Direct Evidence That Well-Ordered, Stoichiometric (Ideal) Dolomites are the Product of Recrystallization*

Stephen E. Kaczmarek[1], and Duncan F. Sibley[2]

Search and Discovery Article #50693 (2012)**
Posted August 20, 2012

*Adapted from oral presentation at AAPG Annual Convention and Exhibition, Long Beach, California, April 22-25, 2012

[1]Geological Sciences, Bridgewater State University, Bridgewater, MA (stephen.kaczmarek@bridgew.edu)
[2]Geological Sciences, Michigan State University, East Lansing, MI

Abstract

Geochemical, structural, and mineral surface data from a broad assemblage of synthetic and natural dolomites suggest that stoichiometric and well ordered (ideal) dolomites form through recrystallization of a nonstoichiometric and/or poorly ordered (nonideal) dolomite precursor. Synthetic dolomite is formed by replacement of calcite in Mg-Ca-Cl fluids at high-temperature (>200°C). The first synthetic dolomites to form are invariably poorly ordered with stoichiometries that strongly reflect the initial Mg/Ca of the fluids. Near reaction completion, when calcite reactants are nearly consumed (>95% dolomite), nonideal dolomite is rapidly replaced by a stoichiometric and relatively well-ordered, ideal dolomite.

Scanning electron (SEM) and atomic force microscope (AFM) observations of synthetic dolomite crystal surfaces reveal that nonideal dolomites are covered with round growth mounds and ideal dolomite surfaces are characterized by flat growth layers separated by elongate steps. When synthetic dolomite crystals are etched in dilute acid, the surfaces of nonideal dolomites remain covered with rounded mounds, whereas ideal dolomites are characterized by flat layers with deep, euhedral etch pits. Comparable surface features are also observed on the surfaces of natural dolomite crystals. Chemically etched nonideal dolomite crystal surfaces have mounds and ideal dolomite crystal surfaces are characterized by flat surfaces with euhedral etch pits.

Mineral surface textures, integrated with dolomite stoichiometry and cation order data, are consistent with a stepwise growth model in which nonideal dolomite first forms by precipitation of growth mounds, and ideal dolomite forms by a spiral growth mechanism only through replacement of a nonideal dolomite precursor. Because layers and etch pits dominate the surfaces of etched ideal dolomites, and ideal dolomites form by replacement of a nonideal dolomite precursor, flat layers with euhedral etch pits are interpreted as direct

physical evidence of recrystallization. An independent evaluation of recrystallization in natural dolomites is valuable because geochemical data are commonly used to interpret the chemistry of dolomitizing fluids. If recrystallization can be established using an independent test, chemical analyses can be more accurately interpreted as to whether they reflect the original dolomitizing fluid or later diagenetic solutions.

Selected References

Kaczmarek, S.E., 2005, Crystal growth mechanisms in natural and synthetic dolomite; insight in dolomitization kinetics: Ph.D. dissertation, Michigan State University, Dept. of Geological Sciences, 230 p.

Kaczmarek, S.E., and D.F. Sibley, 2011, On the evolution of dolomite stoichiometry and cation order during high temperature synthesis experiments; an alternative model for the geochemical evolution of natural dolomites: Sedimentary Geology, v. 240/1-2, p. 30-40.

Kaczmarek, S.E., and D.F. Sibley, 2007, A comparison of nonometer-scale growth and dissolution features on natural and synthetic dolomite crystals; implications for the origin of dolomite: JSR, v. 77/5, p. 424-432.

Kupecz, J.A., and L.S. Land, 1995, Progressive recrystallization and stabilization of early-stage dolomite; Lower Ordovician Ellenburger Group, West Texas, *in* B. Purser, M. Tucker, and D. Zenger, (eds.), Dolomites; a volume in honour of Dolomieu: Special Publication of the International Association of Sedimentologists, v. 21, p. 255-279.

Machel, H.G., 1997, Recystallization versus neomorphism, and the concept of “significant recrystallization” in dolomite research: Sedimentary Geology, v. 113/3-4, p. 161-168.

Direct Evidence that Well Ordered, Stoichiometric (Ideal) Dolomites are the Product of Recrystallization

Stephen E. Kaczmarek[1] and Duncan F. Sibley[2]
Bridgewater State University, Department of Geological Sciences
Michigan State University, Department of Geological Sciences

BRIDGEWATER STATE UNIVERSITY

MICHIGAN STATE UNIVERSITY

The Problem

"One of the most vexing problems in dolomite research is to determine whether the textures and compositions of replacive dolomites represent the conditions of their formation, or whether the present textures and geochemical compositions represent merely the last of possibly several episodes of recrystallization."

Machel (1997, *Sed. Geol.*)

Dolomite Recrystallization

"Some studies of dolomite have suggested that present-day geochemical signatures are the product of recrystallization, not original precipitation."

-Land et al. 1975, Zenger 1981, Gregg & Sibley 1984, Banner et al. 1988, Dorobek & Filby 1988, Moore et al. 1988, Zenger & Dunham 1988, Montanez & Read 1992, and many others.

Kupecz & Land (1994, *IAS Spec. Pub. 21*)

Lack of Direct Physical Evidence

- Without direct physical evidence of recrystallization, we have a circular argument…

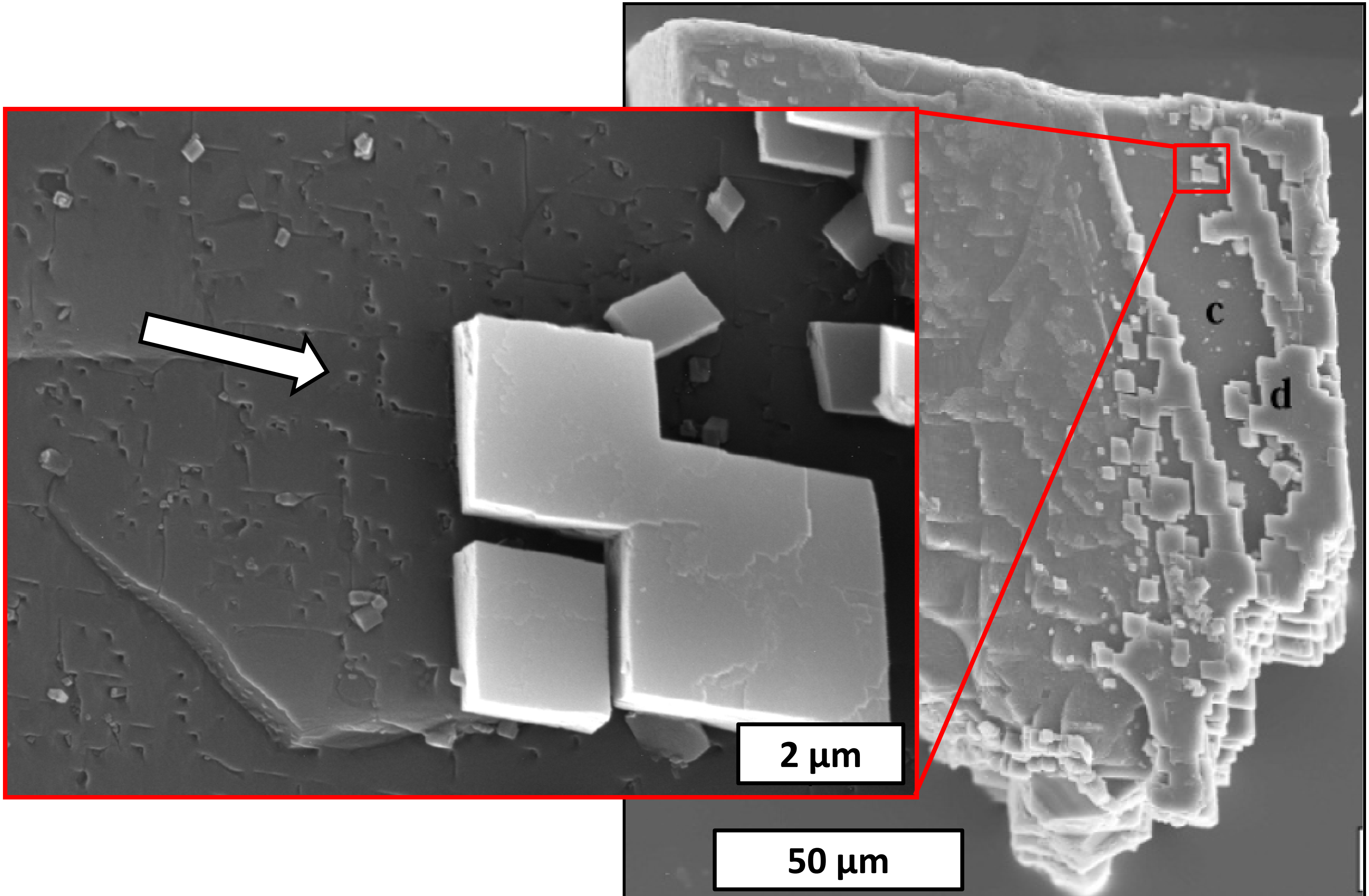
"If the chemical signature of a dolomite appears primary, we can use the chemical signature to interpret the composition of the original dolomitizing fluid."

