pores have wide size range, smaller pores are selectively occluded relative to large pores.
  - –Causes apparent <u>coarsening</u> of pore-size distribution as porosity decreases.
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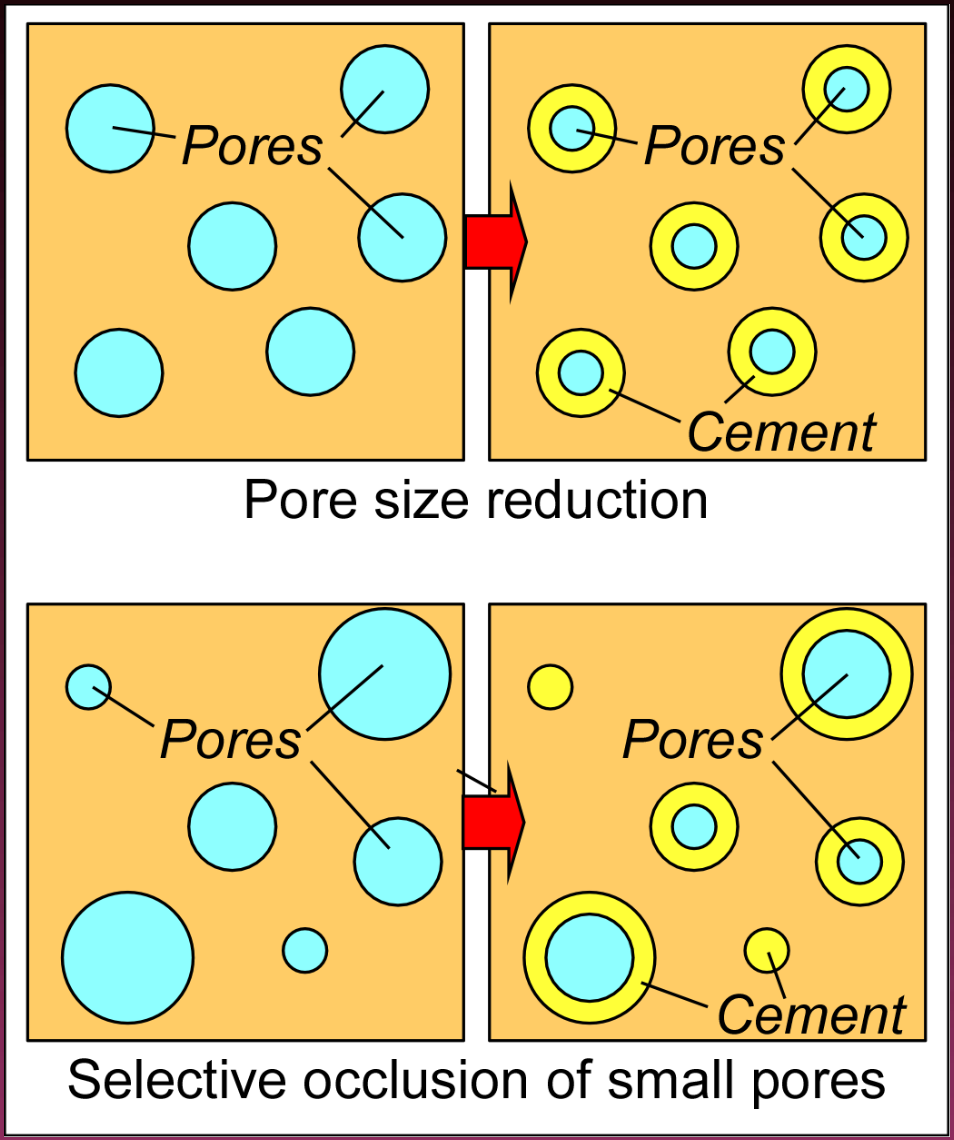
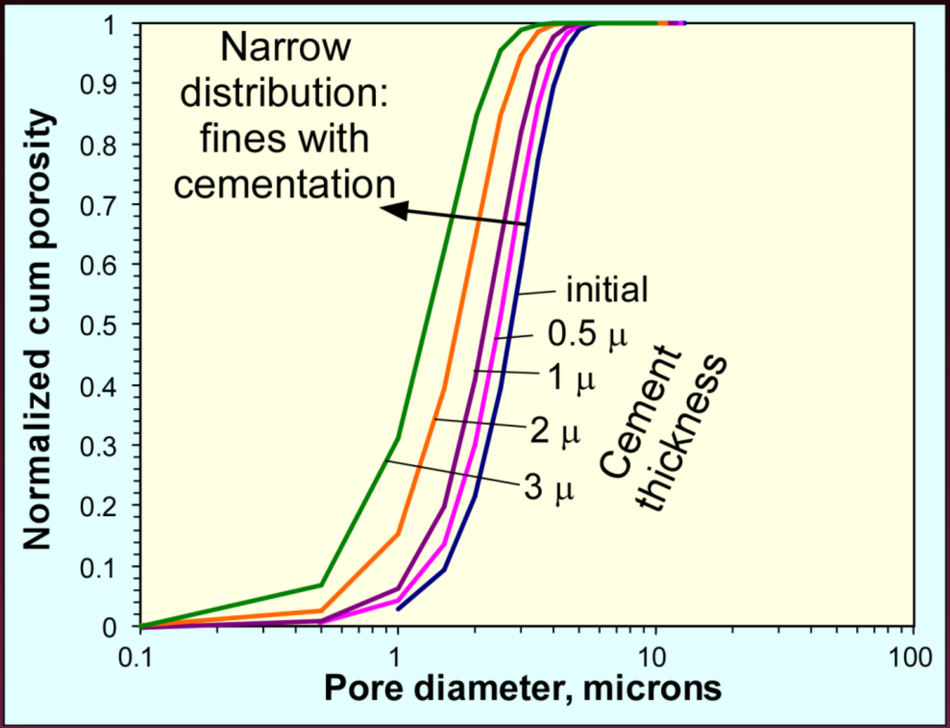
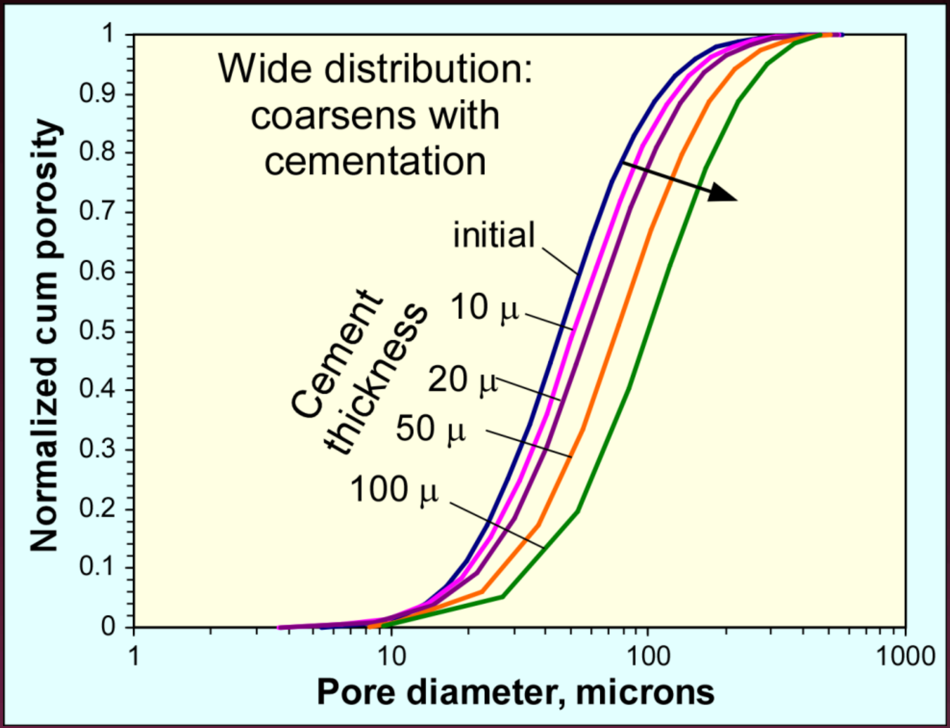


