SAND2022-1955C

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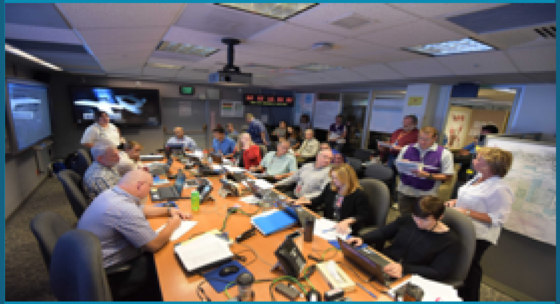
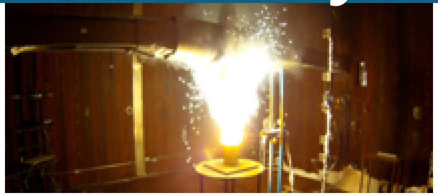
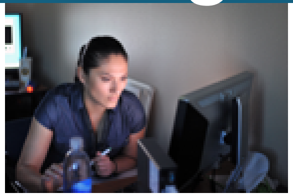
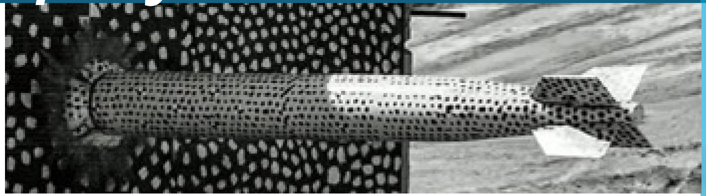
Assessing the evolution of pit growth kinetics during atmospheric corrosion using in-situ X-ray tomography









Philip J. Noell, Michael A. Melia*, Eric J. Schindelholz**, Evangelia Kiosidou**, Erin Karasz*, Andrew Polonsky*, Ian Campbell****

*Sandia National Laboratories, New Mexico

**The Ohio State University

***The University of Washington

Presented by Philip Noell

pnoell@sandia.gov

U.S. DEPARTMENT OF ENERGY — NNSA National Nuclear Security Administration

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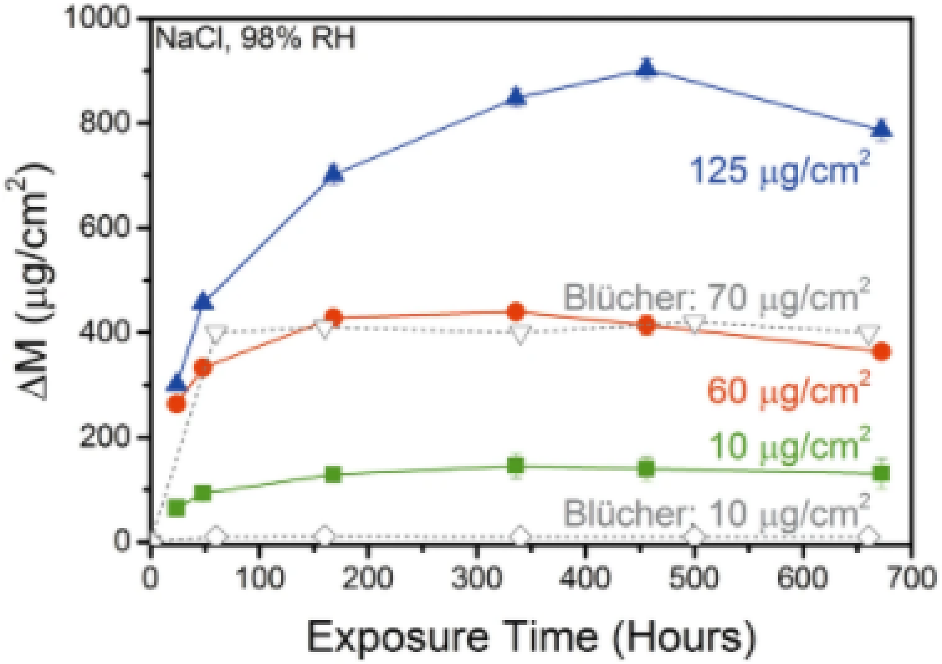
What is the useful lifetime of a component in a humid, chloride environment?

The costs associated with corrosion in the US are estimated at 1-2% of our GDP*. Because we can't monitor corrosion in many applications, we rely on engineering judgement and inspection strategies to mitigate failures.

Long-term damage models are largely empirical in part because we rely on experimental techniques that are largely empirical

Atmospheric test rack from https://www.corrosion-doctors.org/Corrosion-Atmospheric/Corrosion-tests.html



Schaller, R. F., et al. *npj Mat Deg* 2017

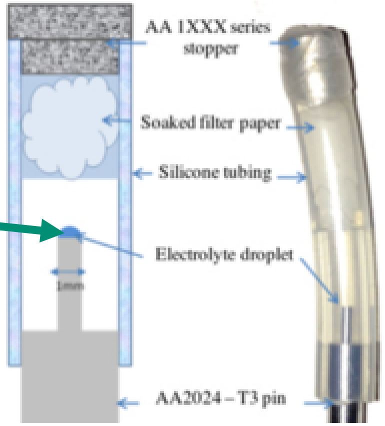
Next generation models need

- Statistical descriptions of the parametric environment-damage relationships and
- A mechanistic understanding of operative processes

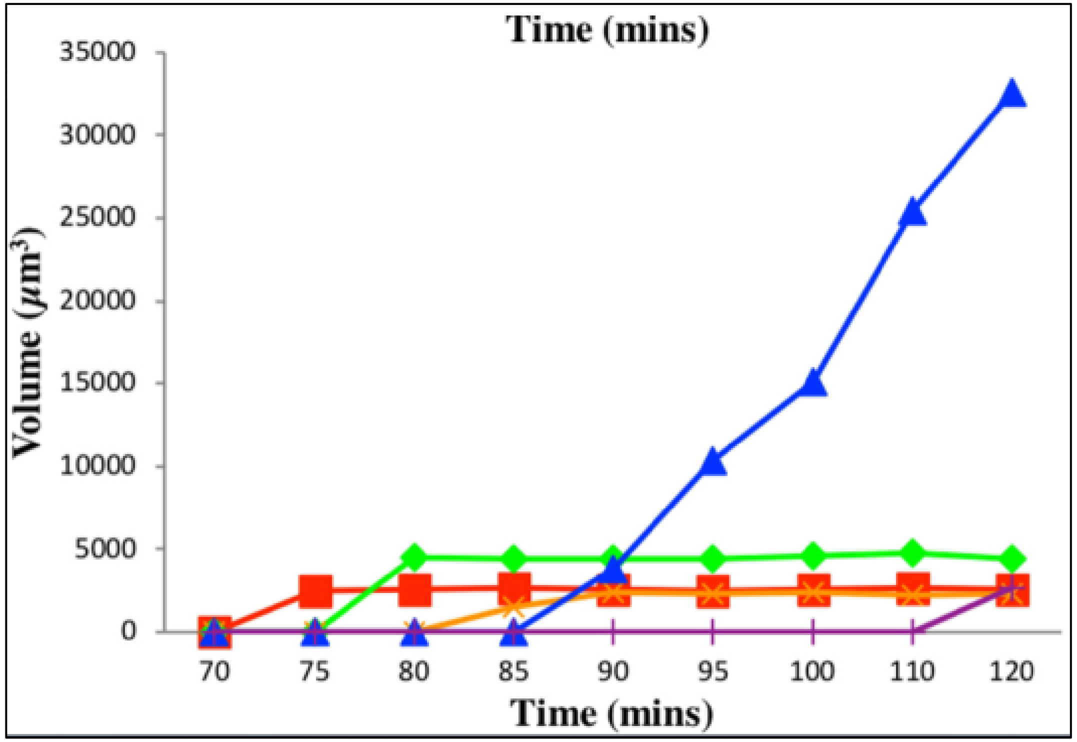
XCT provided such data for models of ductile fracture - can XCT similarly do so for the field of atmospheric corrosion?