High Temperature Dolomite Synthesis

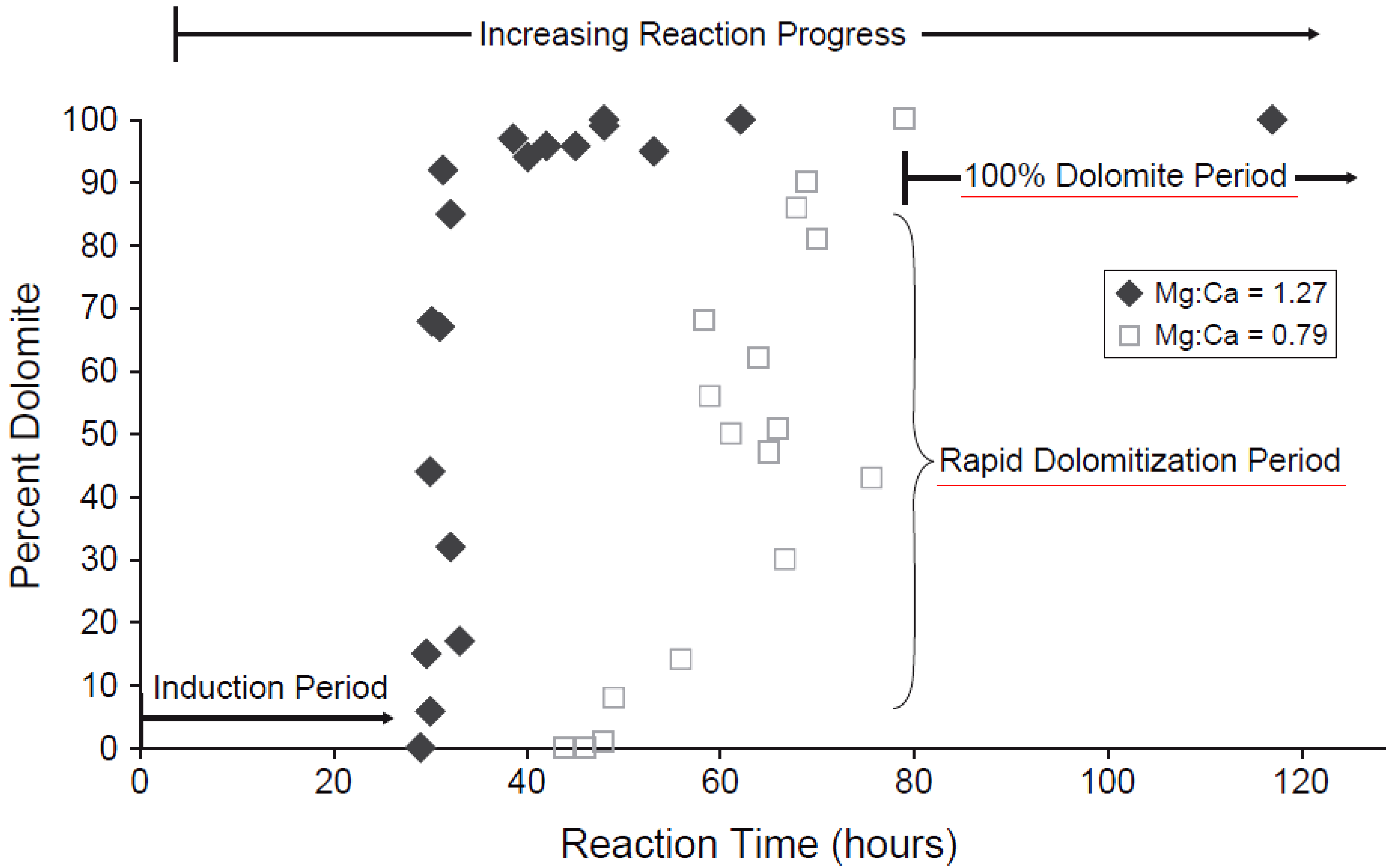
Replacement Reaction

$$Mg^{2+} + 2CaCO_3 \longrightarrow CaMg(CO_3)_2 + Ca^{2+}$$

Dissolution-Reprecipitation Reaction



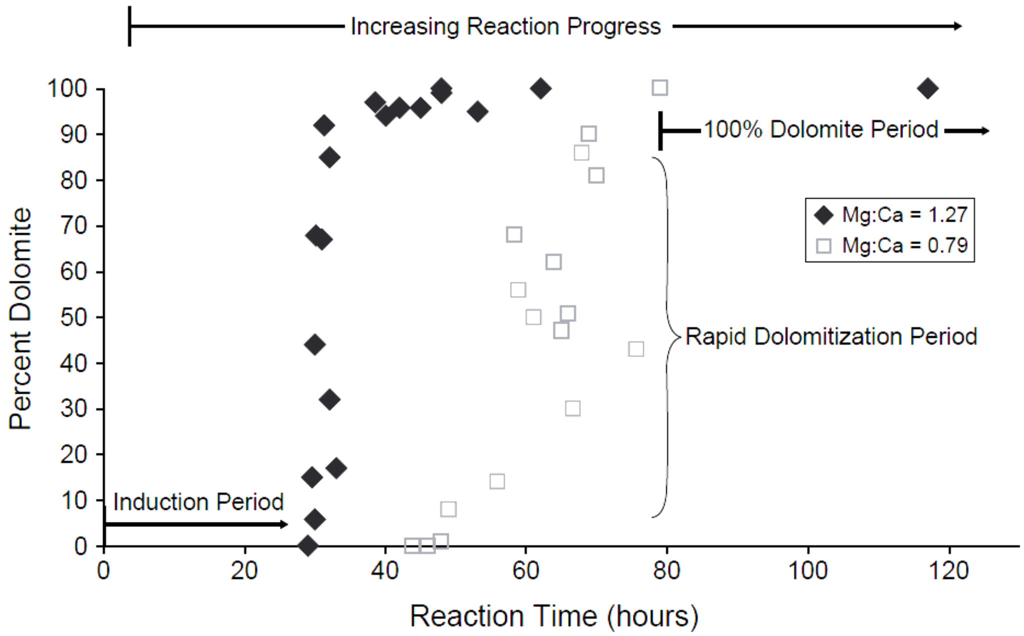
Kaczmarek & Sibley (2007, *J. Sed. Res.*)

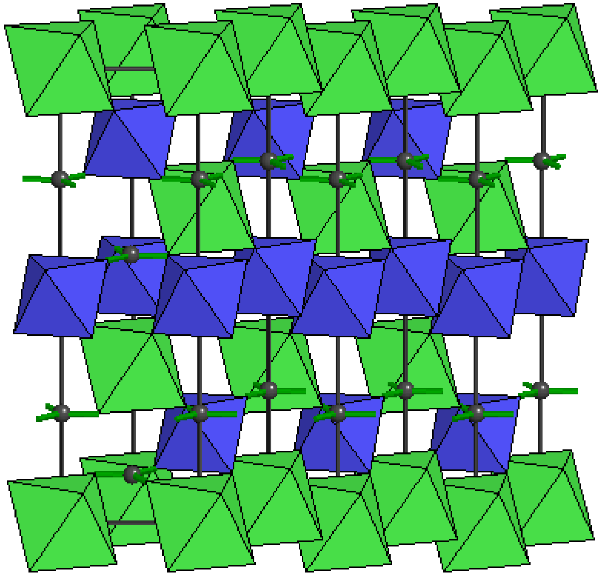


Kaczmarek & Sibley (2011, *Sed. Geol.*)

Nonideal & Ideal Dolomite

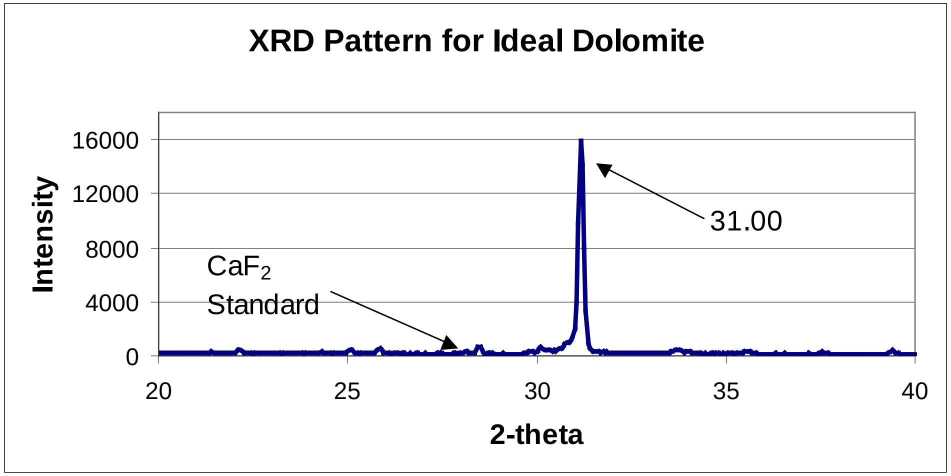
- Stoichiometry & Cation Order
- Composition – Ingredients
- Arrangement – Recipe