Pore-Size Distribution, Equal Growth

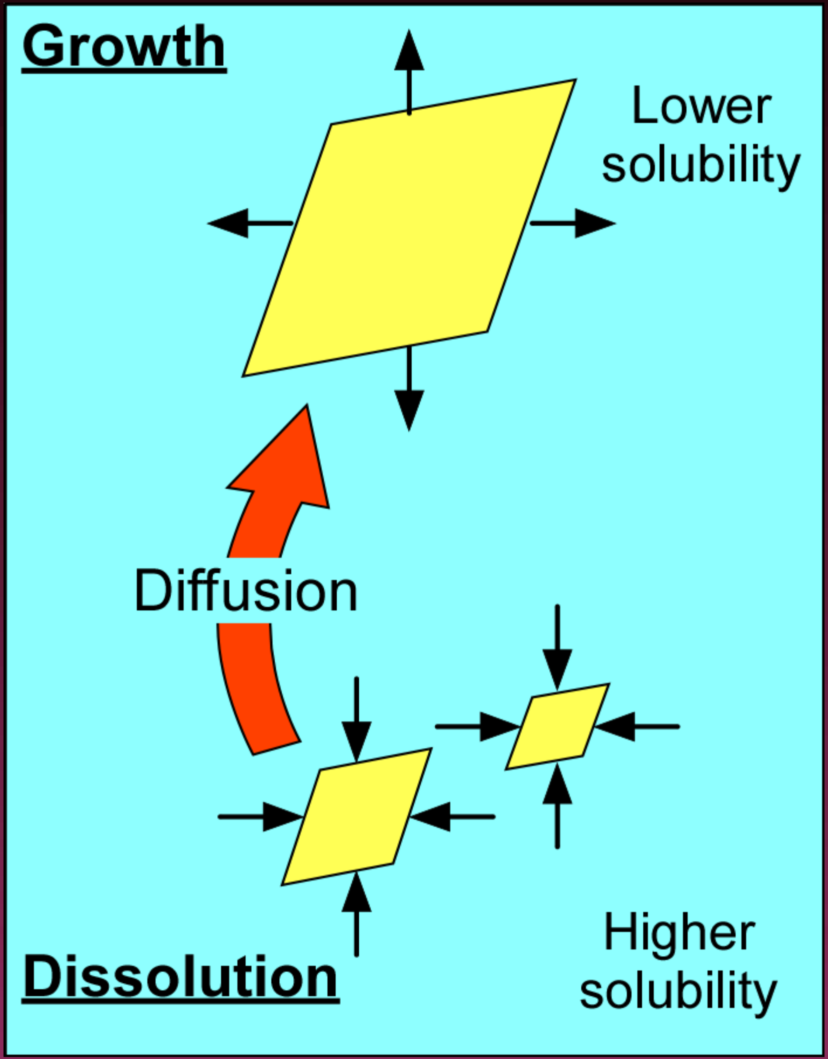




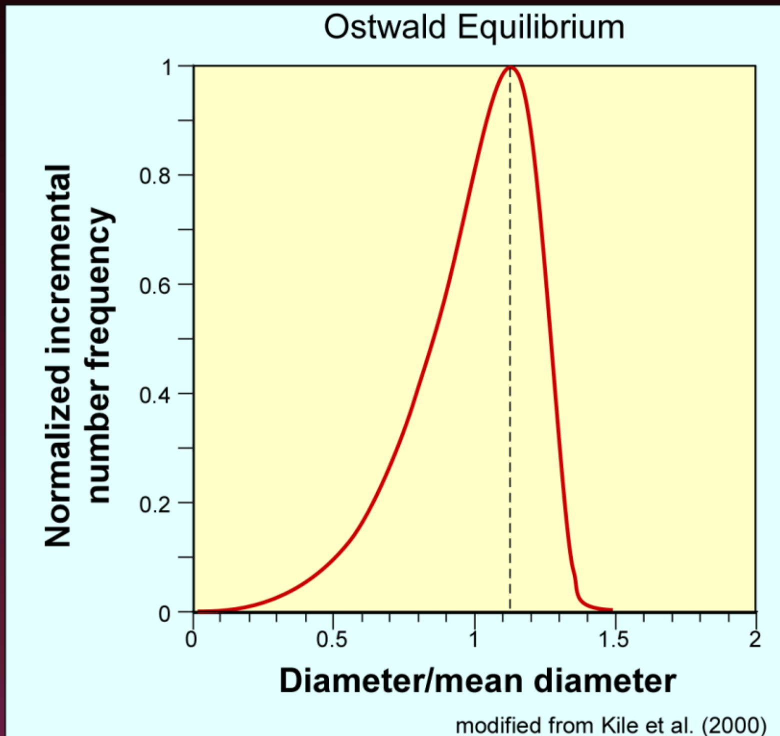
- Narrow initial pore-size distributions evolve towards smaller average diameter due to decrease of all pore sizes.
- Broad initial pore-size distributions evolve towards larger pore size due to selective occlusion of small pores.