* Thompson et al., *Corrosion Reviews,* 2007

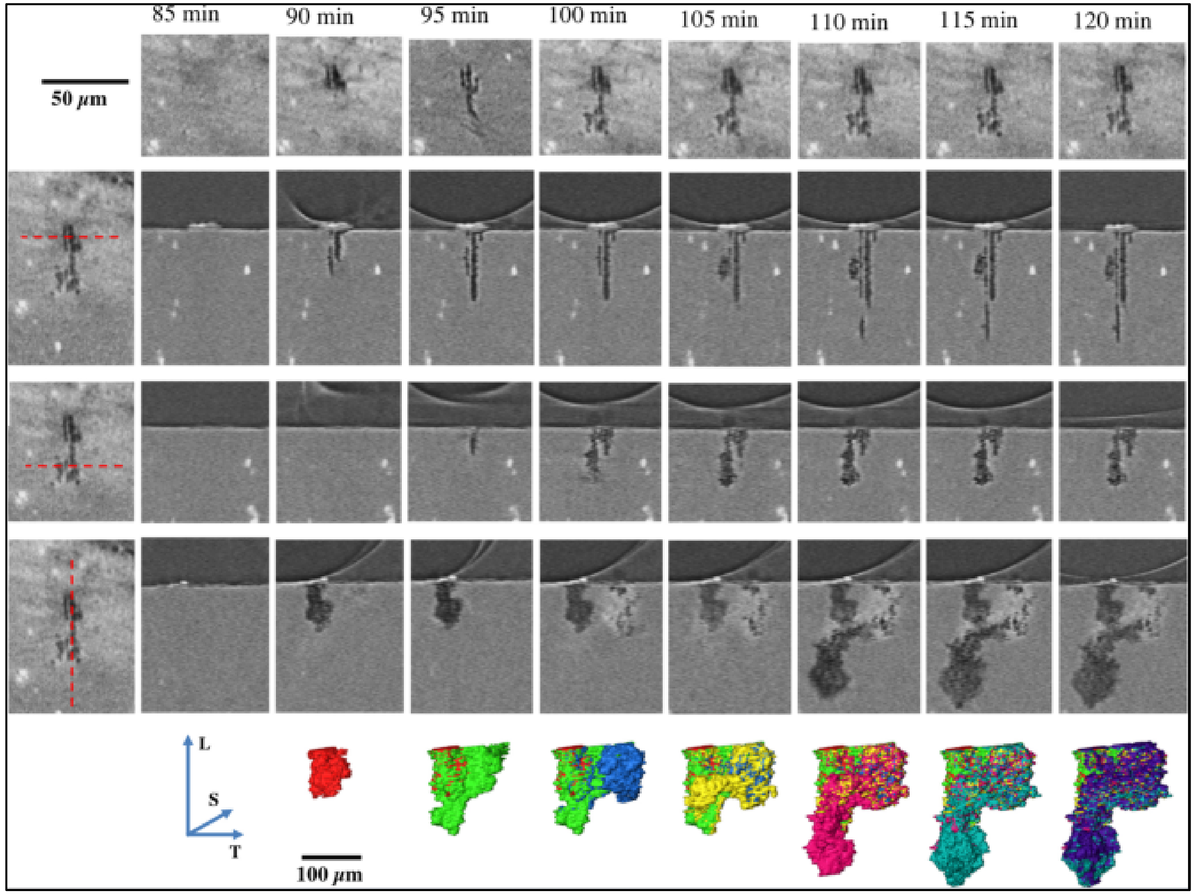
Synchrotron studies: high temporal resolution but challenges when applied to long-term studies



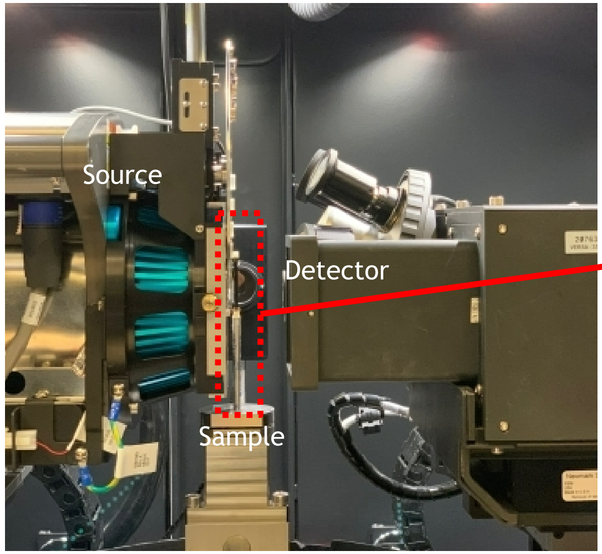
Glanvill, SJM, et al. *J. Electrochem. Soc.*, 2021

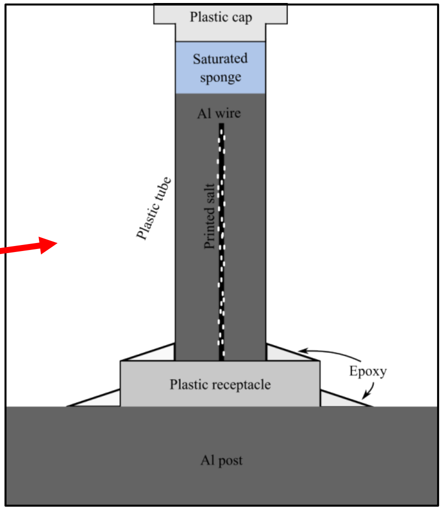


"The largest pit propagated in a highly inhomogeneous manner, with a small fraction of the surface active at any one time, and the remainder passive."

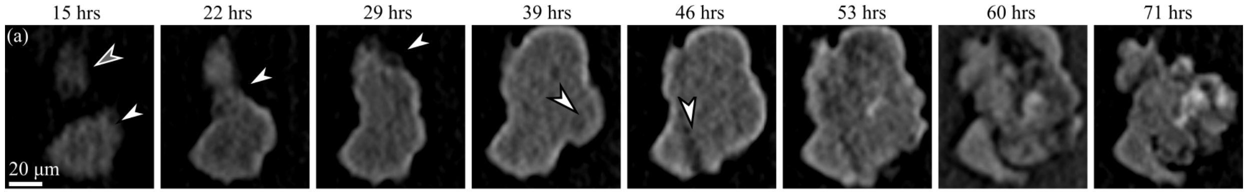


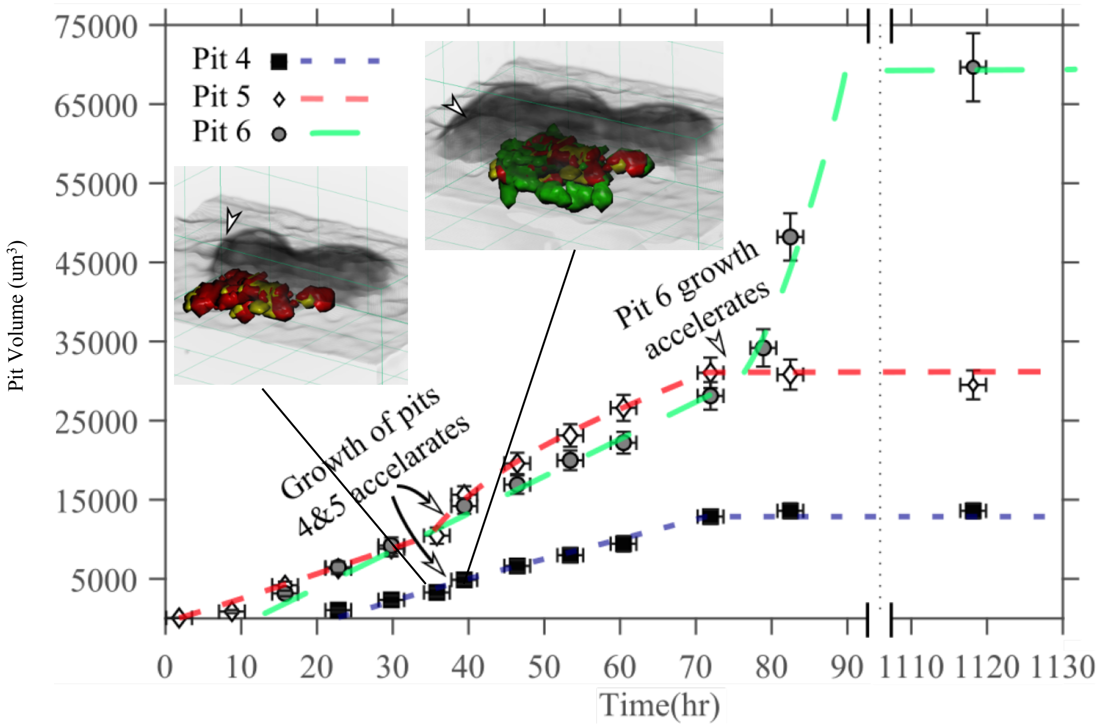
Lab-based XCT: lower temporal resolution but allows samples to be characterized indefinitely





	Pit 1	Pit 2	Pit 3	Pit 4	Pit 5	Pit 6
Final volume (μm^3)	3800	1300	800	13600	30900	69700
Initial growth rate (μm^3/h)	194	39	30	172	370	439
Secondary growth rate (μm^3/h)	–	–	–	240	475	3930
Time growing (h)	12	19	24	46	72	>65





- The growth rate of 9 pits in a 3N-Al wire tracked over 3 months with a ~7 hr. temporal resolution
- Excepting droplet spreading, the rate of pit growth remained relatively constant (linear) from the formation of a ~100 um^3 pit up to repassivation.

Noell, PJ, et al. *npj Mat. Deg.*, 2020

Goals

1) does the rate of pit growth exhibits significant nonlinearities unrelated to droplet spreading?

2) is volume added homogeneously or heterogeneously?

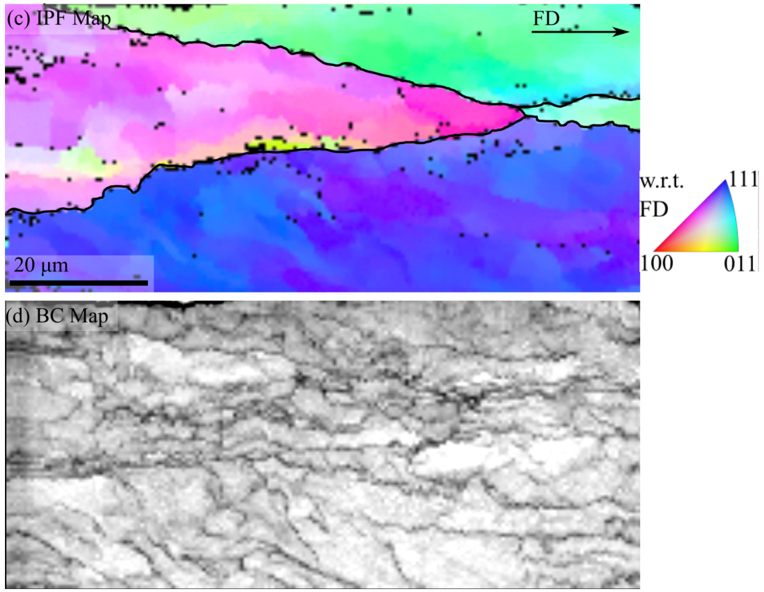
3) what are the operative factors that affect the rate & extent of pit growth and pit morphology?