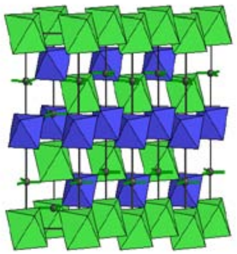


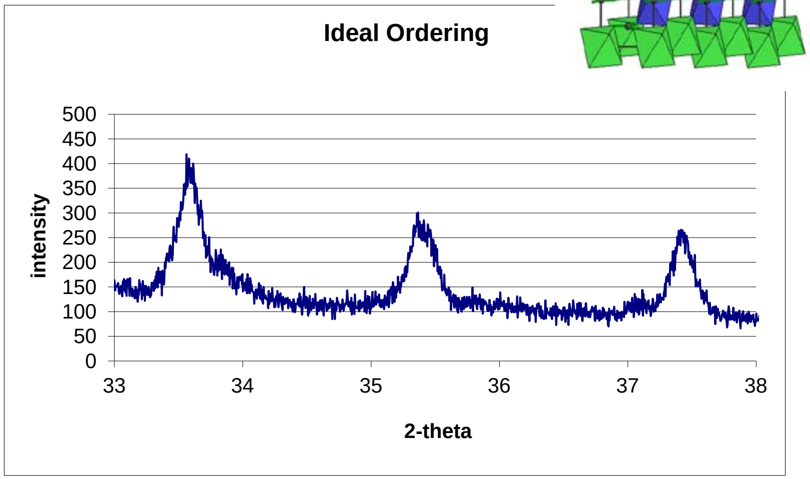


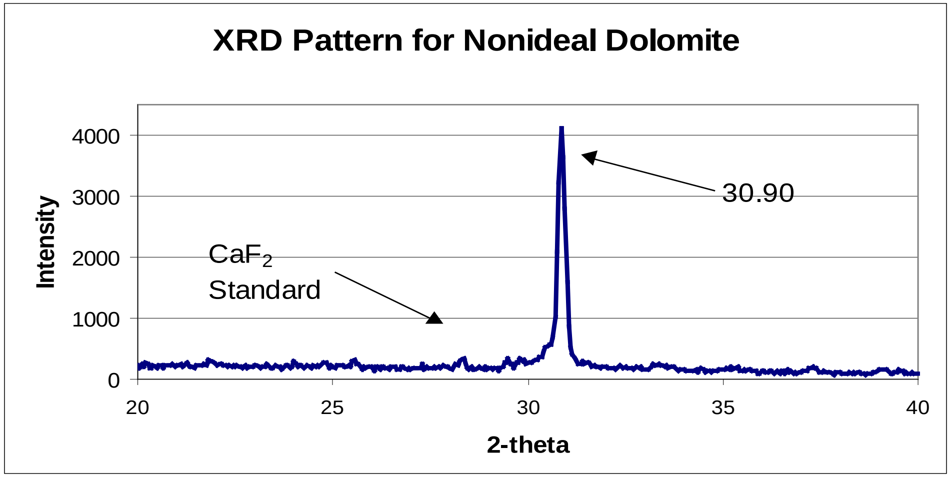
Smyth *(U. Colorado)*

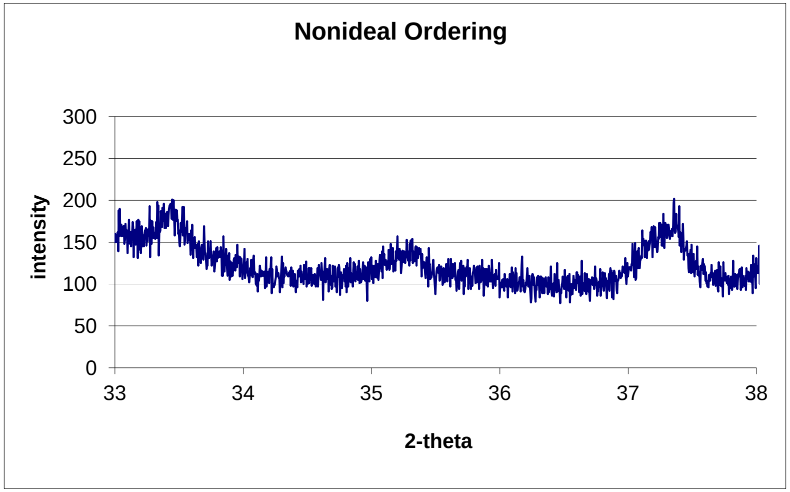
X-Ray Diffraction





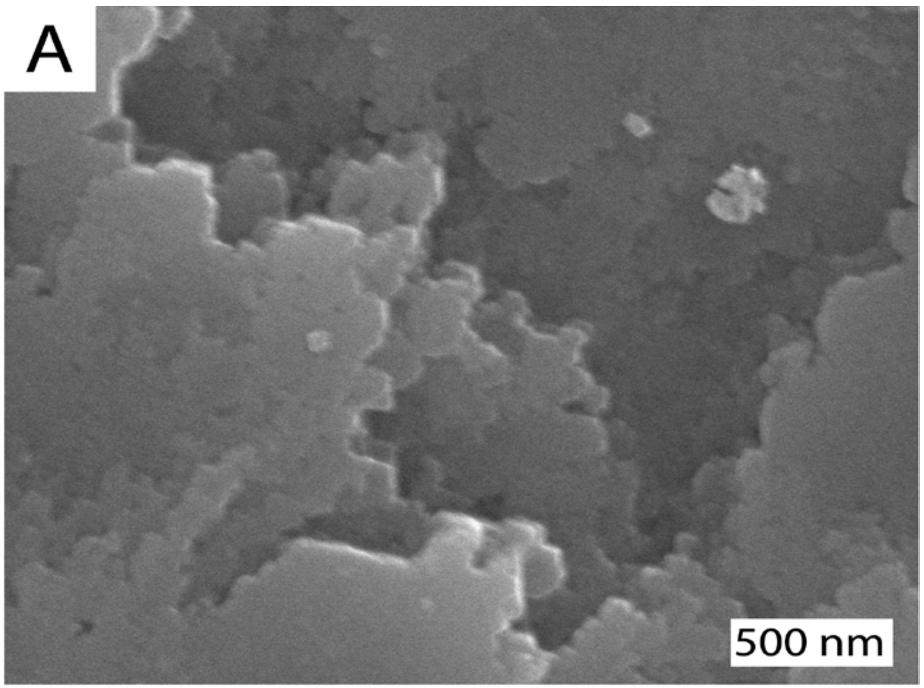




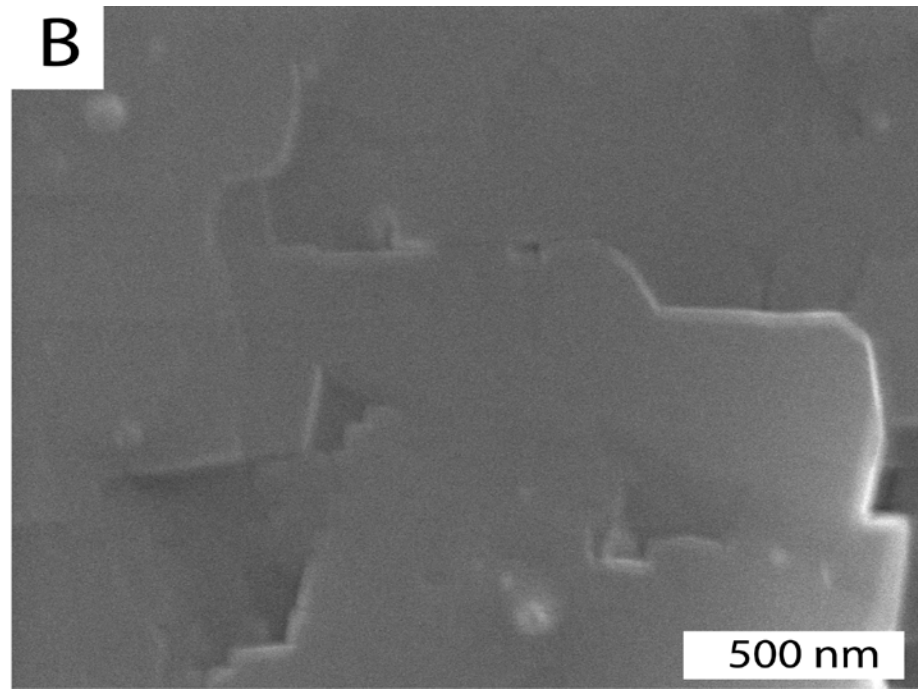


Surface Topography

Nonideal Synthetic Dolomite

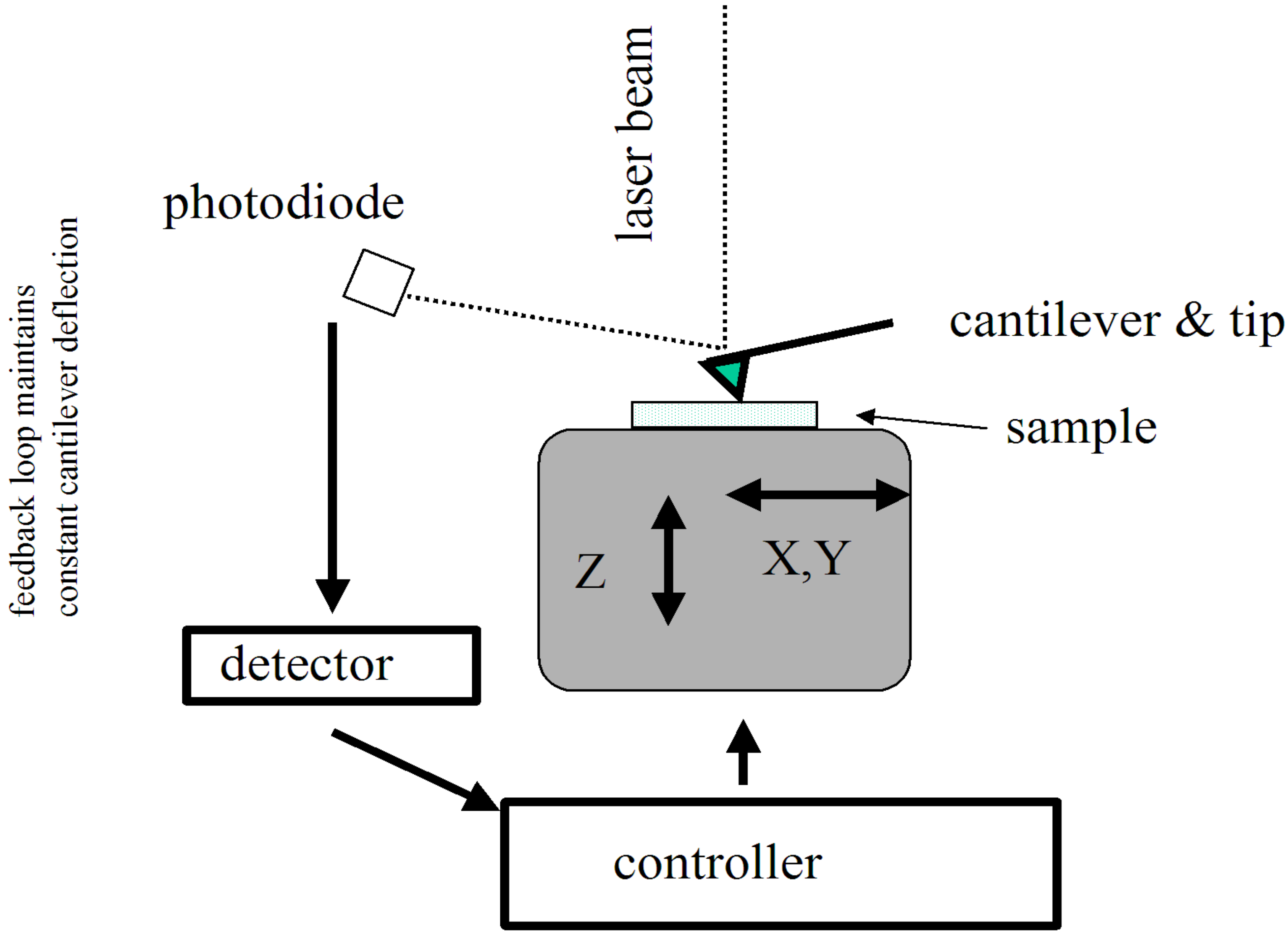


Ideal Synthetic Dolomite



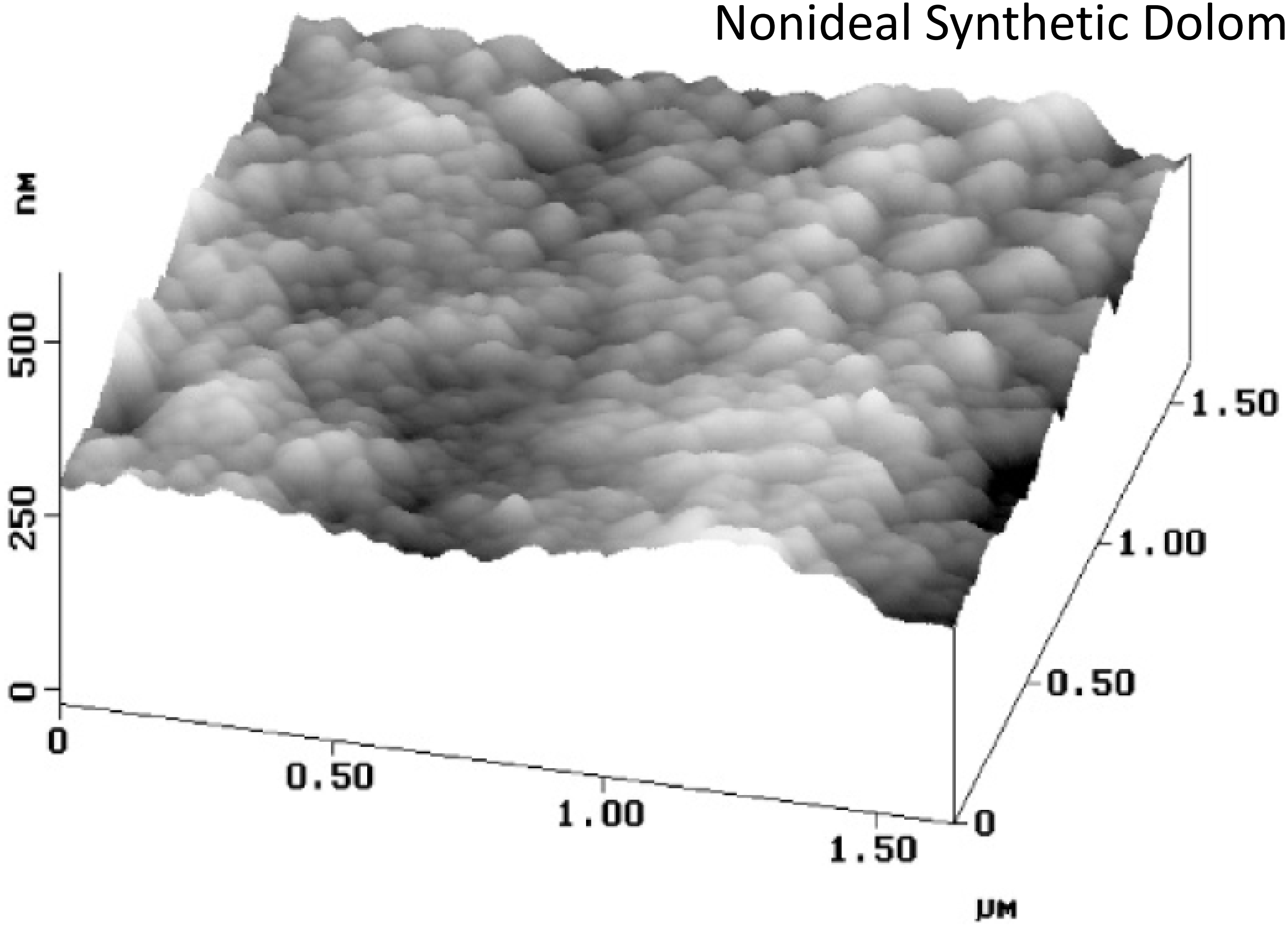
Kaczmarek & Sibley (2007, *J. Sed. Res.*)

