Oxygen Uptake in CH Capsules

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LLNL-PRES-501981

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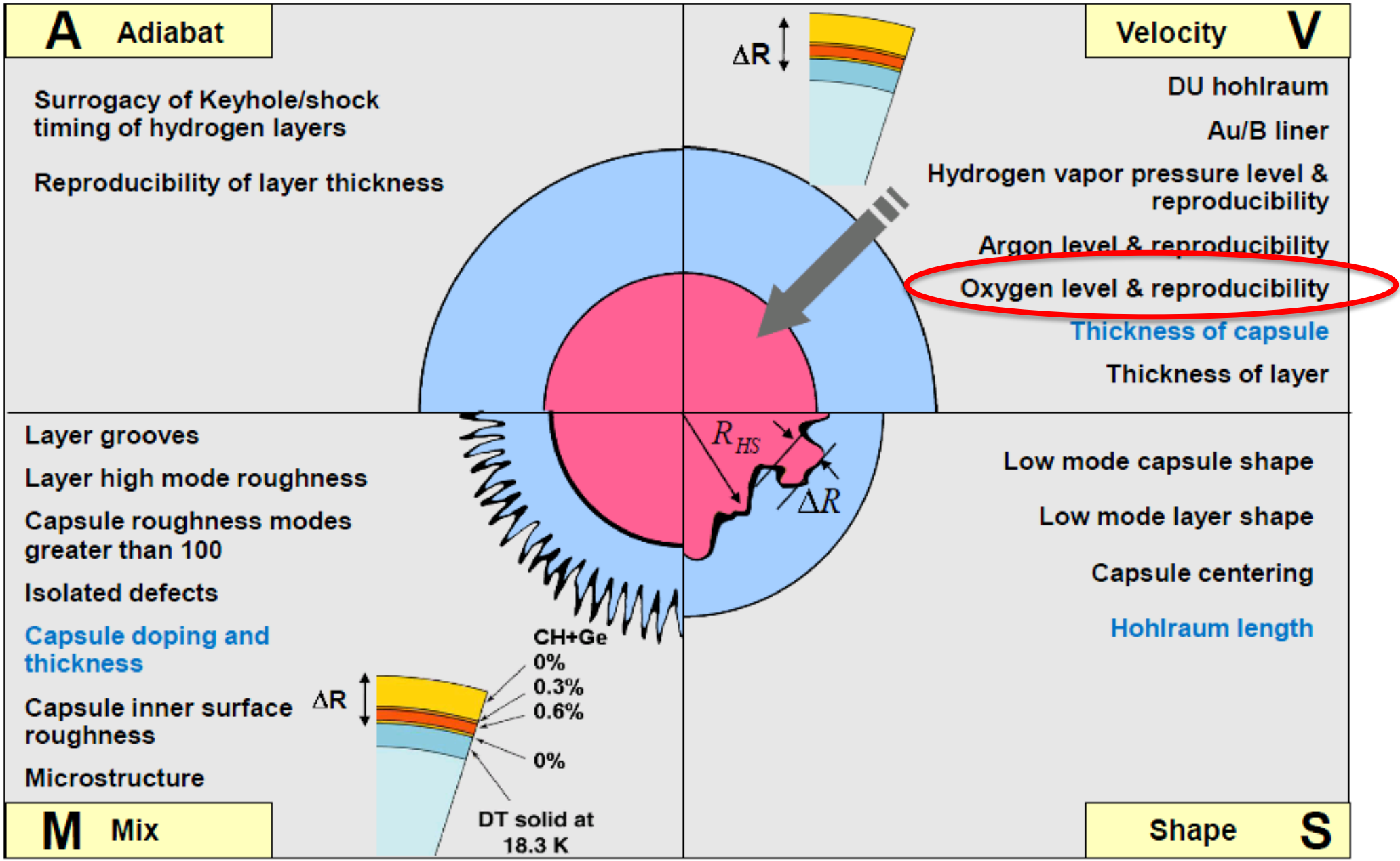
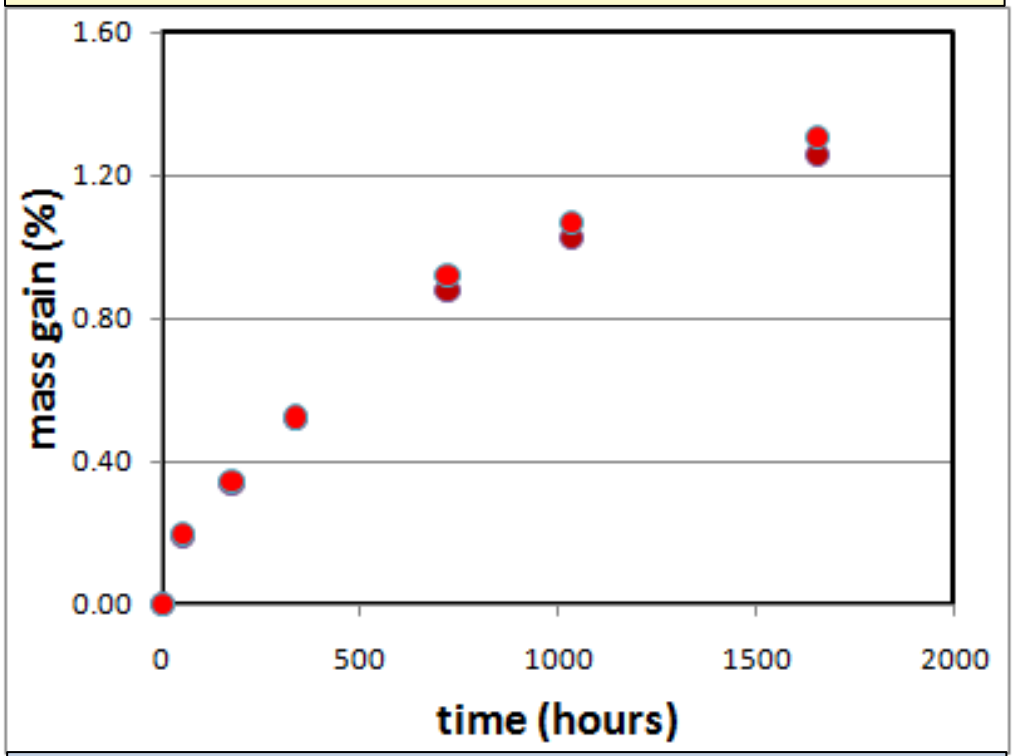
Three target parameters are experimentally tuned but many affect margin and uncertainty