Material and Environment

- Material – 1.02 mm diameter Al wire (99.99% Al)
- Printed with NaCl at 200 ug/cm^2
- Initial Humidity - 84 RH

XCT Characterization Methods

- 1.25 mm length of wire imaged with XCT periodically using a 1.25 um voxel size (15.6 um^3 spatial resolution)
- 4 Samples exposed under these conditions
- Each sample scanned every **1.3 hours** for at least the first 85 hrs. after exposure, then periodically for the next year

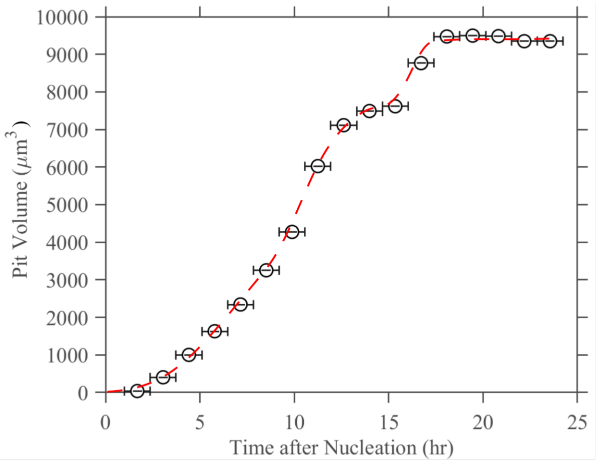


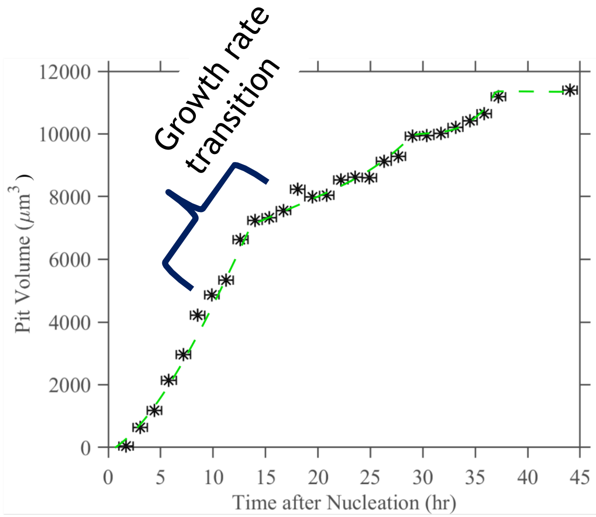
No impurities observed in material, though submicron Fe impurities are typically observed in 4N-Al materials

EBSD data (IPF map and Band Contrast Map) highlight elongated grains and dislocation structure within starting microstructure

The rate of pit growth is not uniformly linear

11 pits observed varying in size between ~400 and ~11,000 um^3



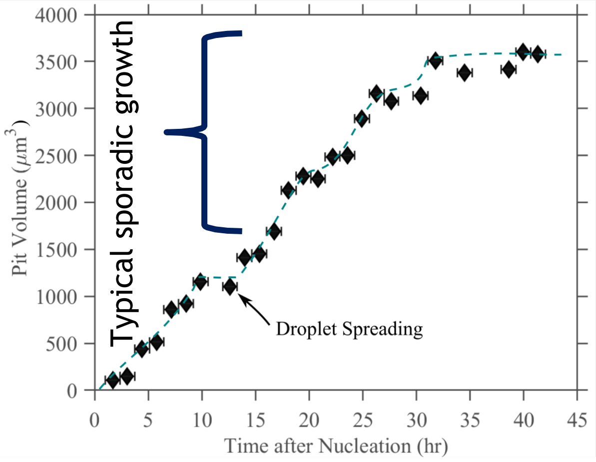


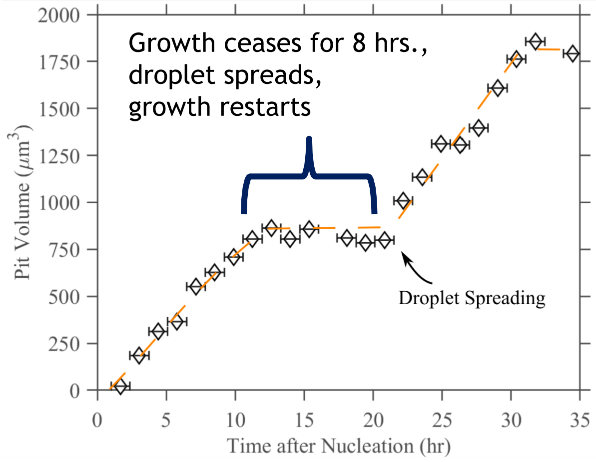
Characteristic aspects of pit growth:

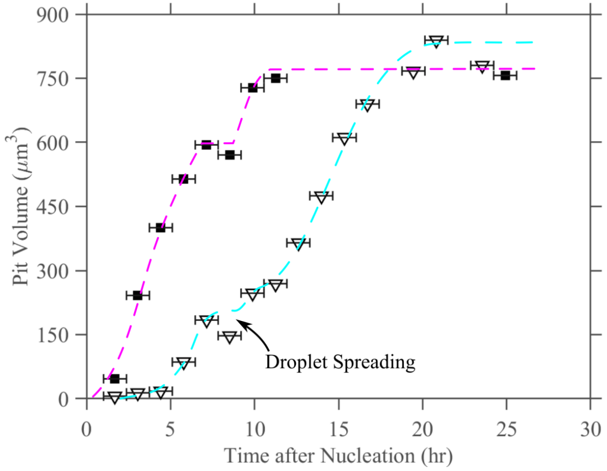
1) Sporadic – growth stops/accelerates

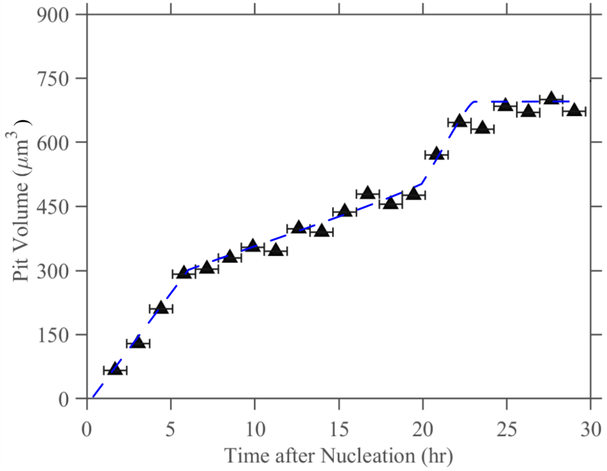
2) Sudden transition from 1 rate to another