AFM – Atomic Force Microscope



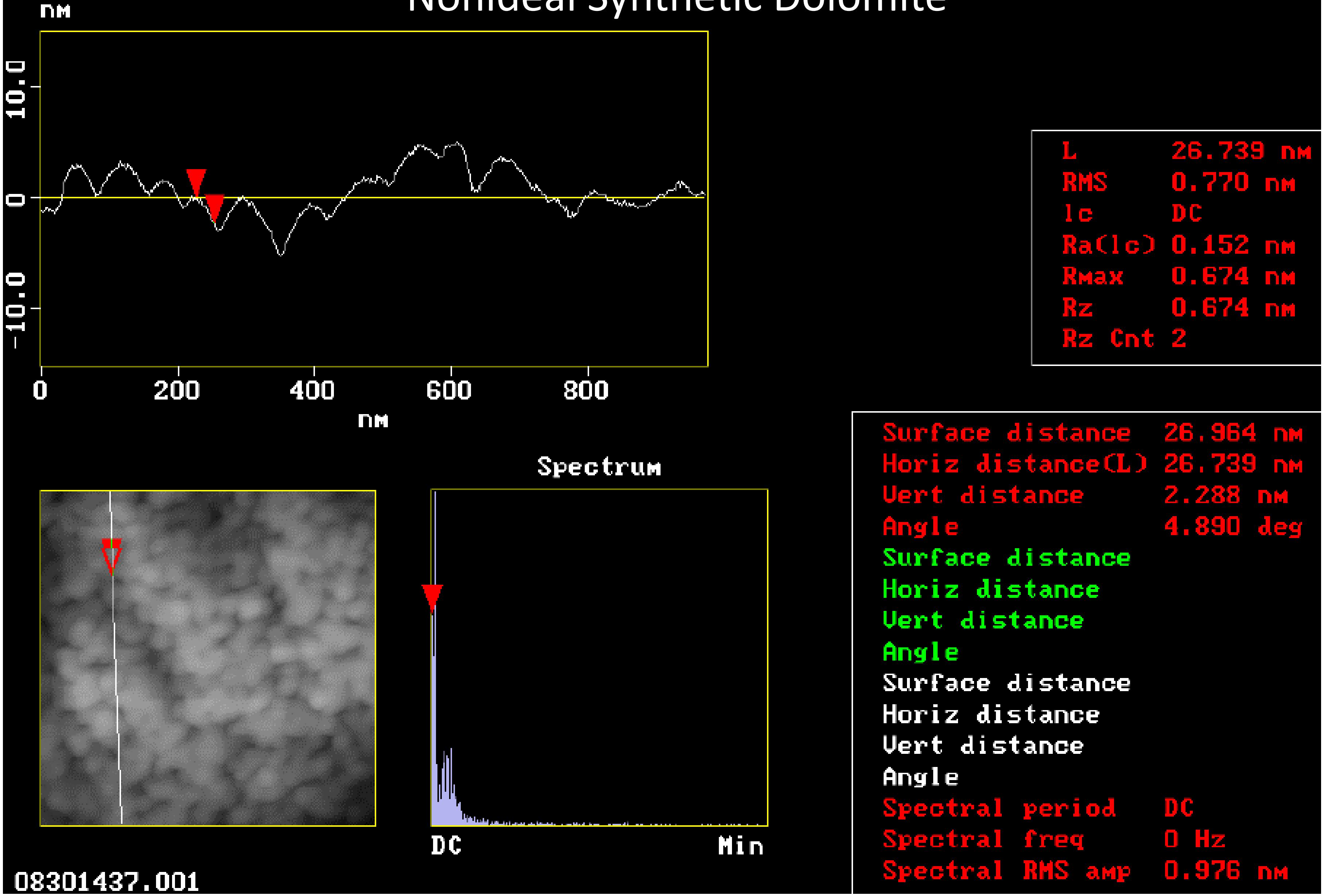
Surface Nanotopography

Nonideal Synthetic Dolomite

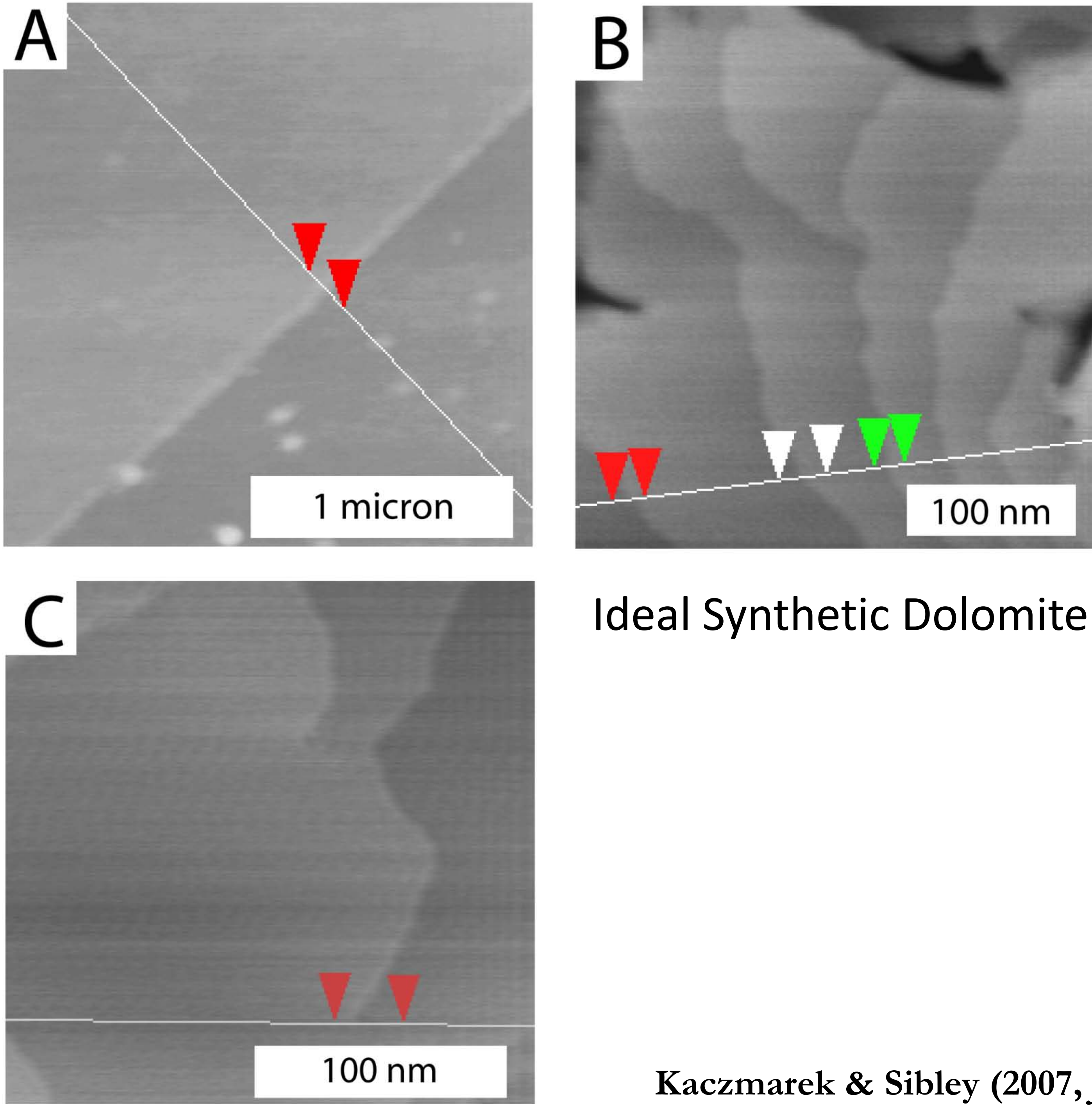


Kaczmarek & Sibley (2007, *J. Sed. Res.*)