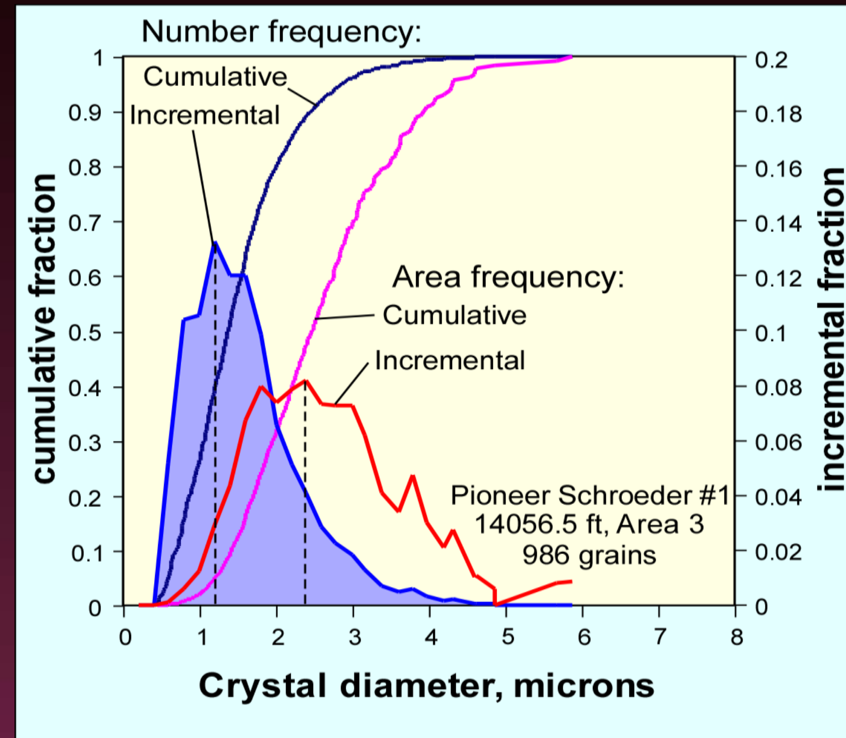
Ostwald Ripening

- Small crystals have greater solubility than large crystals (Kelvin effect).
- Small crystals dissolve and large crystals grow.
- Transfer by diffusion over short distances.
  - –Grain boundary migration in low-porosity rock.
  - –Dissolution - precipitation in high-porosity rock.



Ostwald Ripening Size Distribution





Expected Distribution:

- Very well sorted.
- Mode larger than mean.
- A few small crystals.

Observed Distribution:

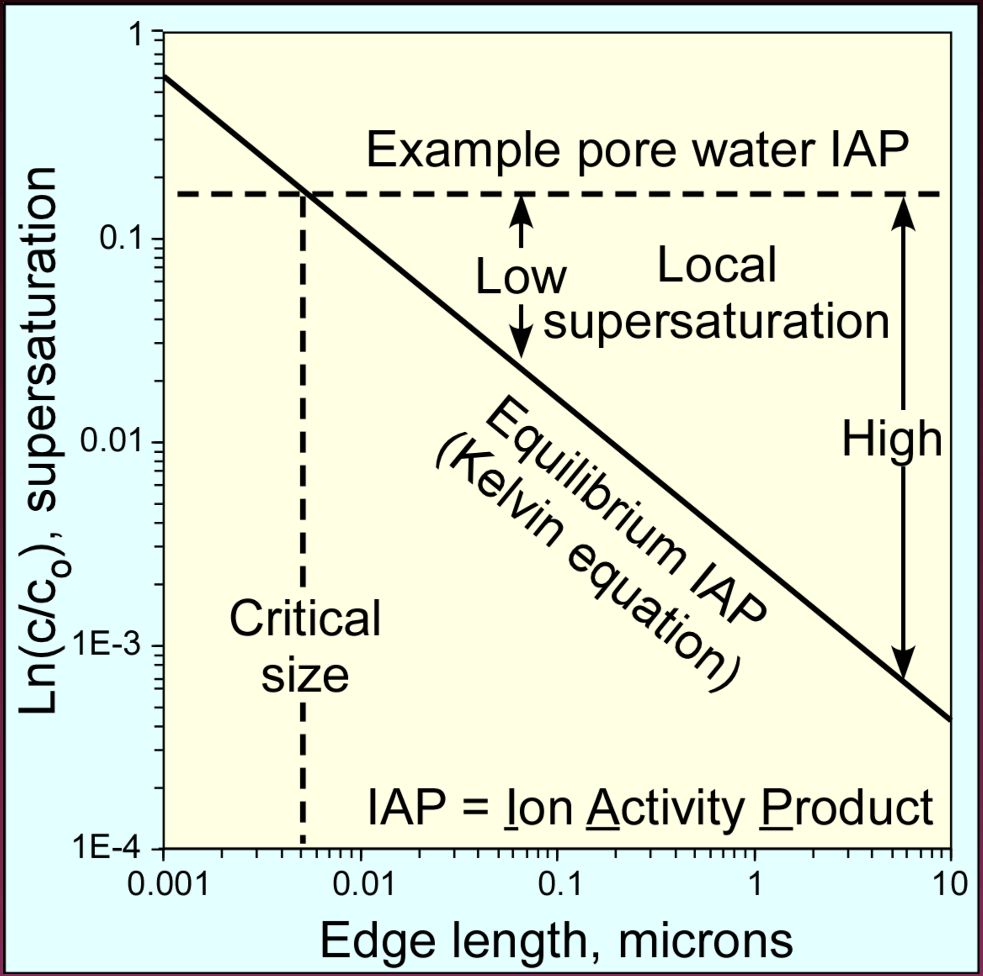
- Too broad for Ostwald ripening.
- Mean larger than mode.
- Dominated by small crystals.