3) Growth ceases before droplet spreading events

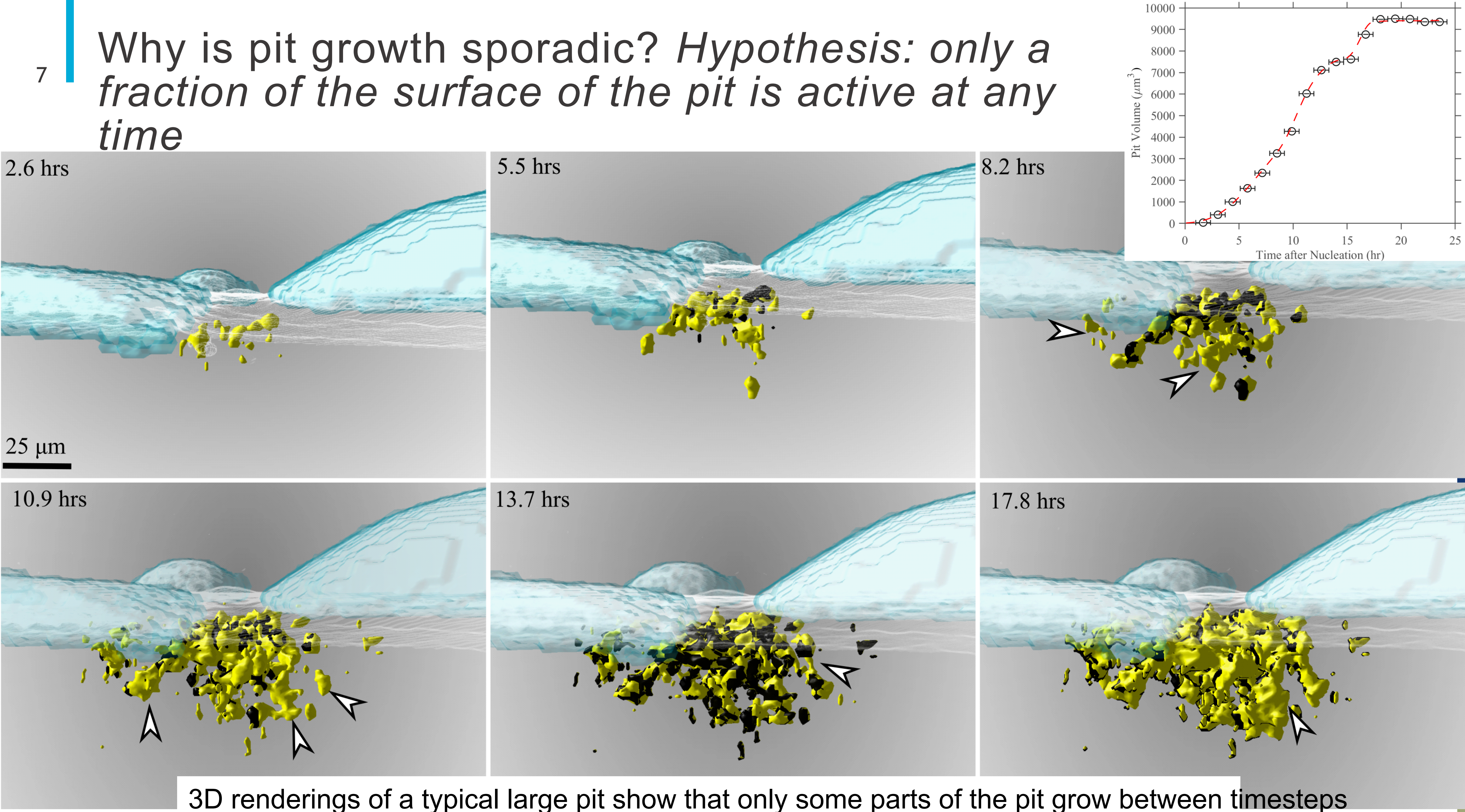






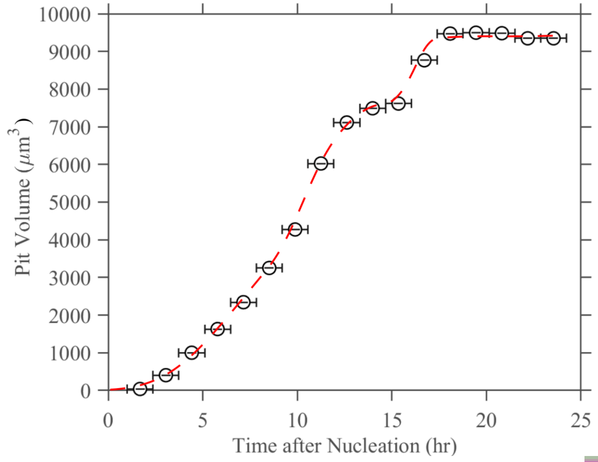


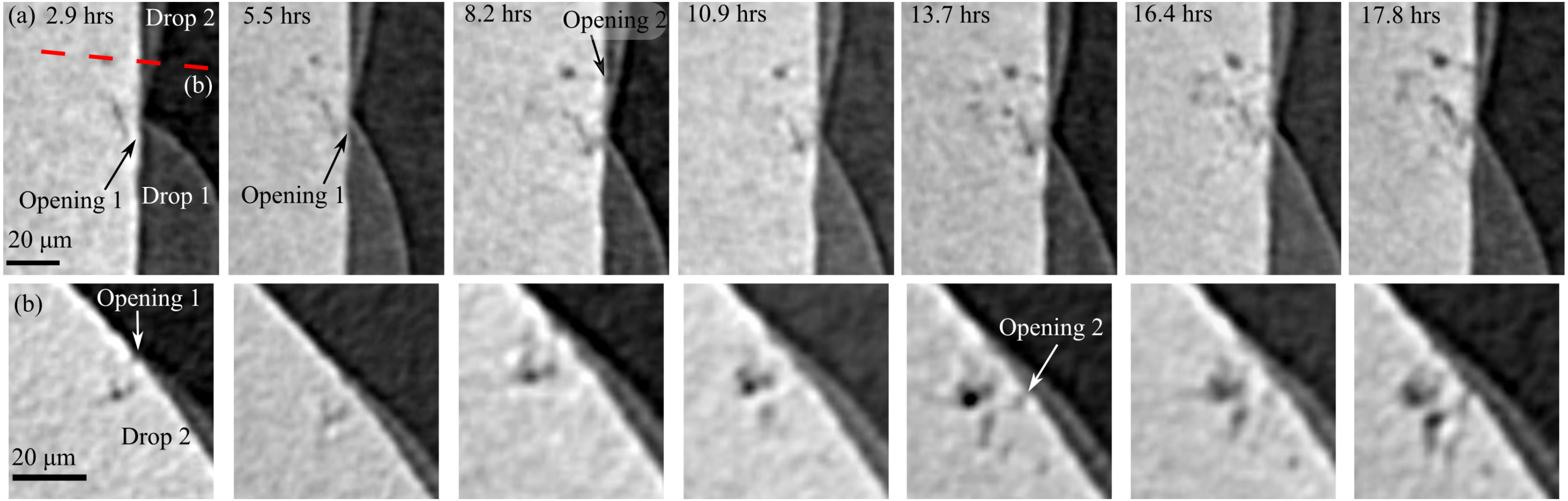
Why is pit growth sporadic? *Hypothesis: only a fraction of the surface of the pit is active at any time*



3D renderings of a typical large pit show that only some parts of the pit grow between timesteps

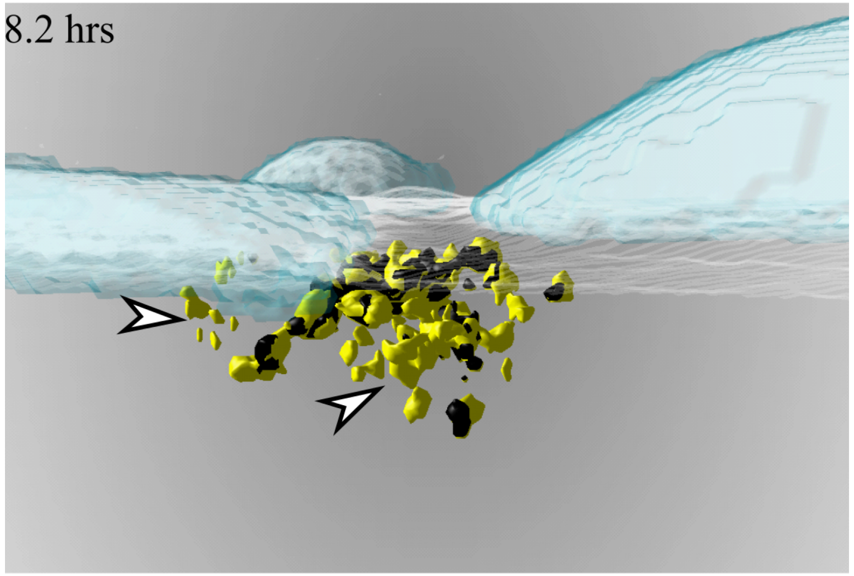
Why is pit growth sporadic? *The "tendrils" of the pit create multiple anodes, none of which is always active*