Nonideal Synthetic Dolomite



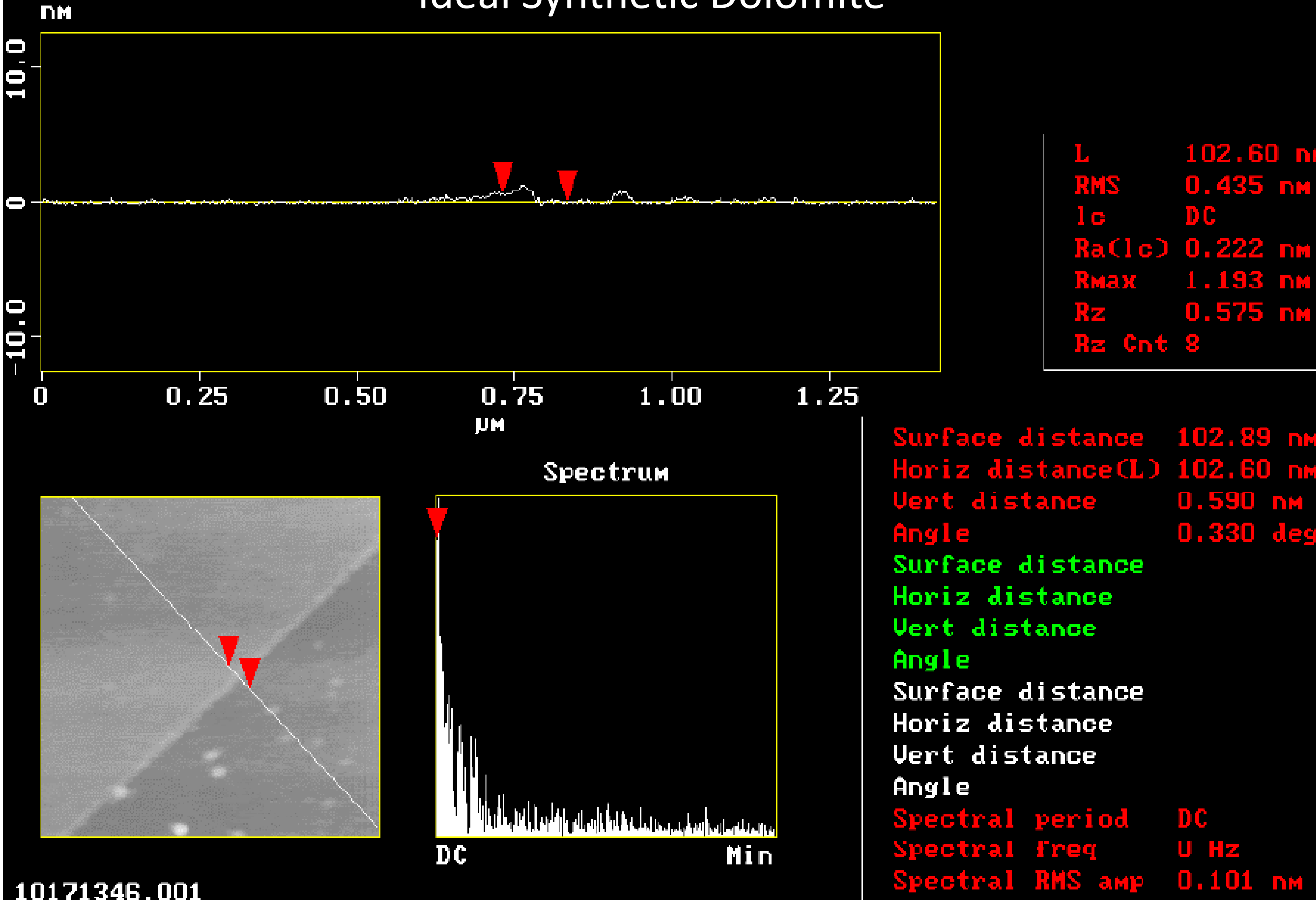
Kaczmarek (2005)



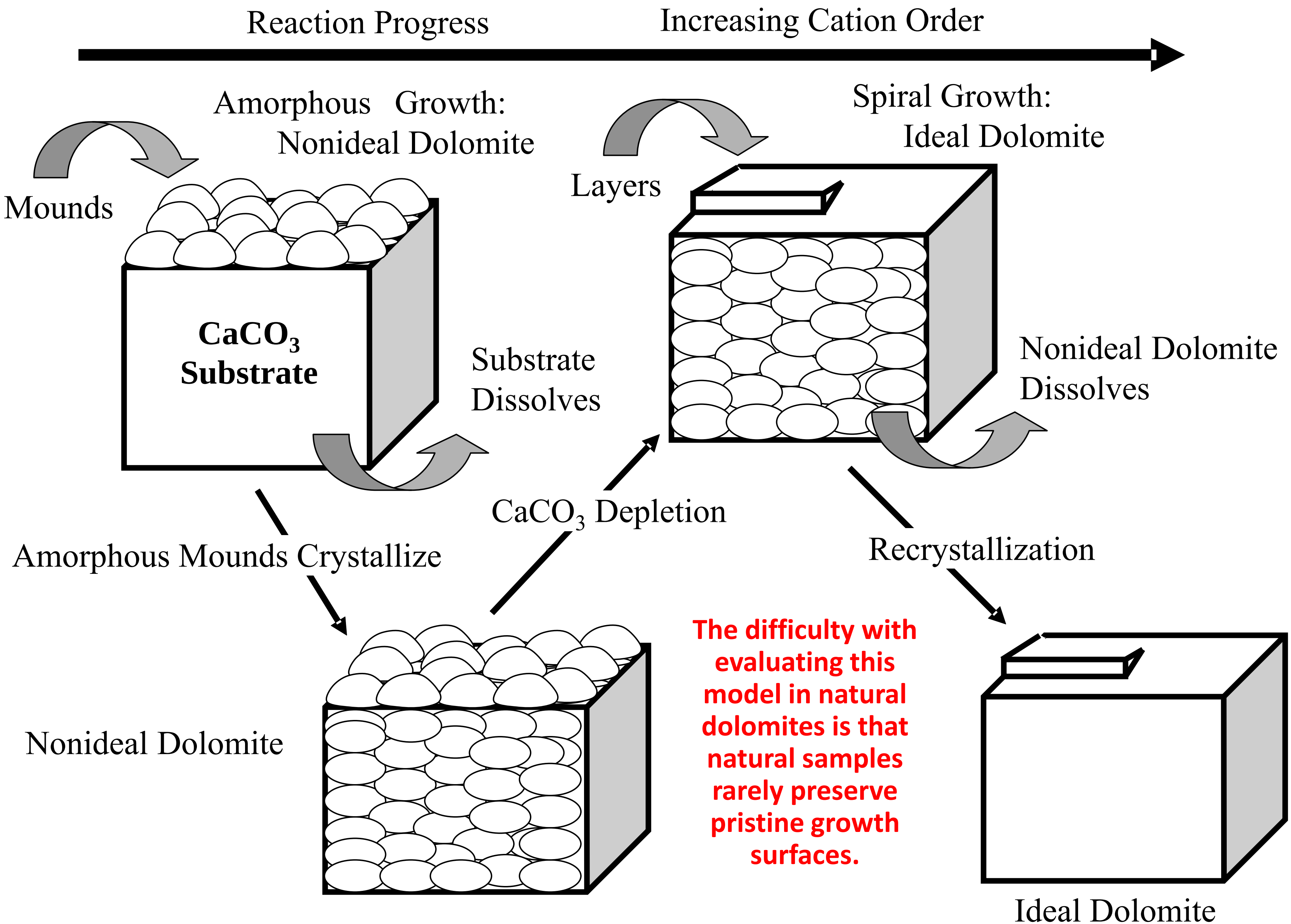
Ideal Synthetic Dolomite

Kaczmarek & Sibley (2007, *J. Sed. Res.*)

Ideal Synthetic Dolomite



Kaczmarek (2005)

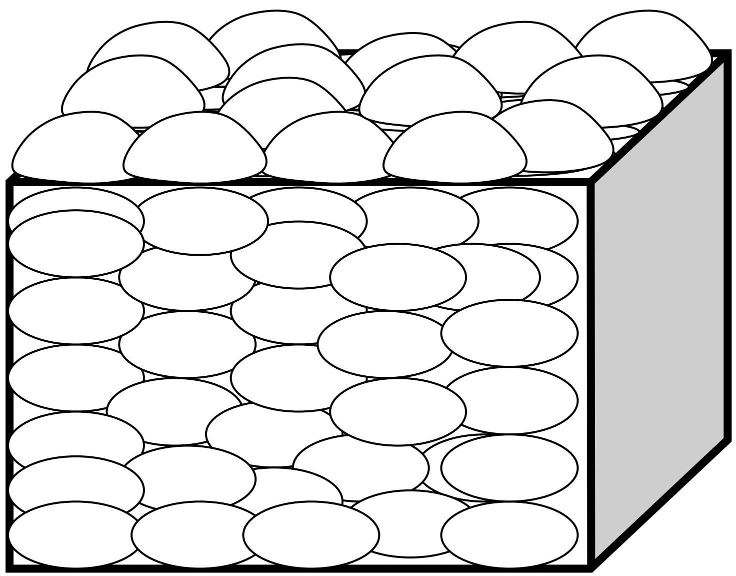


The difficulty with evaluating this model in natural dolomites is that natural samples rarely preserve pristine growth surfaces.

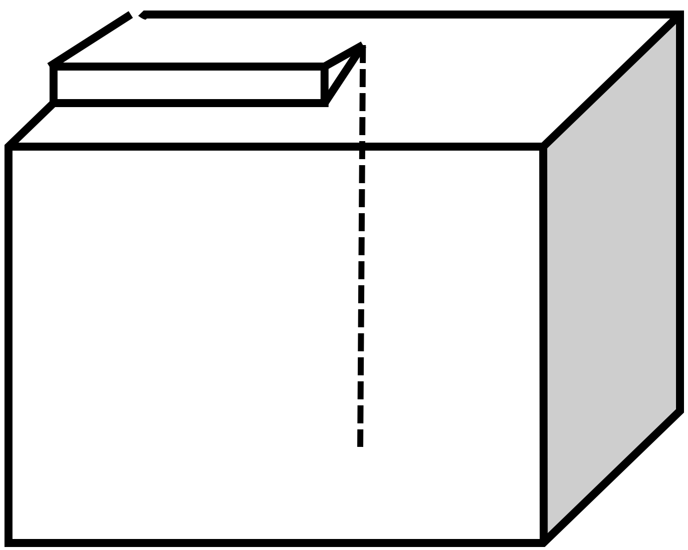
Kaczmarek (2005)

Chemical Etching Experiments

- Attacks chemical and structural imperfections incorporated into crystal during growth



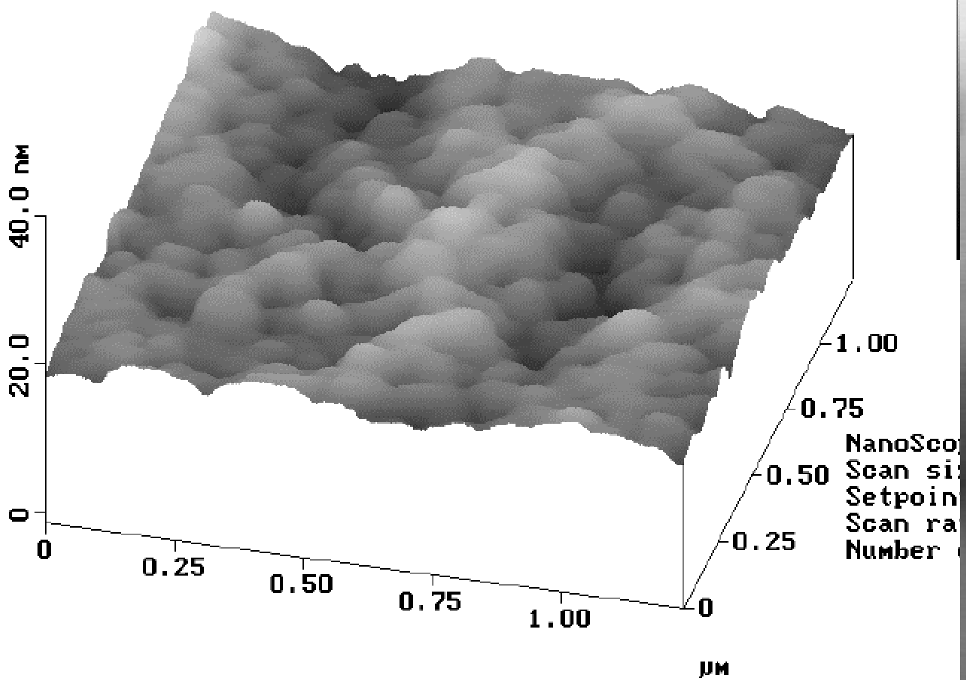
Growth mounds have interfacial free energy (like surface tension between soap bubbles)