NIC
The National Ignition Campaign



Previous measurements of mass gain of pyrolyzed CH capsules indicated limited uptake

Mass gain tracked over 90 days appears to converge around 1.5 wt%



Data indicates mass uptake converges around 1.5wt%; 0.5at% oxygen at most

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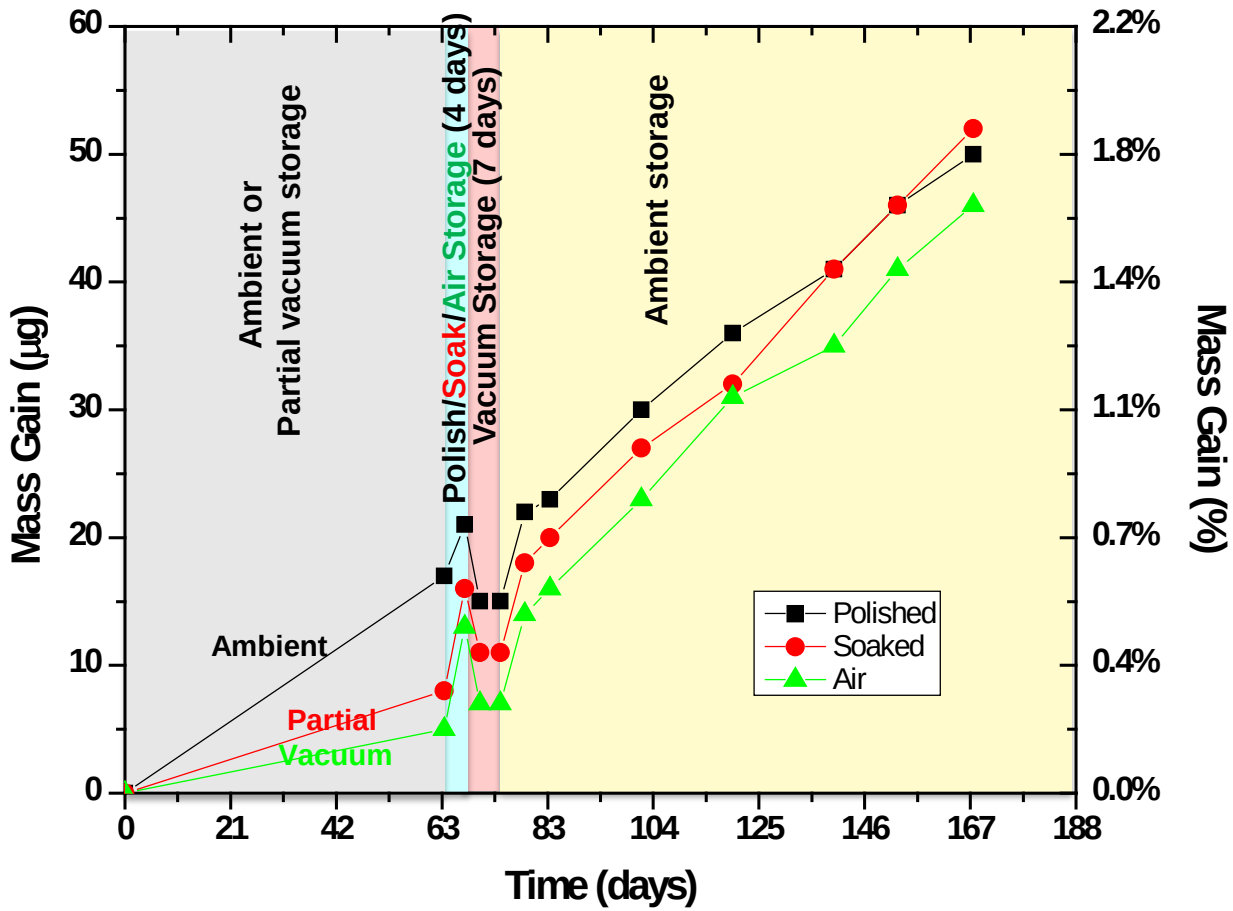
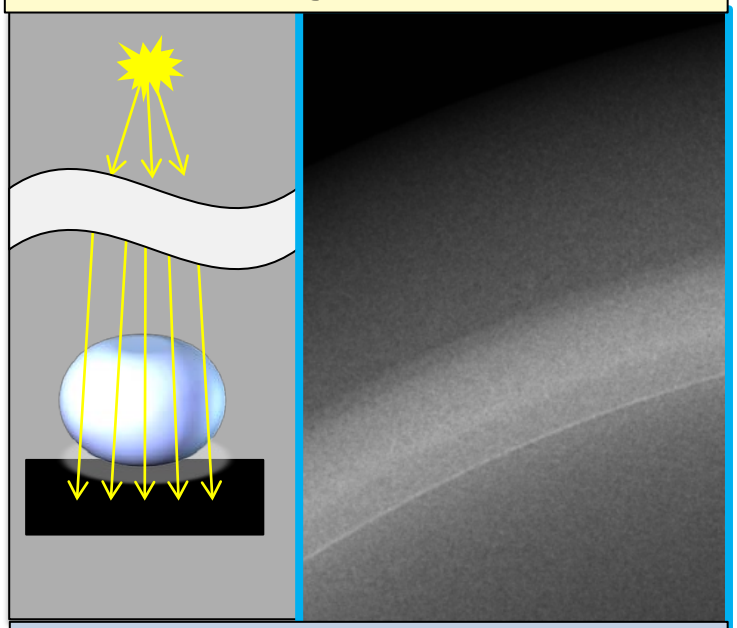
Capsule weight gain is dependent on environment and is partially irreversible