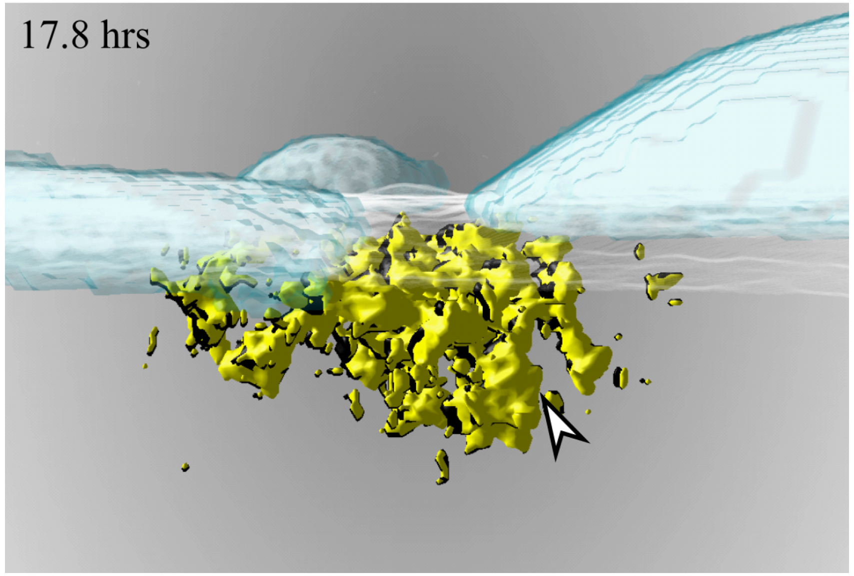


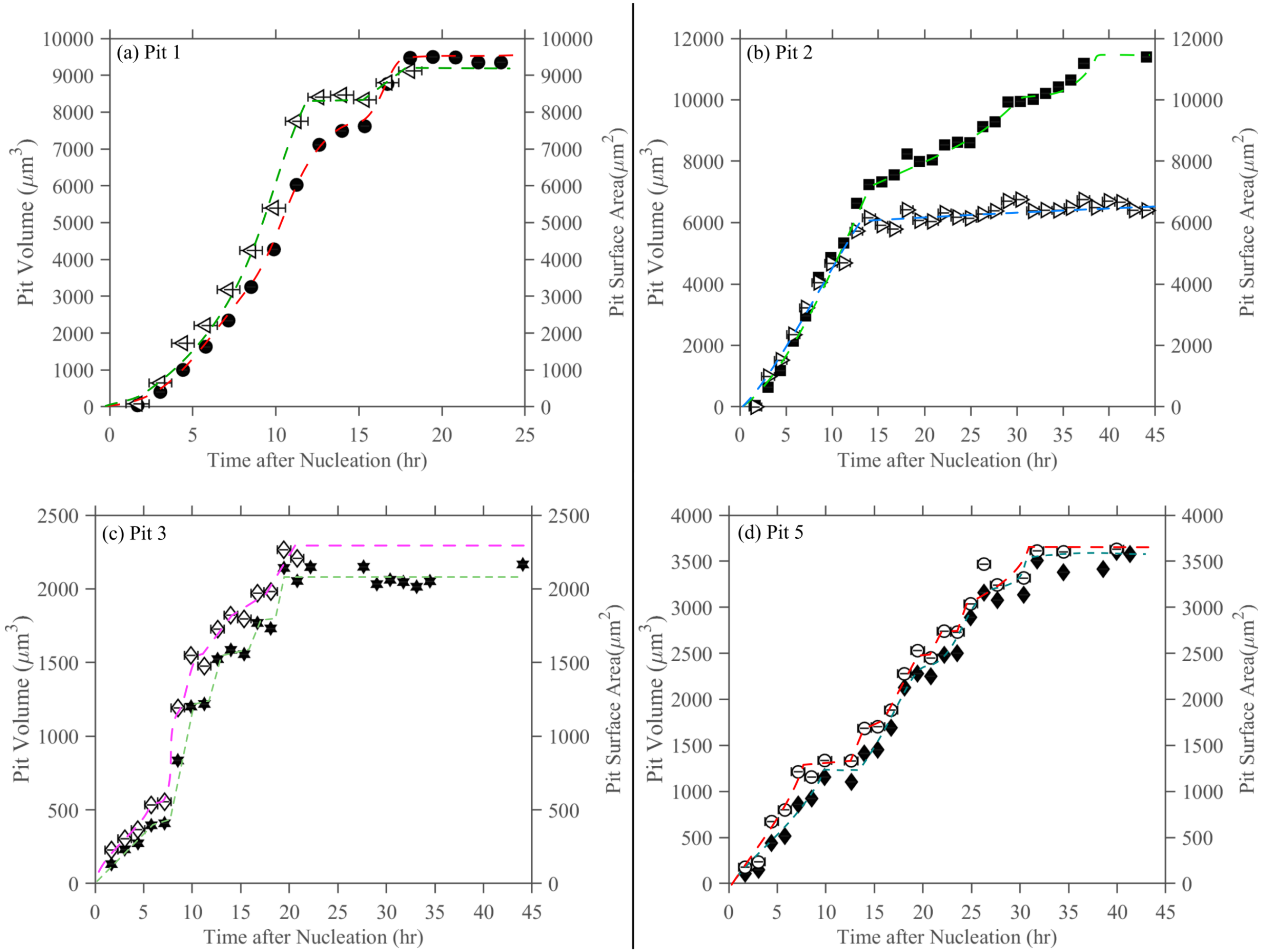


2D slices of the same pit similarly show that only some surfaces of the pit are active at

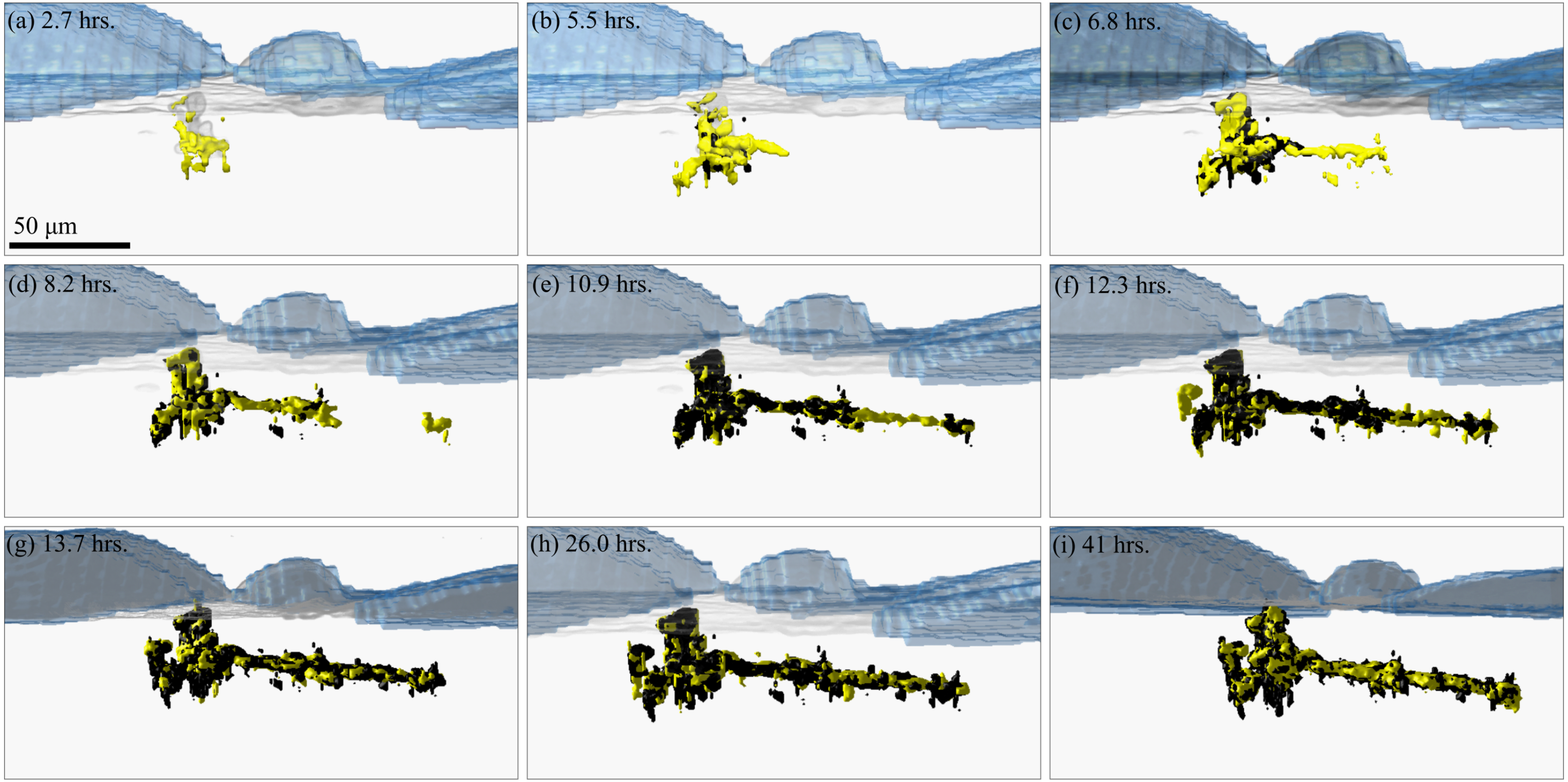
3D data suggest two distinct modes of pit growth

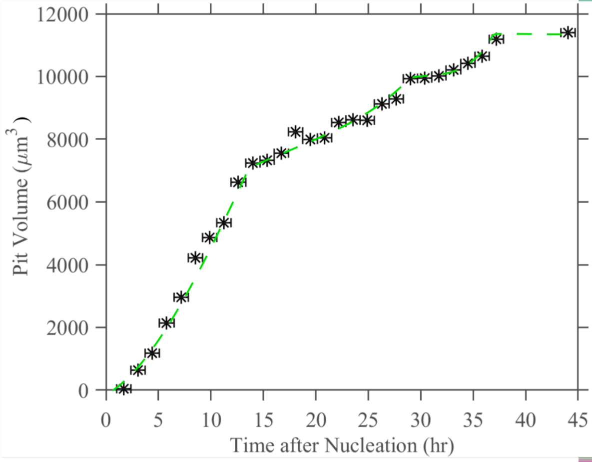






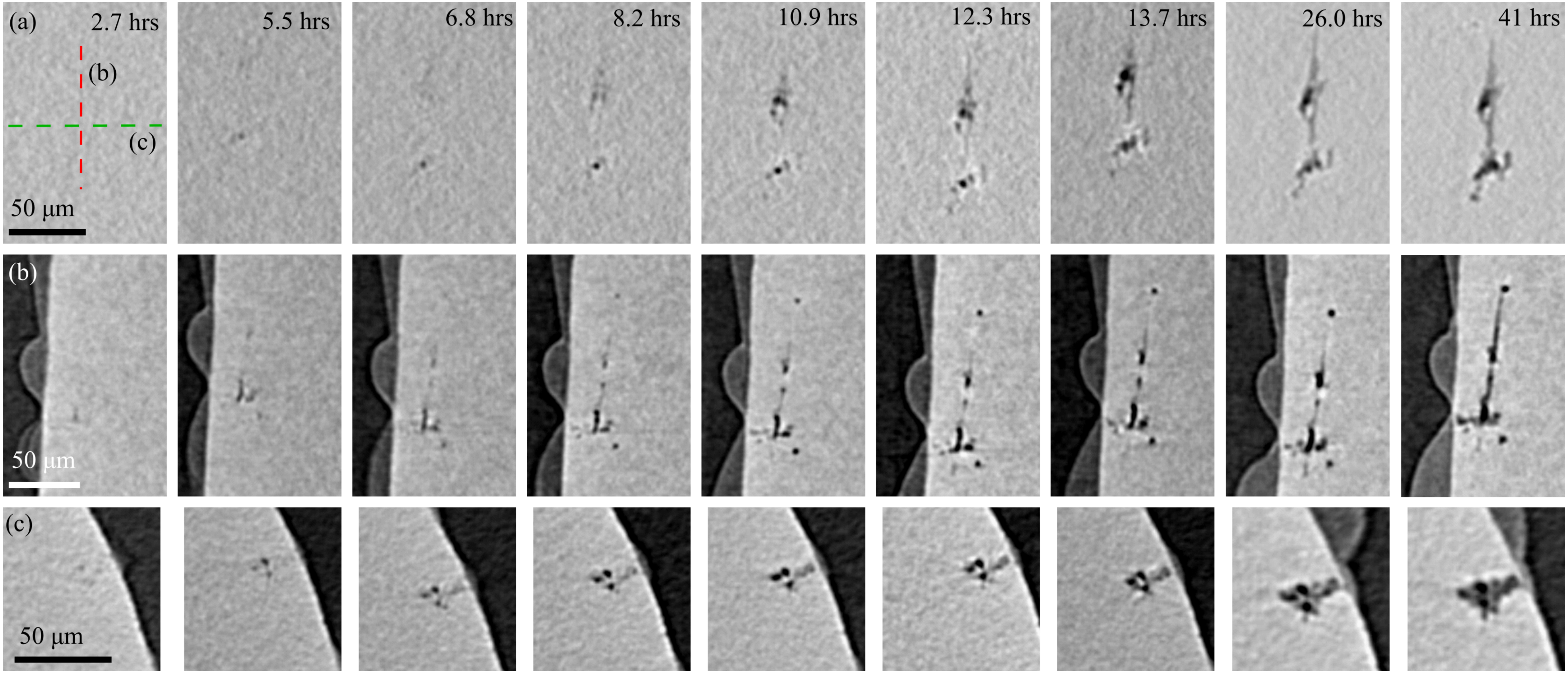
Mode 1 – pits primarily add volume by some combination of creating new tendrils and the lengthening of pre-existing tendrils.
Mode 2 – existing tendrils expand radially, no new tendrils form