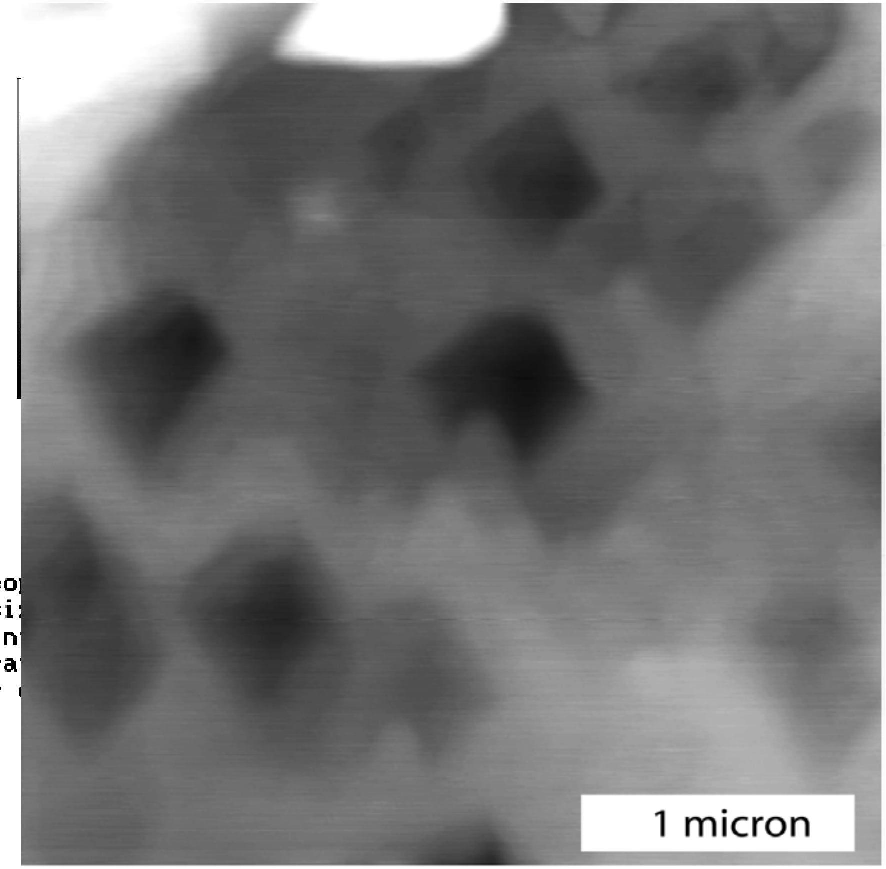
Dislocations produce strain in the crystal lattice (like a loaded spring)

Chemically Etched Synthetic Dolomite

Nonideal Synthetic Dolomite

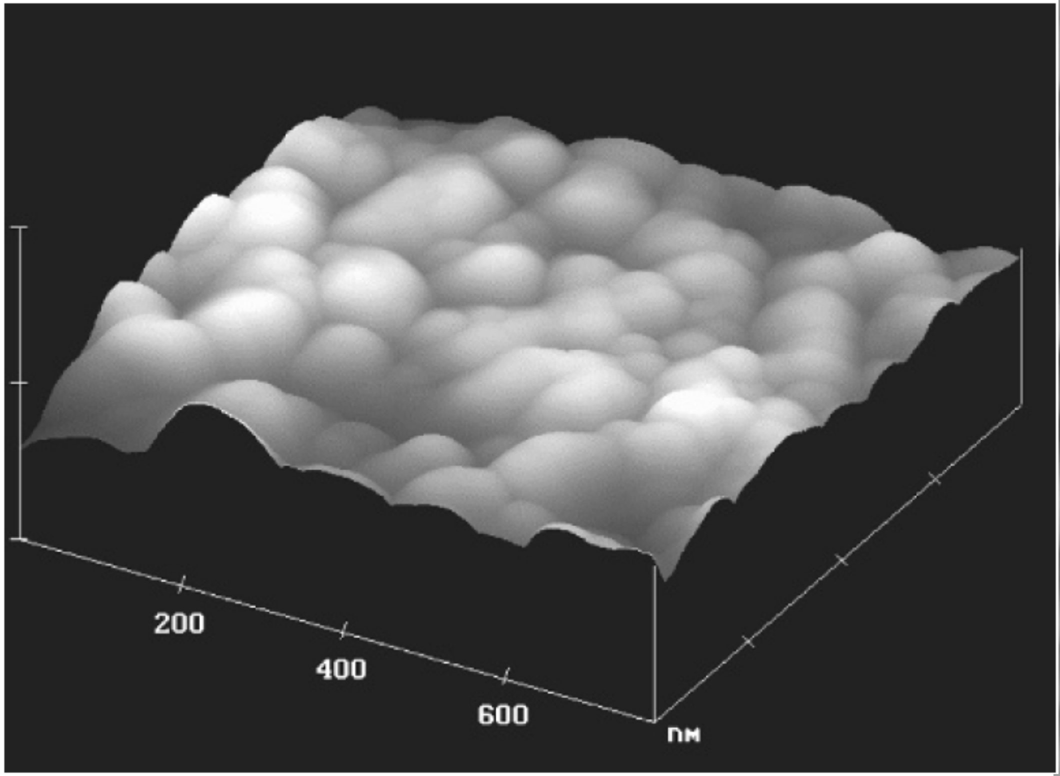


Ideal Synthetic Dolomite

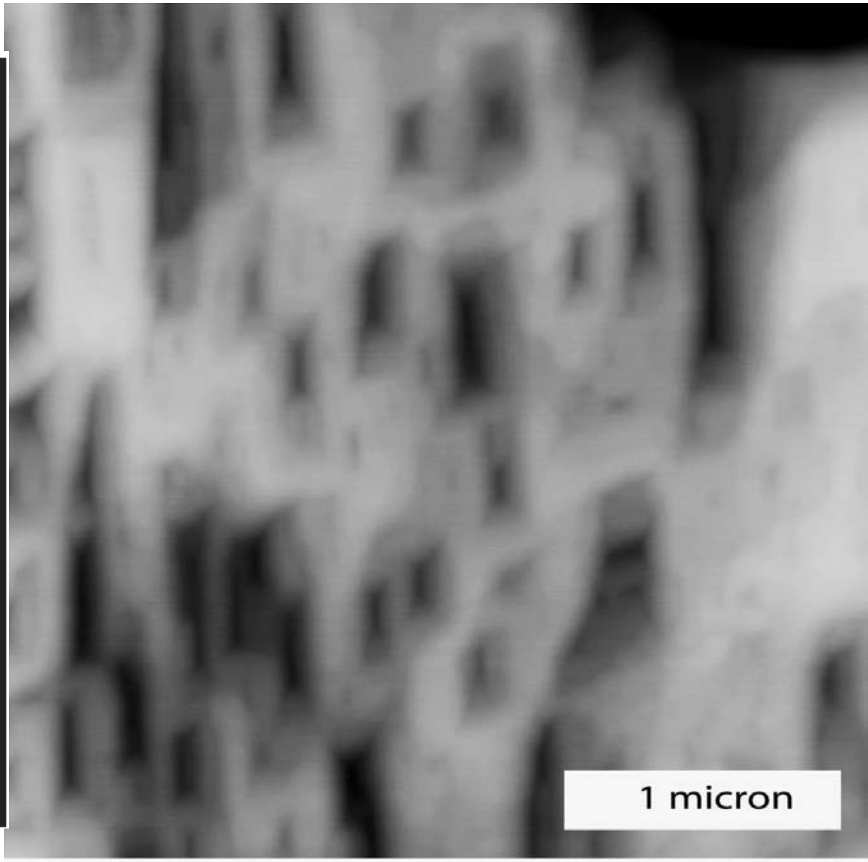


Chemically Etched Natural Dolomite

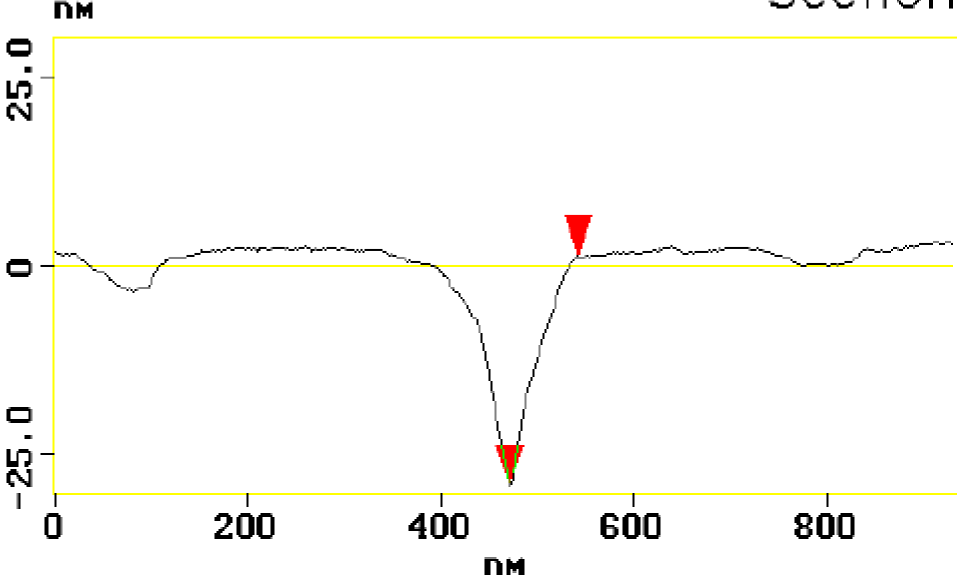
Nonideal Natural Dolomite



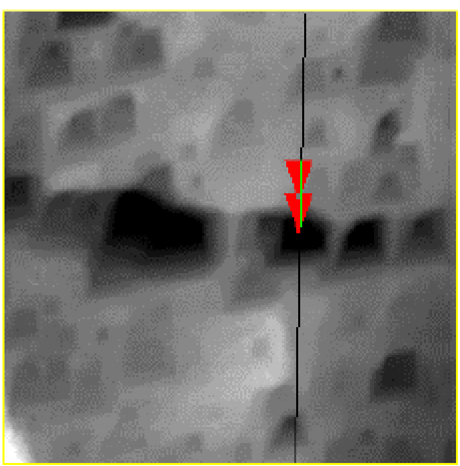
Ideal Natural Dolomite

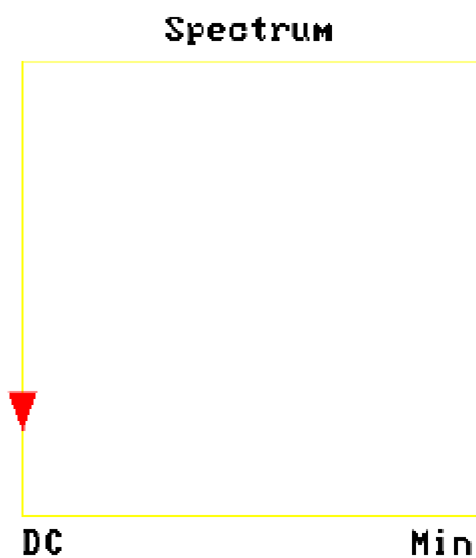


Section Analysis



L	71.244 nm
RMS	9.259 nm
lc	DC
Ra(lc)	1.368 nm
Rmax	5.777 nm
Rz	5.777 nm
Rz Cnt	2