Measured capsule weight as function of time and process



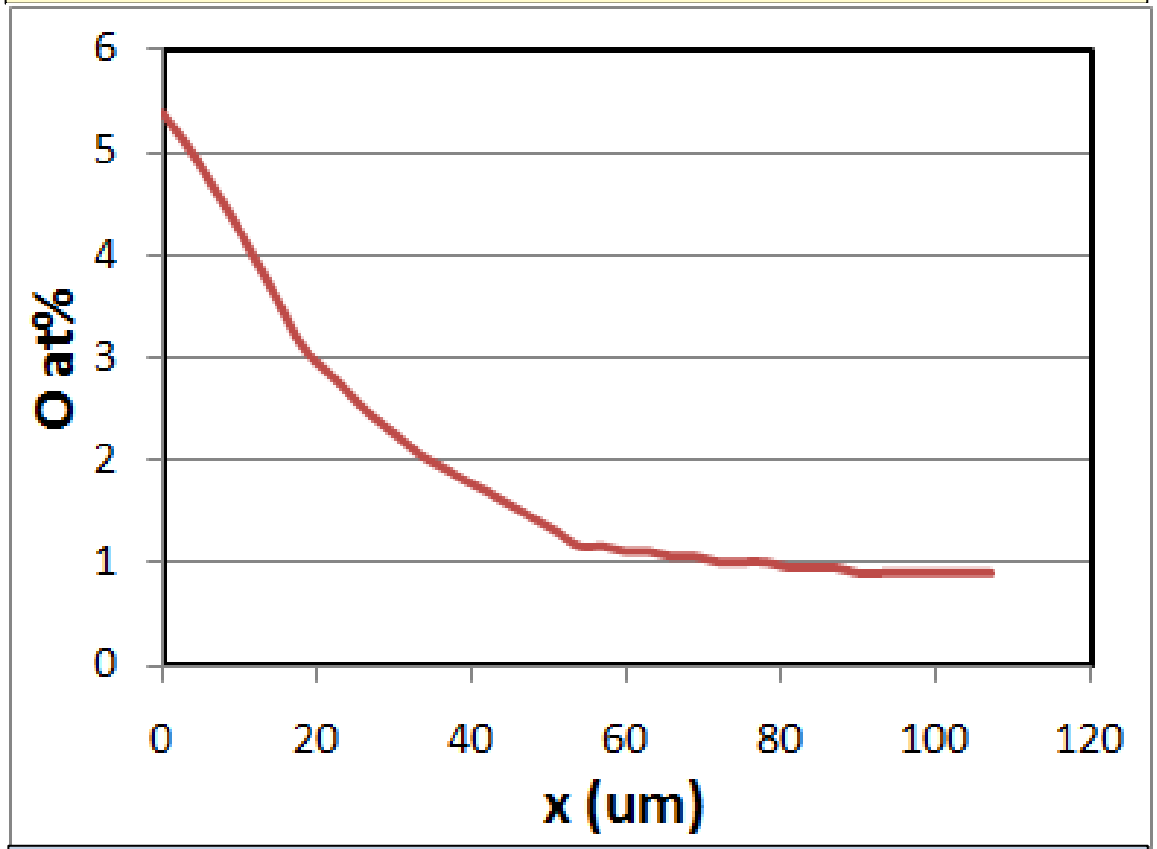
Contact radiography measurements confirm increased uptake of oxygen