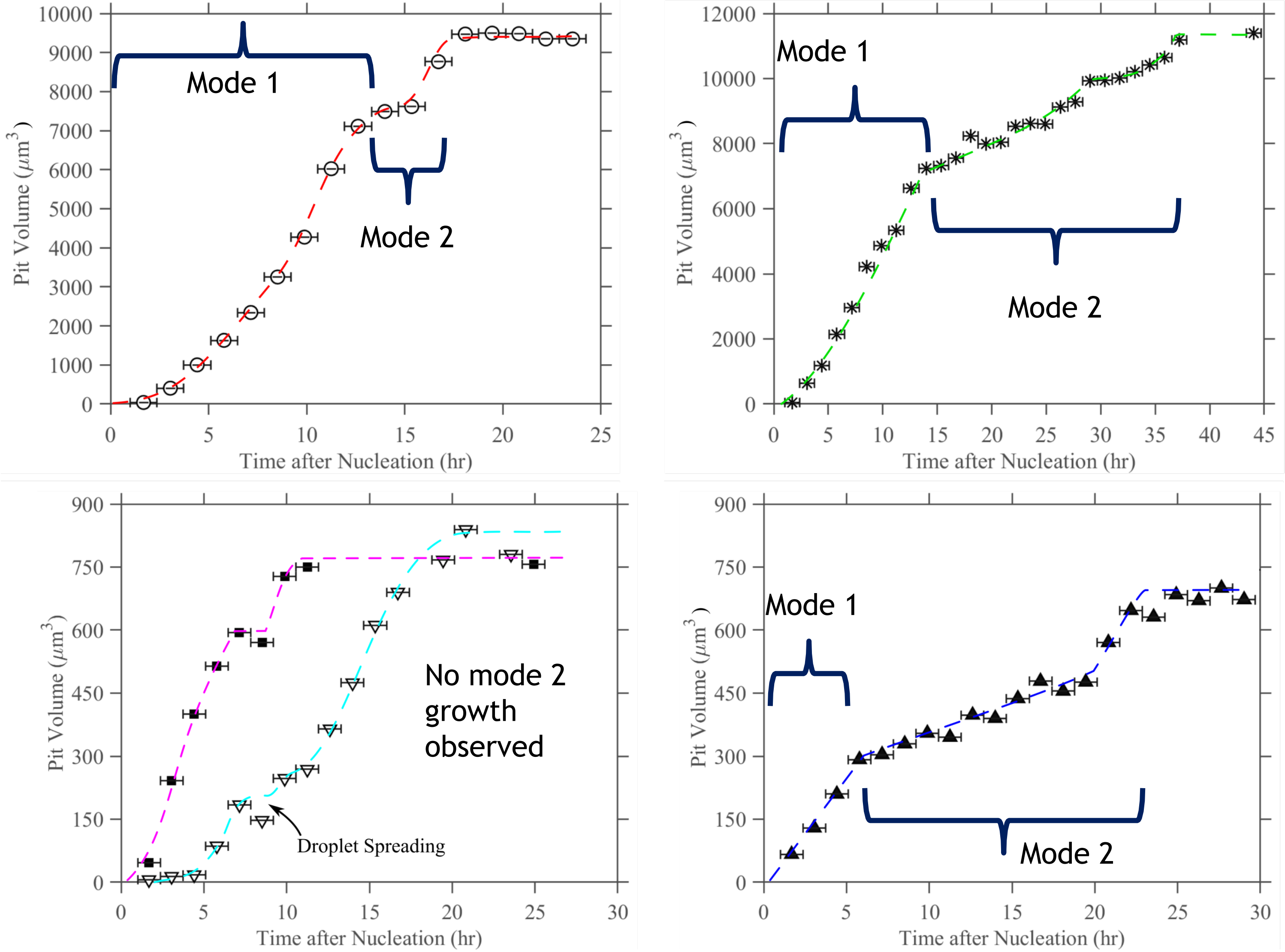


3D renderings of pit that exhibited this behavior show that at ~12 hours after nucleation, this pit transitions from growing into new material to expanding radially

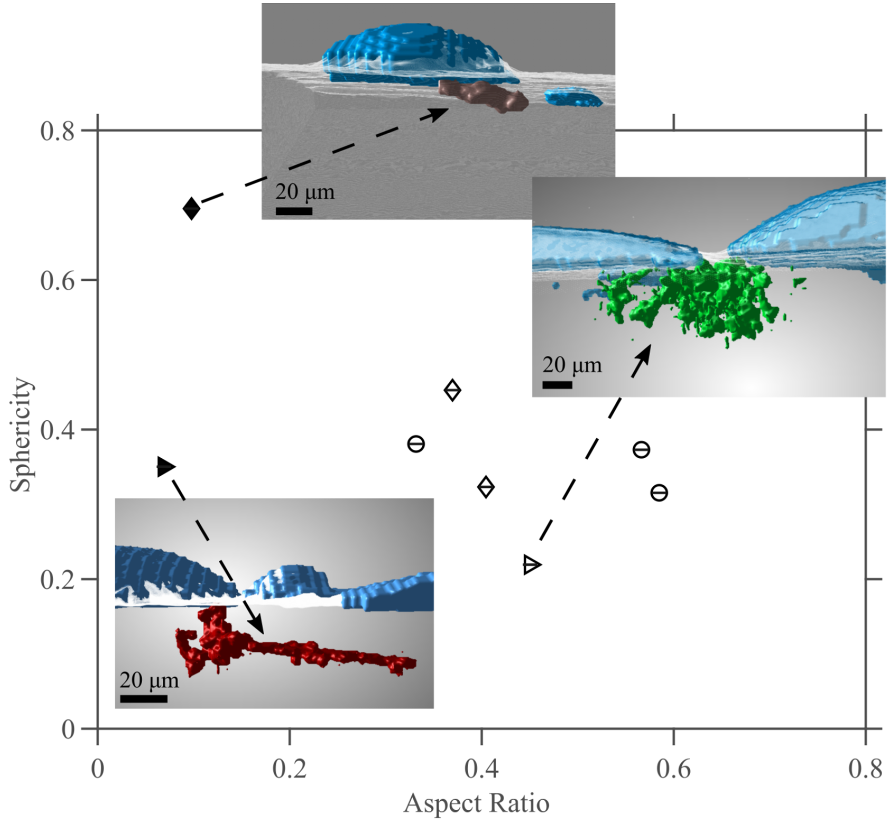
2D renderings also show that this pit primarily grew by radial expansion of existing tendrils for ~2/3 of its life



For all but two pits, the dominant growth mode for most or all of its life was mode 1. Why this difference?