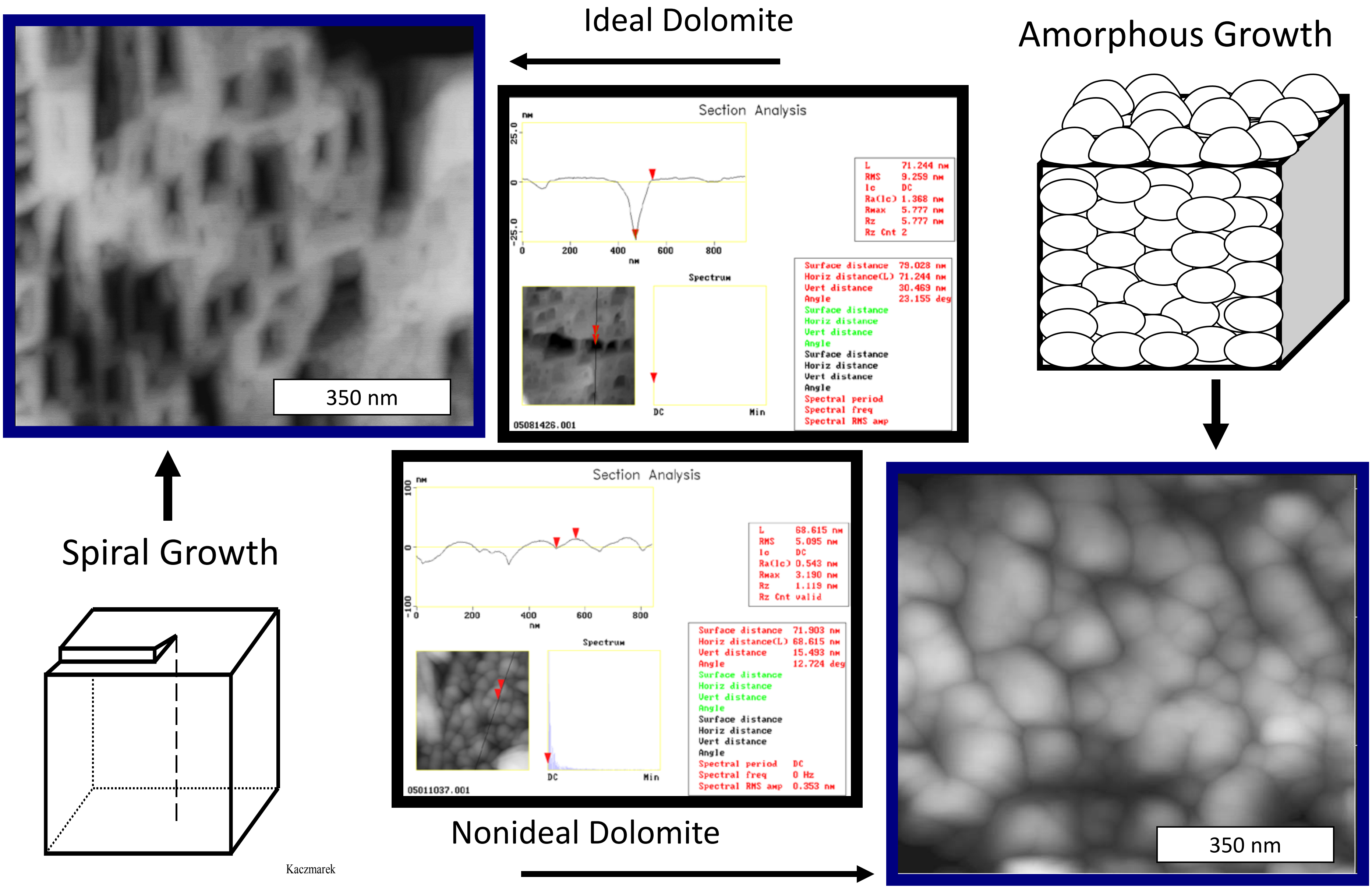




05081426.001

Surface distance	79.028 nm
Horiz distance(L)	71.244 nm
Vert distance	30.469 nm
Angle	23.155 deg
Surface distance	
Horiz distance	
Vert distance	
Angle	
Surface distance	
Horiz distance	
Vert distance	
Angle	
Spectral period	
Spectral freq	
Spectral RMS amp	

11 Formations - Ordovician to Cenozoic



Conclusions

- Synthetic dolomite grows by same mechanisms as natural dolomite
- Stepwise Replacement Growth Model
  - Nonideal Dolomite rapidly replaces calcite
    - Mound Growth
  - Ideal Dolomite more slowly replaces nonideal dolomite
    - Layers/Spiral Growth

Conclusions

- Etch pits are evidence for layer/spiral growth in ideal dolomite
- Layer/spiral growth occurs only during replacement of nonideal dolomite precursor
- Etch pits are direct physical evidence of recrystallization in ideal dolomite

Direct Evidence that Well Ordered, Stoichiometric (Ideal) Dolomites are the Product of Recrystallization

Stephen E. Kaczmarek[1] and Duncan F. Sibley[2]

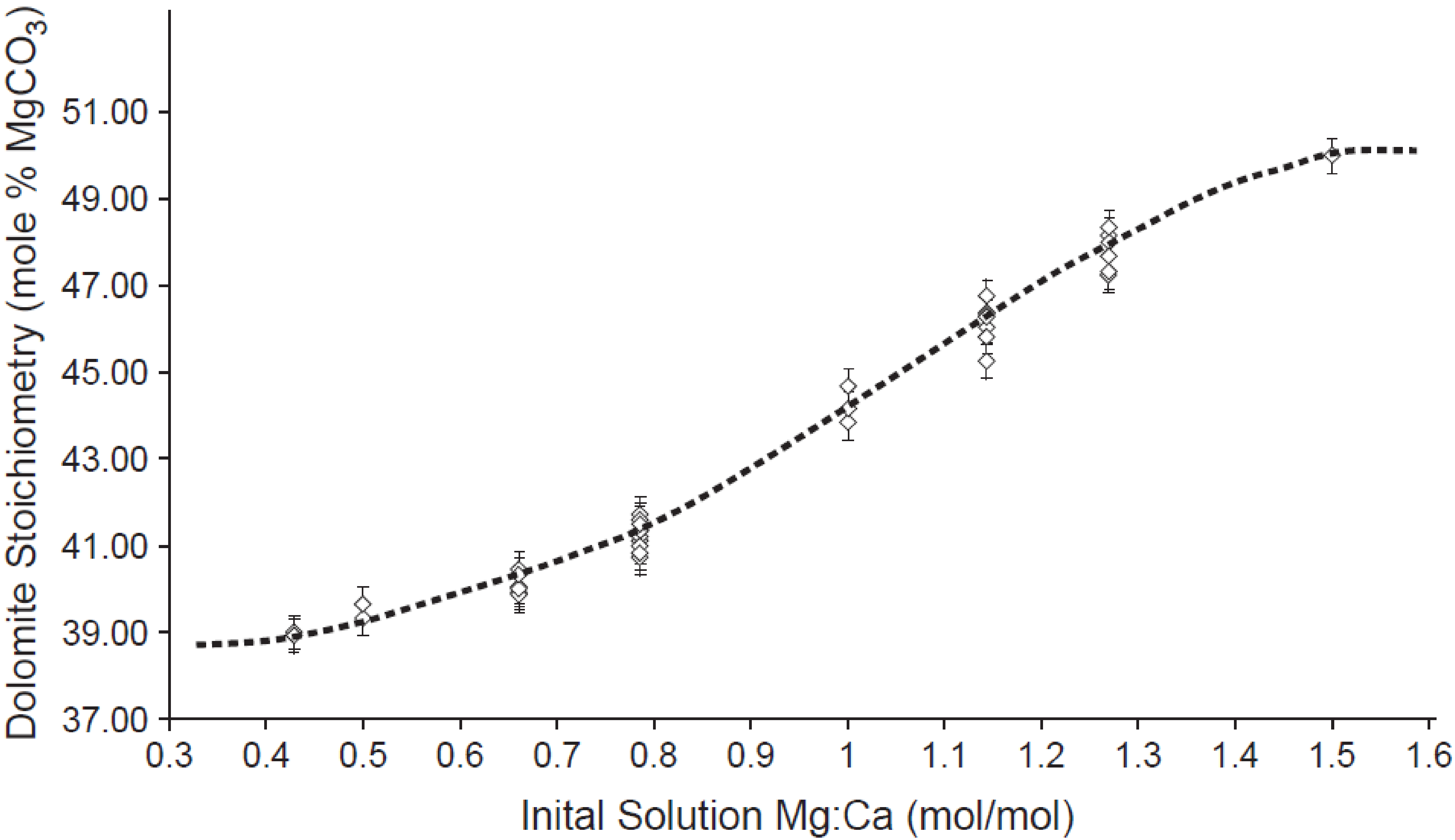
Bridgewater State University, Department of Geological Sciences