- Conclusion: microrhombs are <u>not</u> a product of Ostwald ripening.

Size Effect on Growth Rate

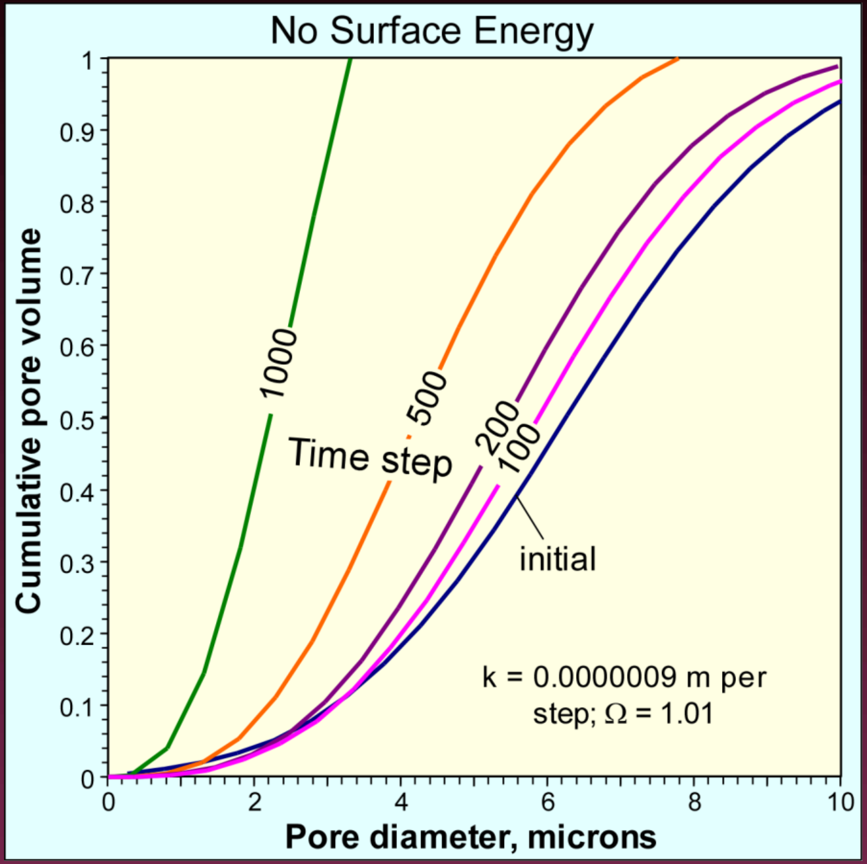
Surface Energy Affects Growth Rate

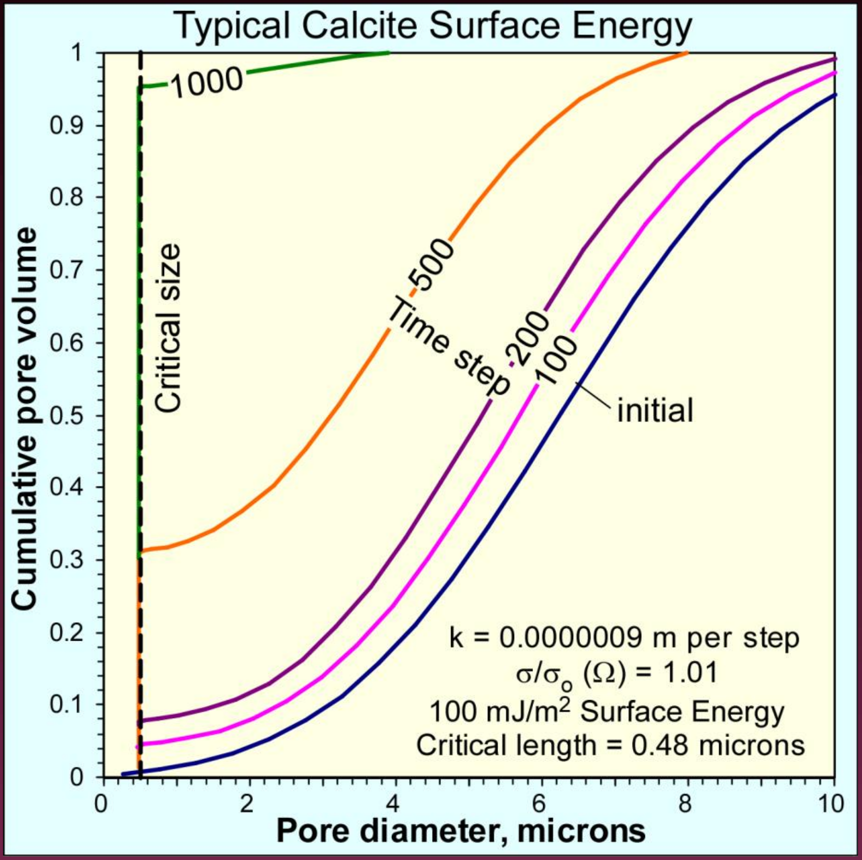
- At any supersaturated pore water ion activity product, small crystals have less supersaturation than large crystals.
- Lower supersaturation causes slower crystal growth.
- Emmanuel and Berkowitz (2007) propose that pore size has a similar effect.
- Result: selective preservation of pores near critical size.



Concept from Emmanuel and Berkowitz (2007).