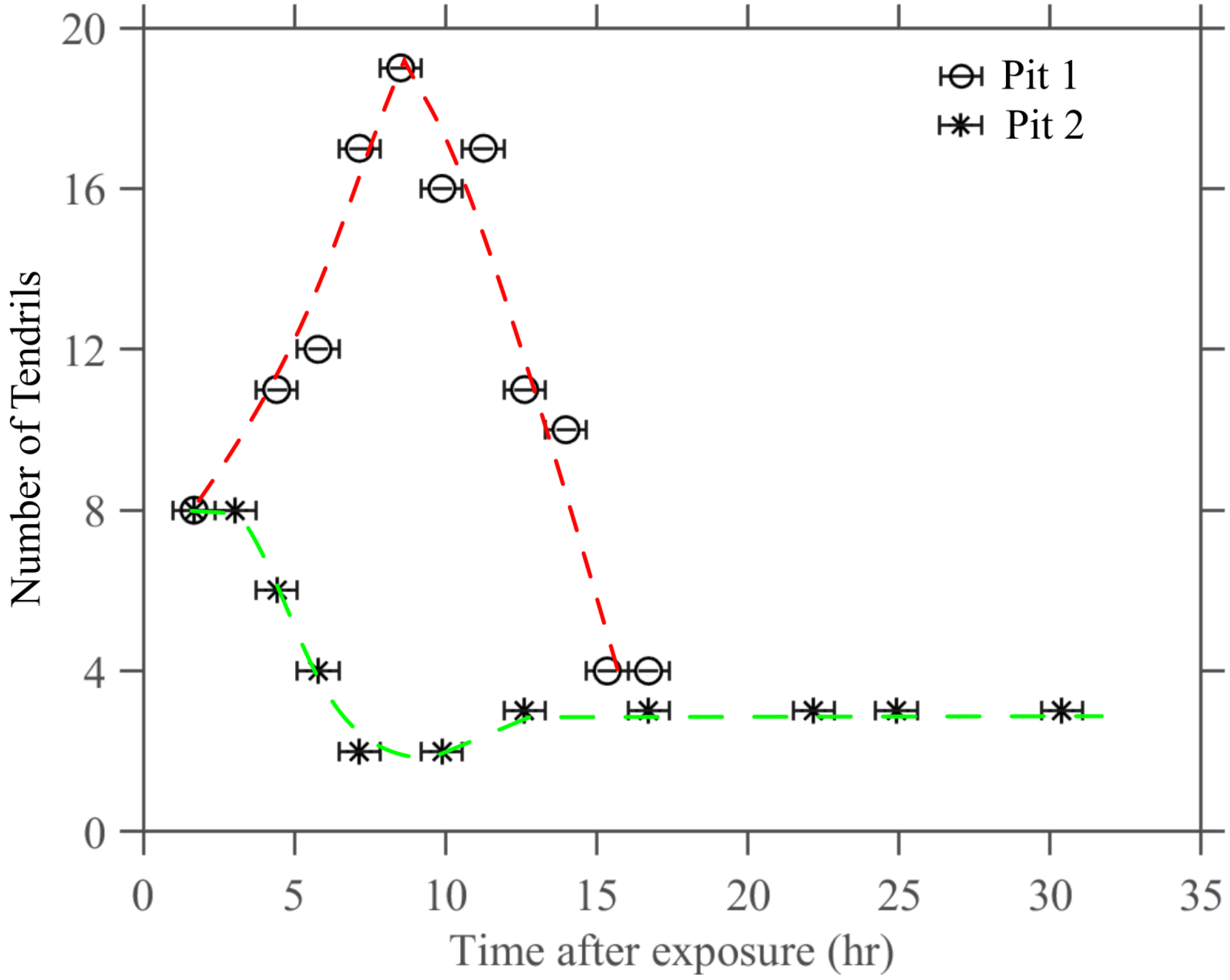


Is mode 2 growth dependent on pit morphology?



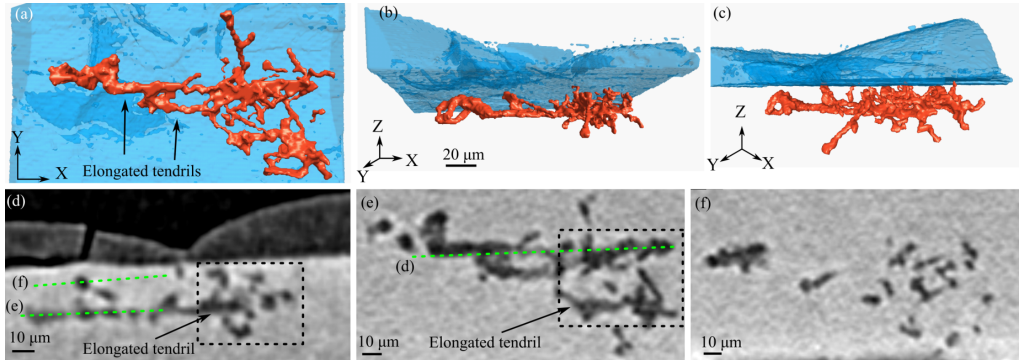
Plots of final pit sphericity versus final pit aspect ratio (for pits larger than 600 um[3]) indicate that sustained mode 2 growth is associated with elongated pits

Two distinct trends in the number of tendrils associated with a pit observed

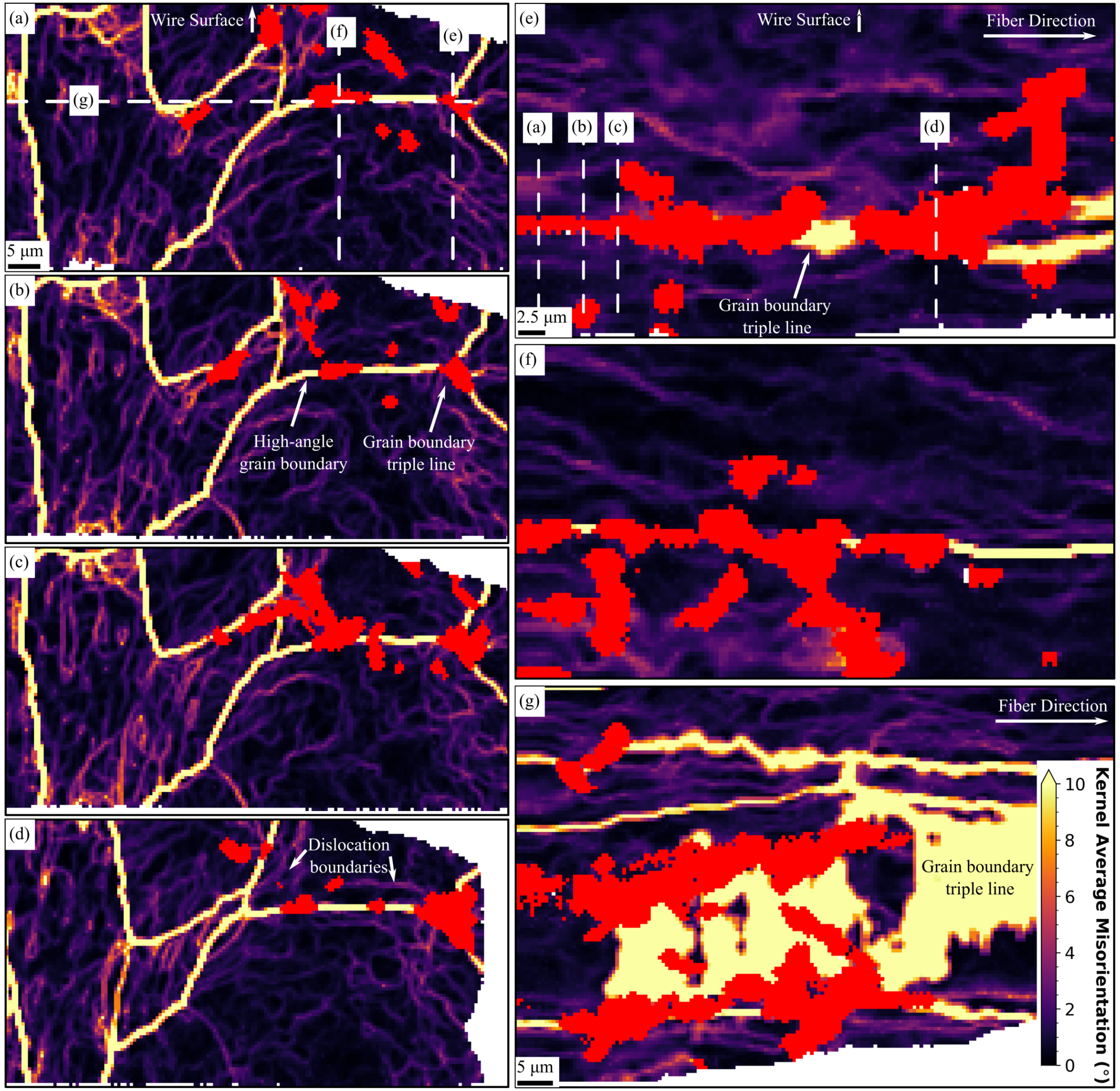


Morphology appears to influence the duration of mode 2 growth!

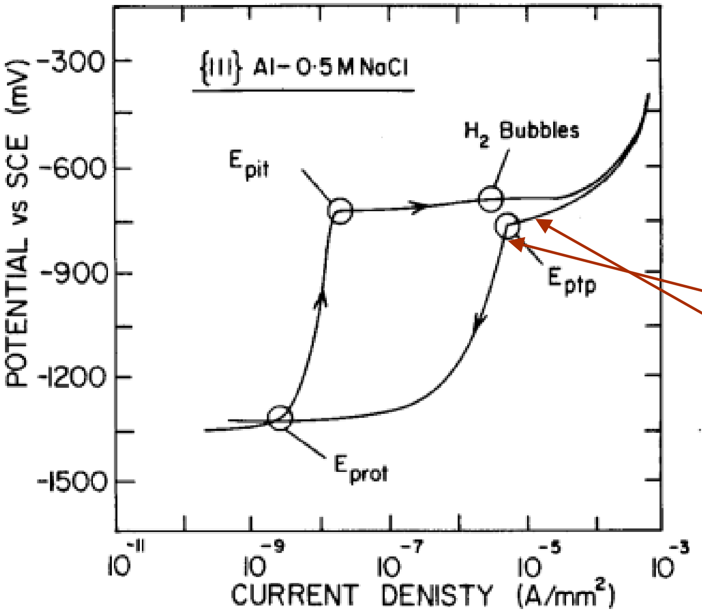
Local microstructure appears to strongly influence pit morphology, particularly the formation of elongated tendrils