Michigan State University, Department of Geological Sciences

BRIDGEWATER STATE UNIVERSITY

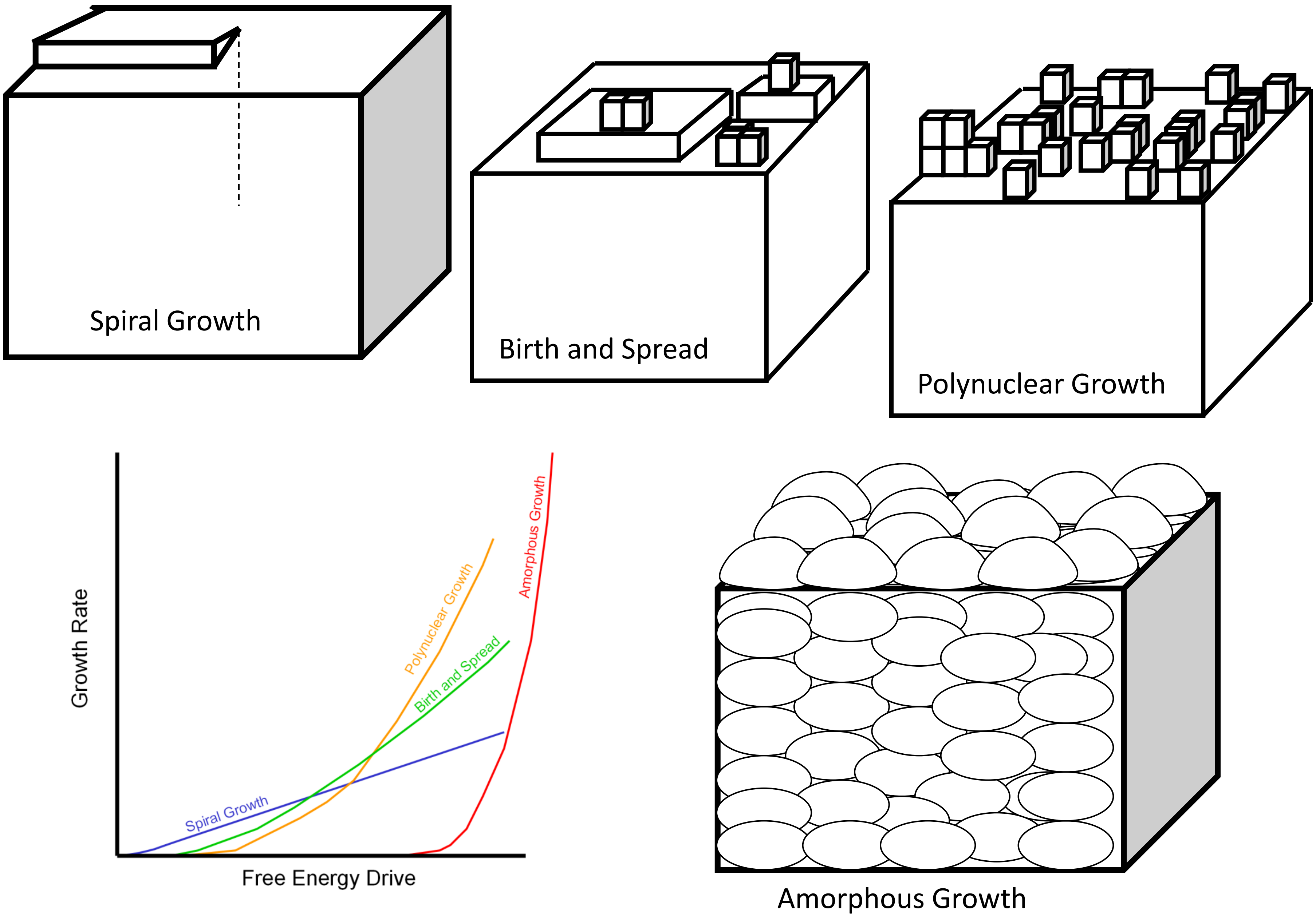
MICHIGAN STATE UNIVERSITY

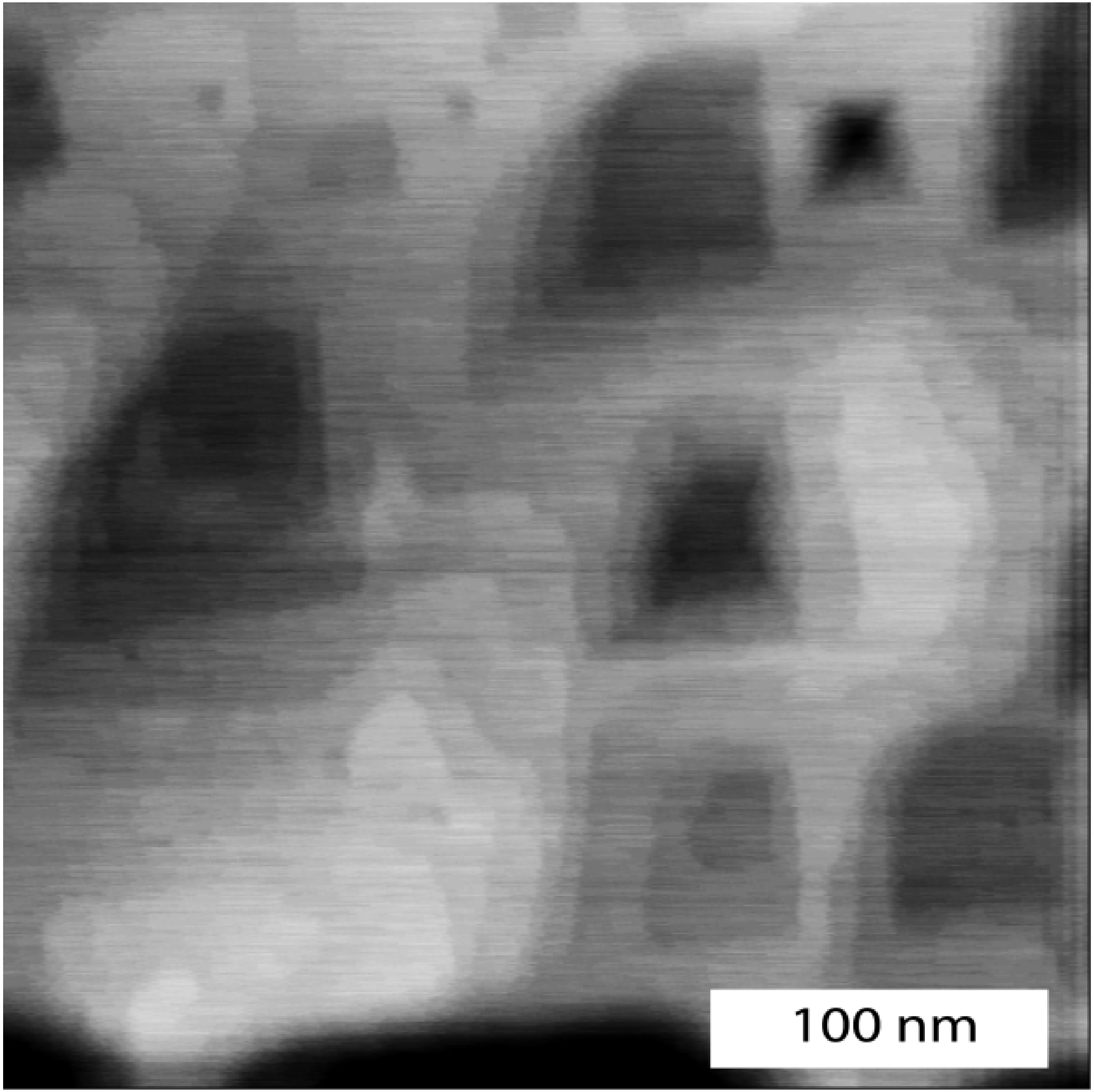
Solution Chemistry & Stoichiometry



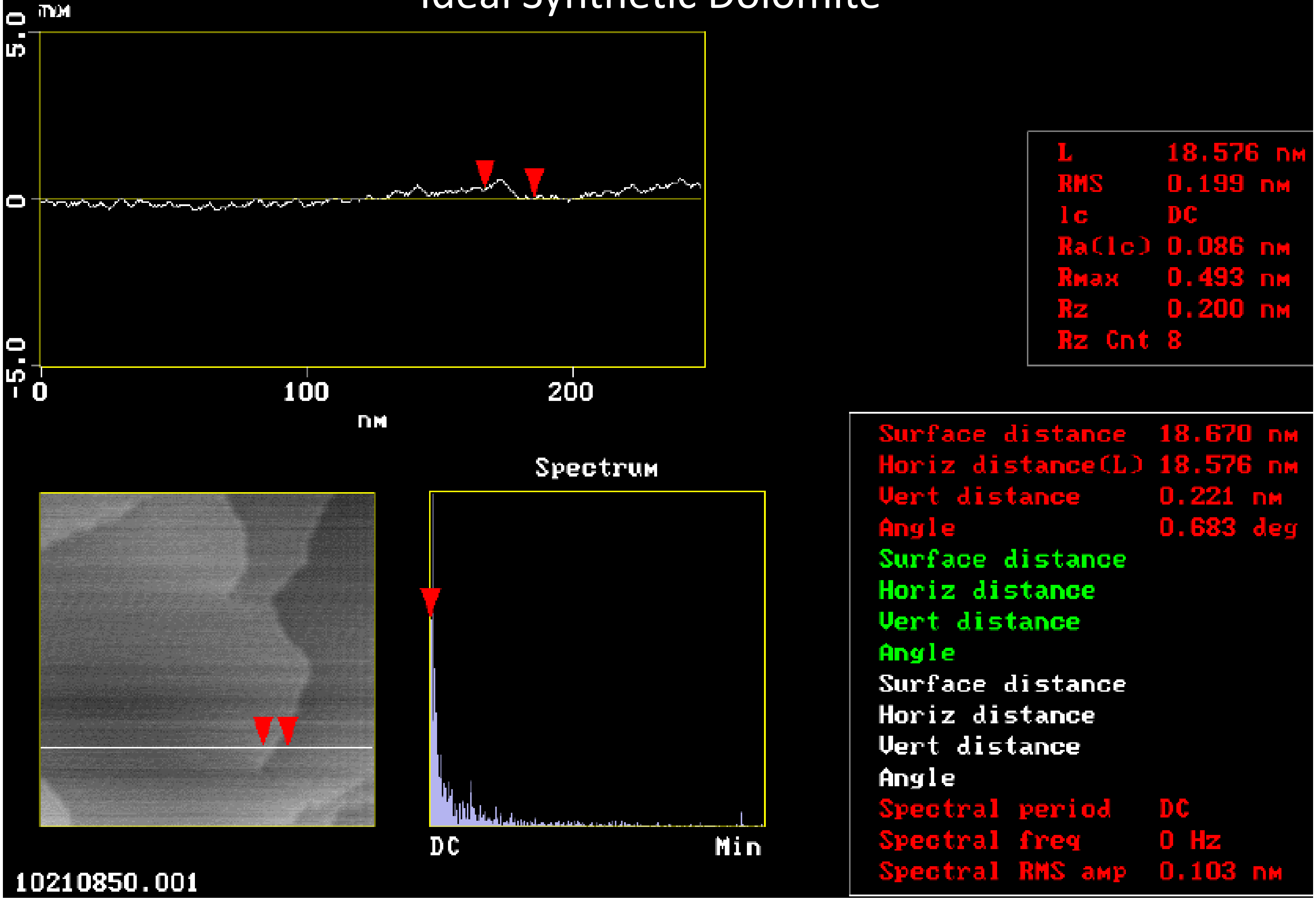
Kaczmarek & Sibley (2011, *Sed. Geol.*)

Crystal Growth Models




100 nm

Ideal Synthetic Dolomite



Kaczmarek & Sibley (2007, *J. Sed. Res.*)

Significant Recrystallization

'Significant recrystallization' is a modification via recrystallization of the original texture, ordering, chemical composition, or magnetic properties that is larger than the original range during dolomite formation. Significant recrystallization is recognized, if recrystallization modified at least one of the above properties to a range larger than the original

Machel (1997, *Sed. Geol.*)