Modeled Pore Size Distributions

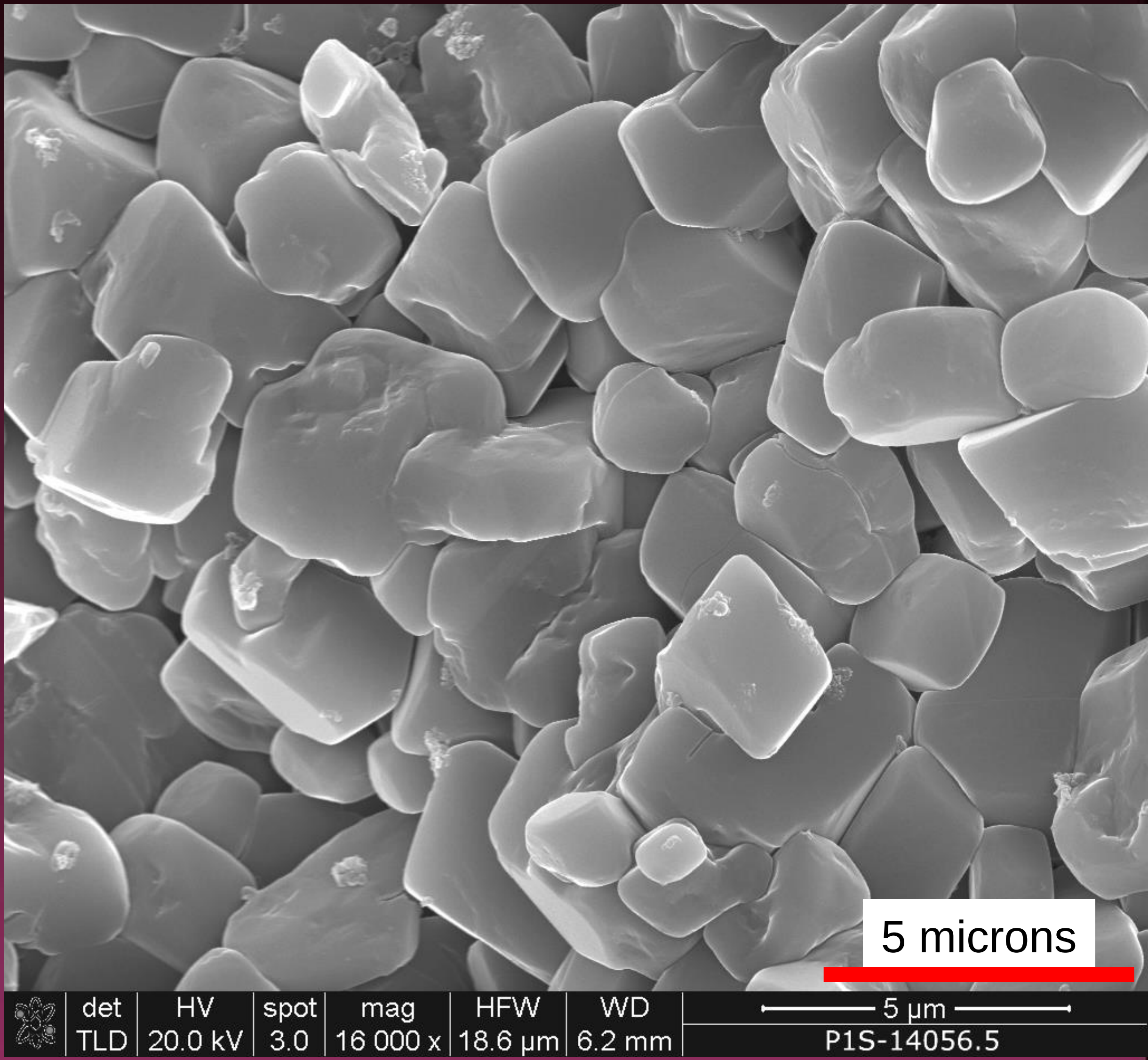




- No surface energy: decreasing average diameter with time.
- Surface energy: increasing fraction of pores at critical size. Larger pores form population similar to rescaled initial population due to equal cement growth.