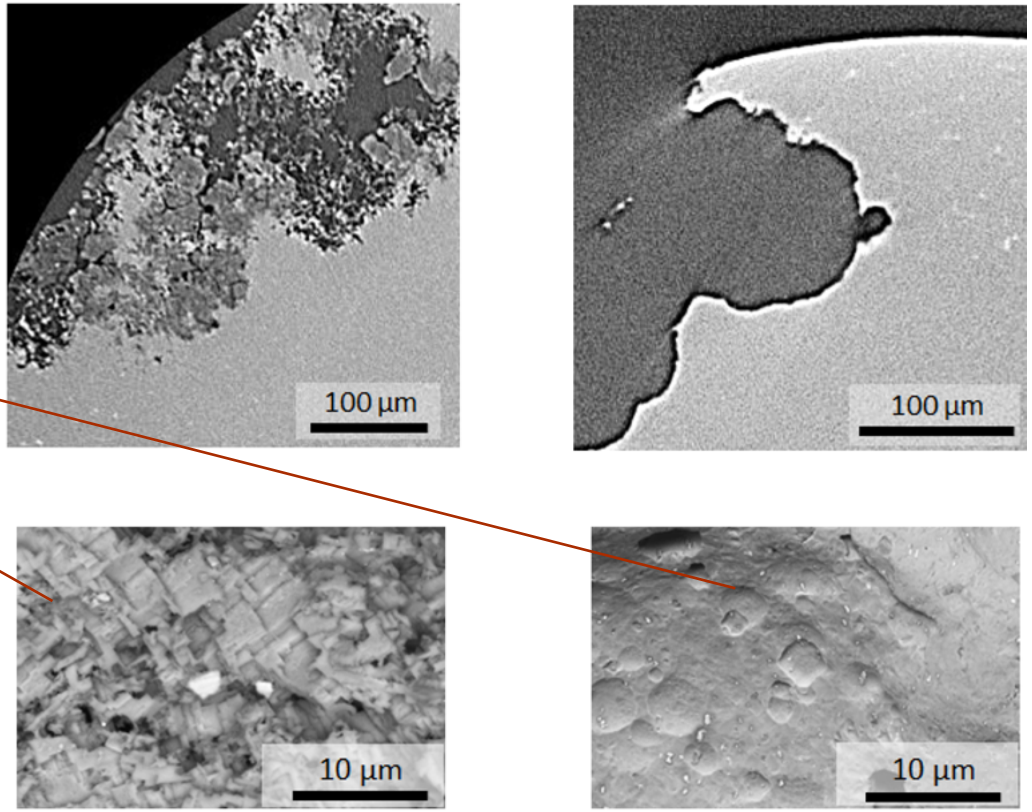
- An additional pit (pit 12, see above) was serial sectioned and characterized using EBSD
- EBSD data are plotted as a kernel average misorientation map to highlight grain and dislocation boundaries.
- The two elongated tendrils in this pit grew along a grain boundary triple junction and a high-angle grain boundary, respectively



Why two different growth modes?



Yasuda et al., J Echem. Soc, 1990



(a) -740 mV_{SCE} (E_{ptp}+50mV)

(b) -790 mV_{SCE} (E_{ptp})

Cyclical polarization experiments show that pitting in Al (and some other passive alloys) is associated with three critical potentials: E_{pit}, E_{ptp}, and E_{prot}

Early work showed that E_{ptp} is related to repassivation but it remains obscure

Potentiostatic holds above and below E_{ptp} in a similar Al material show that pit morphology above and below E_{ptp} resembles those observed for mode 1 and mode 2 growth

We speculate that the two growth modes result from the potential within the pit dropping below E_{ptp}

Conclusions

- Pit growth in 4N-Al is not uniformly linear. Many nonlinearities are related to the repassivation of old tendrils and initiation of new tendrils during mode 1 growth.
- During mode 1 growth, pits add volume in a heterogenous manner
- During mode 2 growth, most (all?) of the surface of the pit remains active up to pit repassivation
- A clear transition in the rate of pit growth was observed when the pit ceased growing into new material and instead began to expand roughly uniformly
- These two manners of growth produced pits with very different morphologies
  - **in-situ data suggests that certain pit morphologies (elongated/tunnel-like) result in sustained/constant growth**

pnoell@sandia.gov

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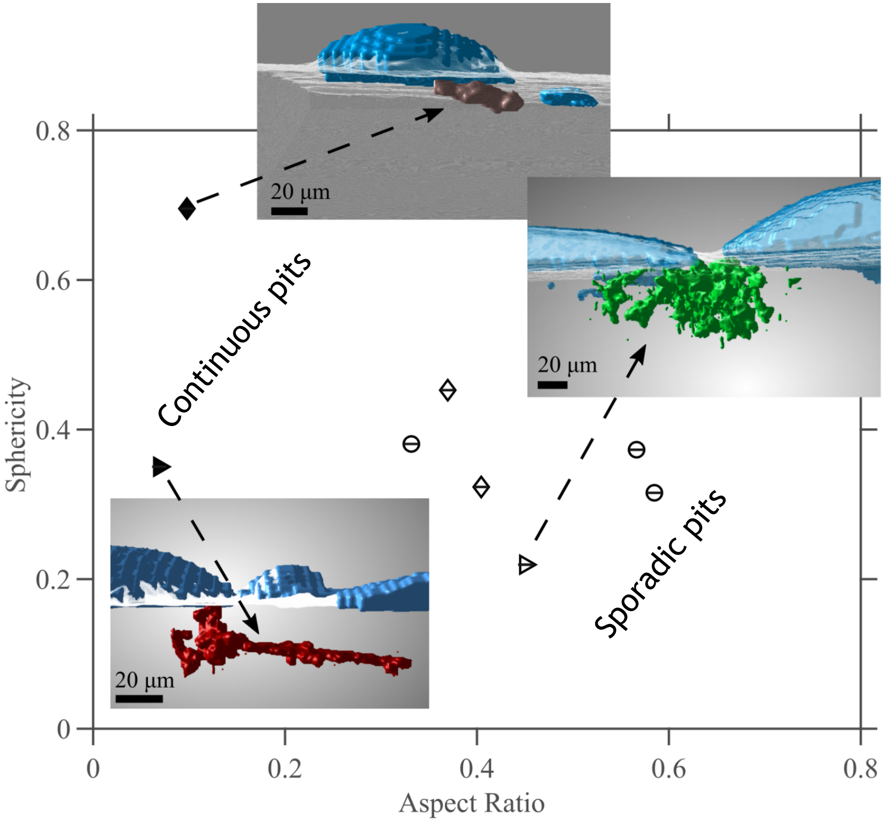
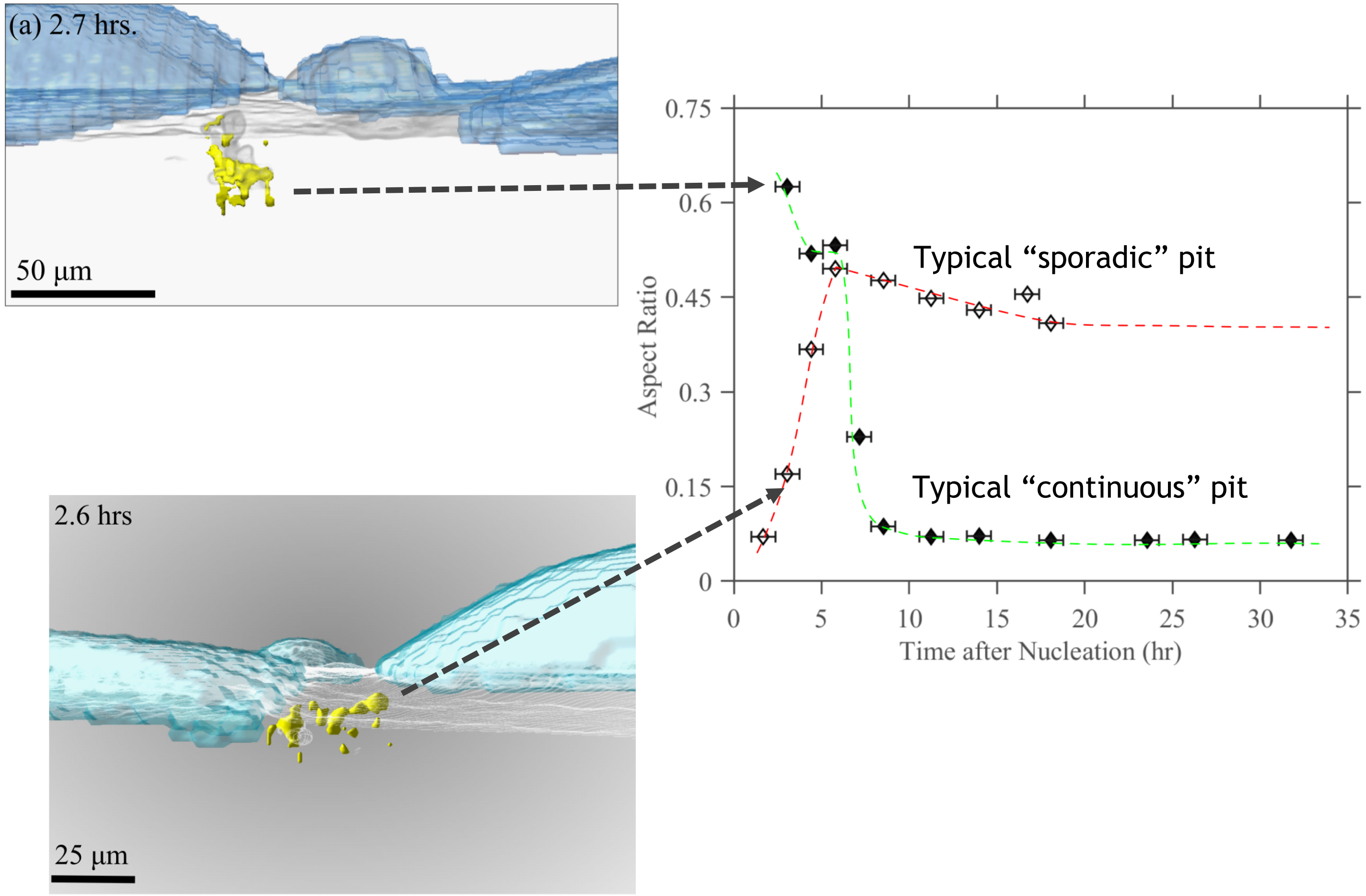
Is mode 2 growth dependent on pit morphology?



Plots of final pit sphericity versus final pit aspect ratio (for pits larger than 500 um) indicate that sustained mode 2 growth is associated with elongated pits

But which comes first? Does pit morphology control pit growth kinetics or vice versa?



In-situ date indicates that aspect ratio is roughly constant after the first 5-10 hours of growth. ***Morphology appears to influence pit growth kinetics!***