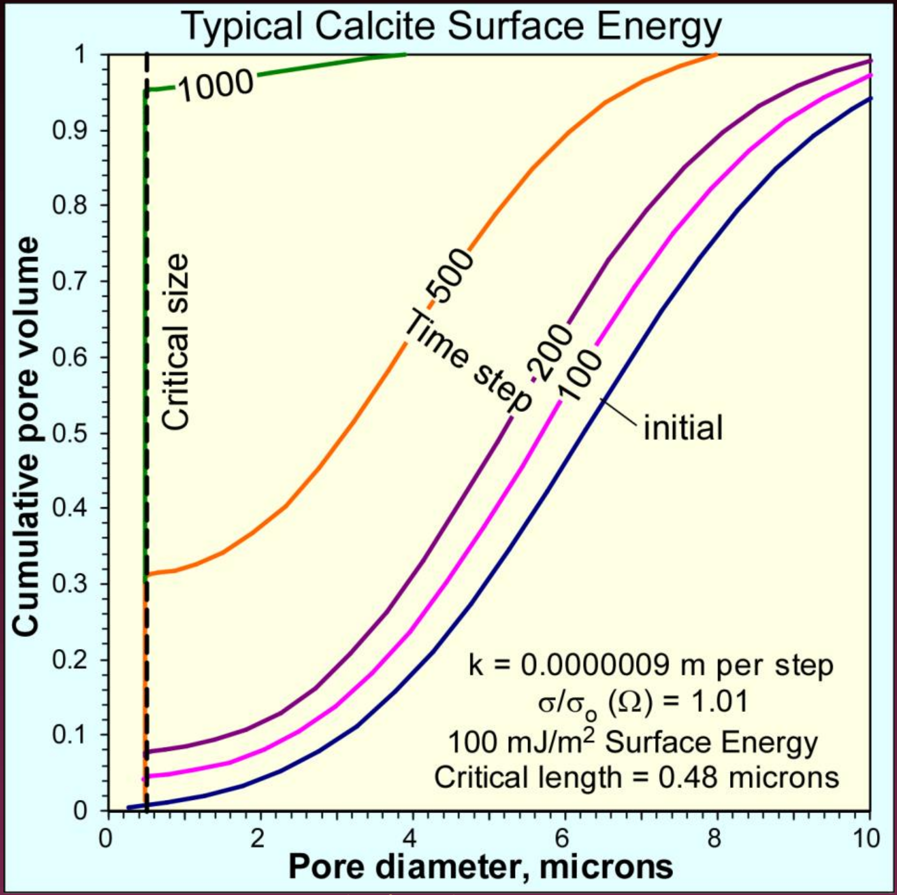
Pore Sizes in Microrhombic Fabric

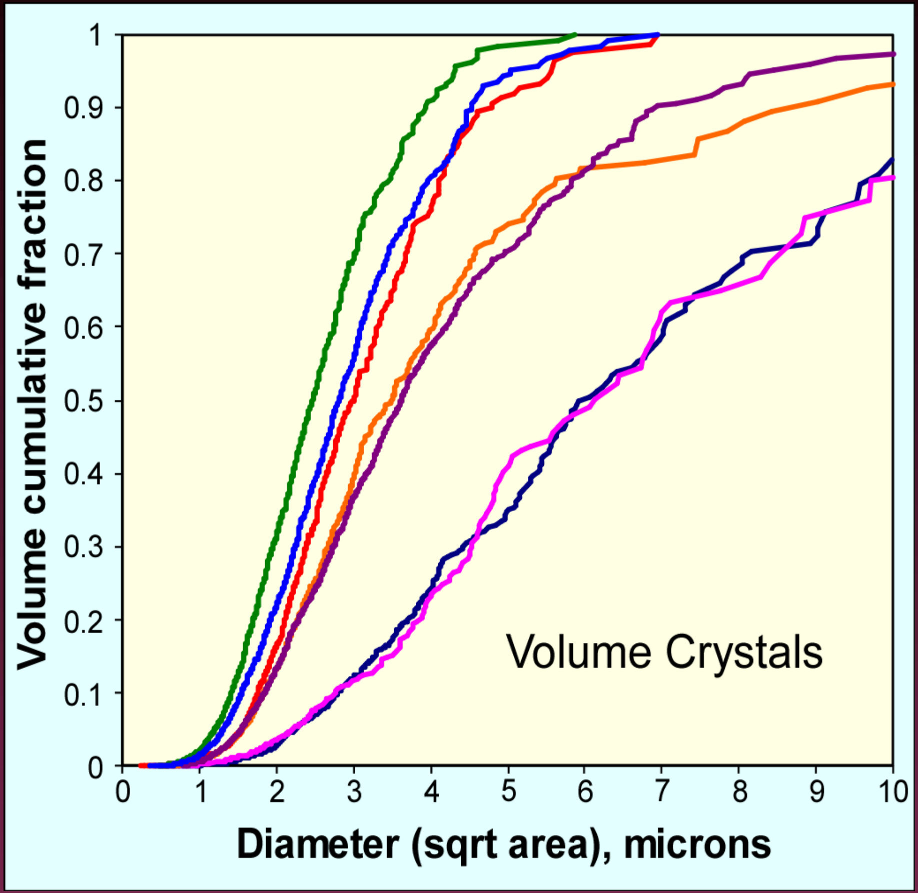
- Large pore-size variation.
- Well sorted rhombs.
- Inconsistent with predictions from size-controlled growth



Fracture surface, Pioneer Schroeder #1 14056.5 ft.
Image from Bob Loucks, UT BEG

Crystal Size in Microrhombic Fabric





Modeled Pores:

- Narrow volume distributions with coarse tail.
- Distinct critical length effect in best sorted distributions.

Crystals:

- Wider distributions with broader coarse tail.
- No critical length effect.

Growth Model Validity

- Surface Energy model predicts:
  - –Most pores reach critical size as rock cements.
  - –Small pores are relics of heavily cemented initially, large voids.
  - –Overall rock should have large, irregular cement volume with narrow pore-size distribution.
- None of these predictions match observations

Growth model is <u>not</u> controlling selective micropore preservation at Pawnee Field

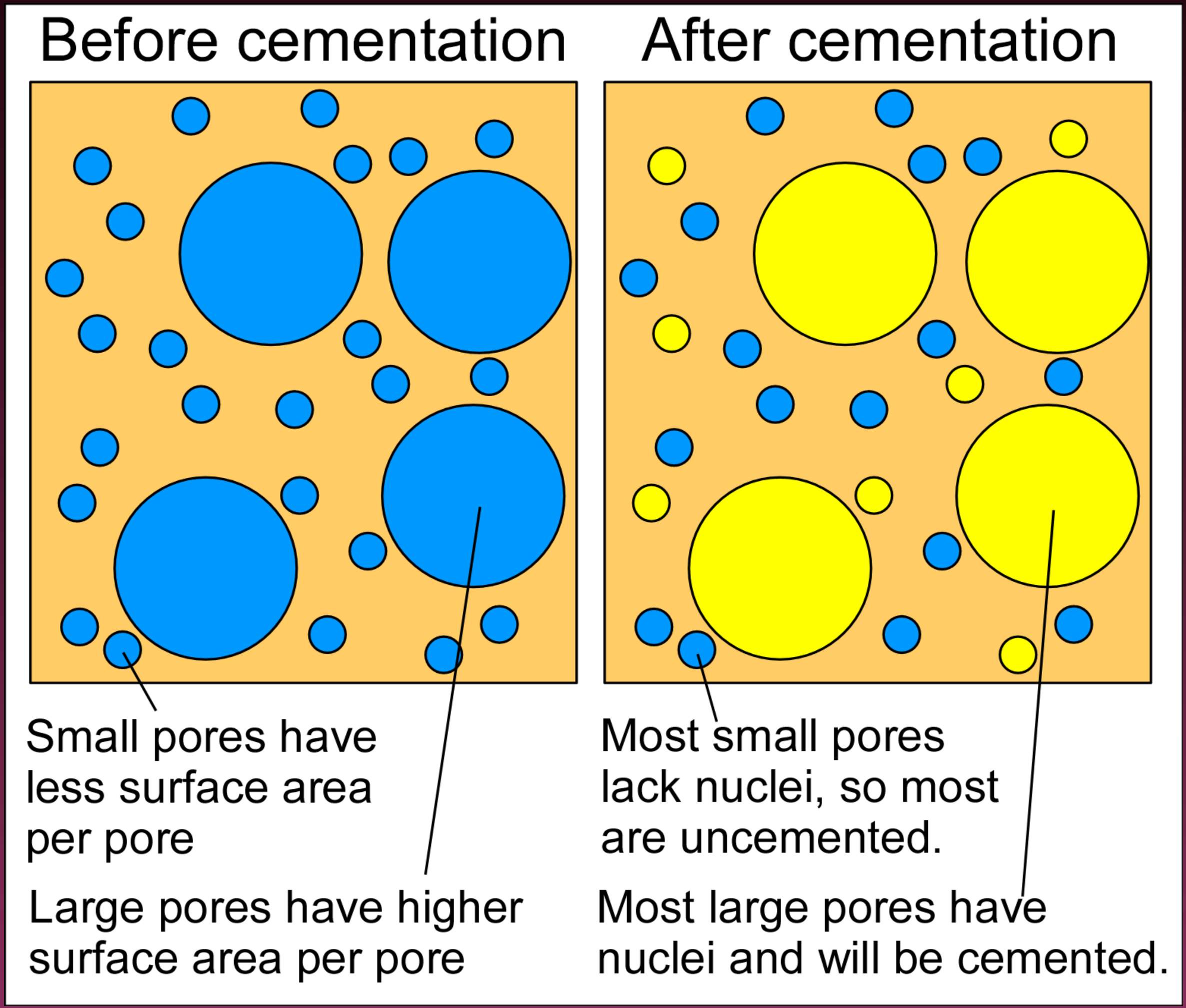
Nucleation-Limited Cementation

Nucleation-Limited Cementation

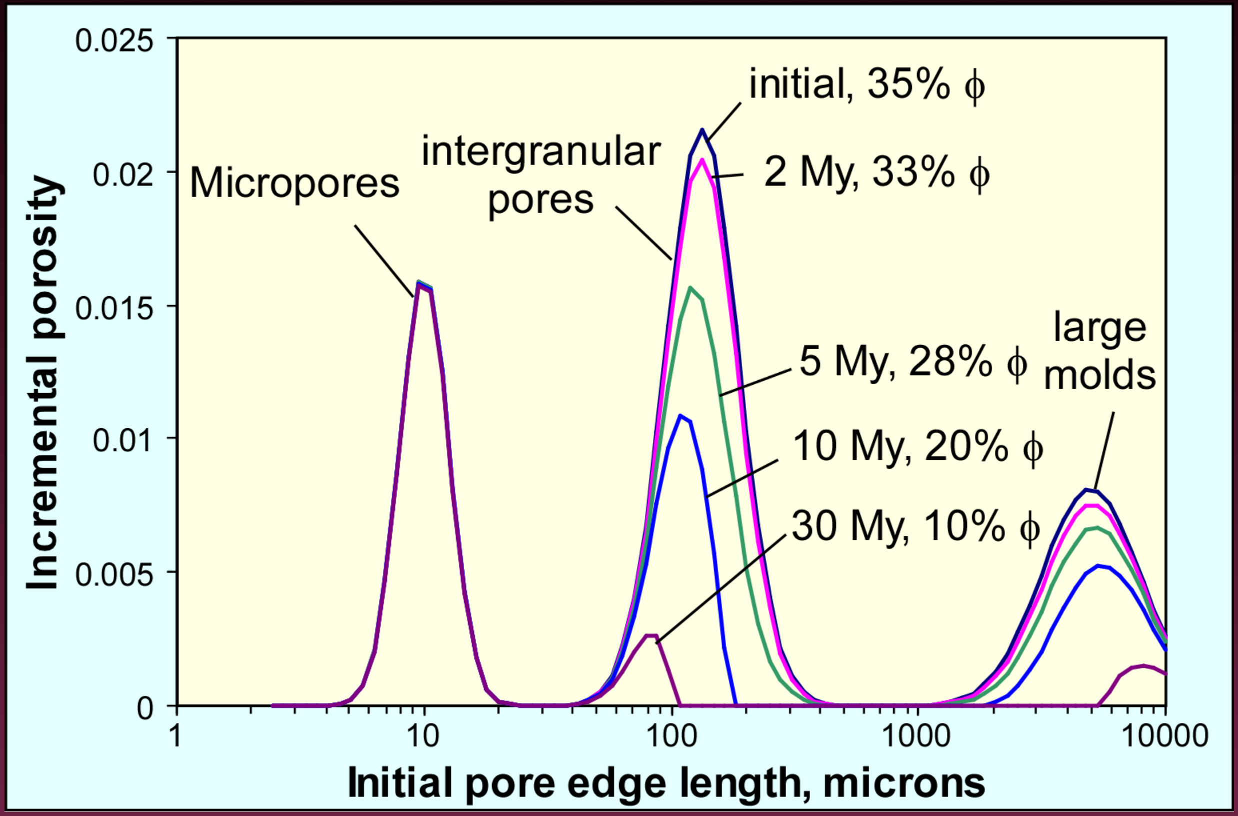
- Cementation requires both nucleation and growth. Pores without nuclei remain uncemented.
- Probability of nucleation within each pore is controlled by its surface area.
  - A small pore has less surface area per pore and is less likely to have a nucleation site.
  - Less likely nucleation equals fewer small pores are cemented. More porosity in small pores are preserved than in larger pores.
- Surface energy does not directly affect concept; size selection is applicable at all scales.

Nucleation Model

- Small pores have higher total surface area per unit porosity, but less surface area per pore.
- Fewer small pores with nucleation sites.
- Therefore, more small pores remain uncemented.



Combined Equal Growth and Nucleation



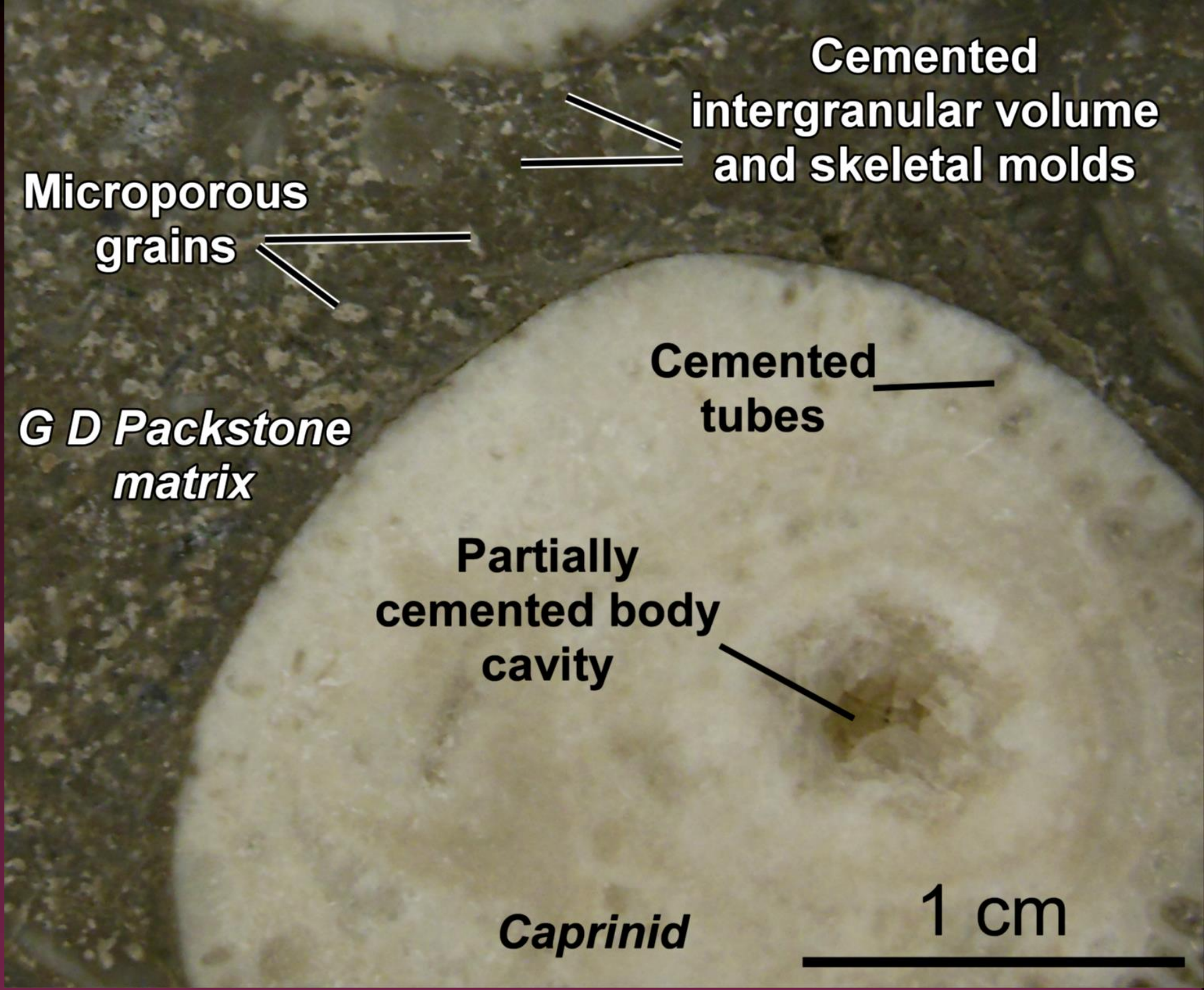
Constant rates.

Nucleation rate: 10 nuclei/cm^2/My

Growth rate: 0.03 mm/My

- Some larger vug pores are still porous due to incomplete cementation.
- Smaller interparticle pores selectively preserved due to less nucleation.
- Almost all micropores are preserved due to low nucleation rate.

Pawnee Field Porosity Preservation



Caprinid floatstone, Schroeder #1, 14064 ft.

- Minor porosity (vugs) in partially cemented, caprinid-body cavity.
- Smaller caprinid pores cemented by calcite.
- All sand-sized molds and IGV are calcite-cemented (dark).
- Initially microporous grains retain microporosity (light).

Nucleation Controlled Cementation

- Nucleation model with relatively simple, reasonable assumptions explains size-selective porosity preservation in Pawnee Field reservoir samples.
- Vugs:
  - Incompletely cemented primary intragranular voids.
  - Porosity is preserved where initial void size exceeds cement thickness.
- Micropores:
  - Porosity is preserved because pores are sufficiently small to have low probability of nucleation. Without nucleation, cements cannot grow.
- Sand-sized molds and IGV:
  - Porosity is essentially completely lost due to size sufficiently large for nucleation and sufficiently small for complete cementation.

Application of Nucleation-Controlled Porosity Model

- Sandstones:
  - Narrow range of initial pore sizes = less deviation from equal cementation model because most pores will be nucleated.
  - Growth-rate dominated: relatively simple prediction of average porosity by quartz cementation modeling.
- Carbonates:
  - Wide range of early diagenetic pore sizes = significant effect of nucleation and growth rates on cementation patterns and overall cement volume.
  - Difficult to predict average limestone porosity by simple-equal-calcite-cementation rate models during burial.
  - Micropores between microrhombs have high preservation potential in settings with low nucleation rates, such as the burial environment.

Conclusions

- Ostwald ripening is not responsible for the well sorted crystal sizes in microrhombic limestone.
- Surface energy effects on growth rates, such as those proposed by Emmanuel et al. (2007, 2010) are not likely to selectively preserve porous microrhombic fabrics in limestone.
- Nucleation limits cementation in small pores and is the most likely reason for preservation of porous microrhombic fabrics in the Pawnee field reservoir.

Acknowledgements

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