Capsule is illuminated with X-ray source



Oxygen profile can be calculated from gray scale

Contact radiography of a 21-month old capsule shows up to 5 at% O concentration

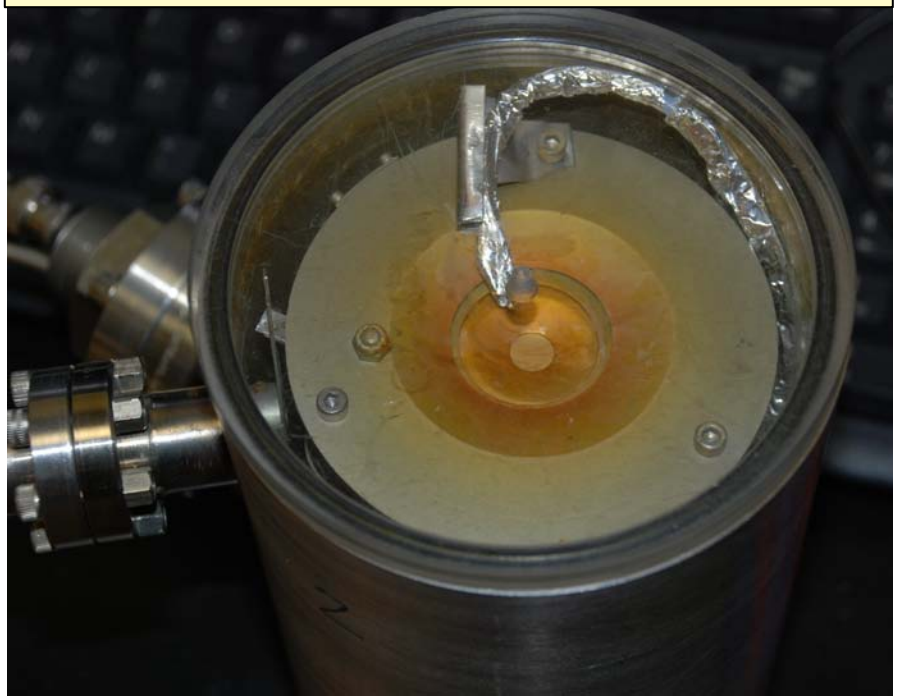


Oxygen concentration is non-uniform across the wall thickness

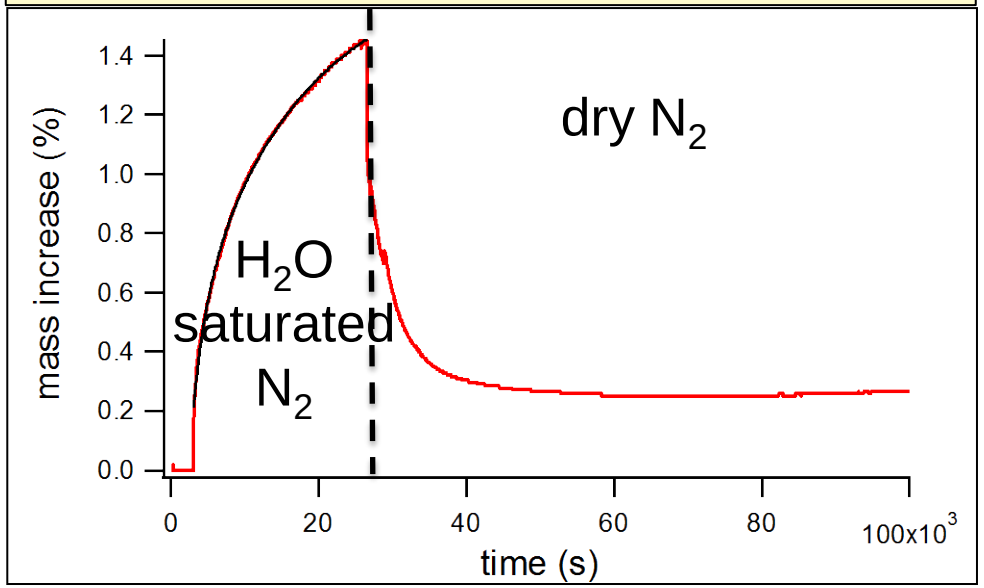
P-27 **Oxygen Uptake Characterization and Analysis in NIF GDP Ablator Capsules**
H. Huang

Quartz crystal microbalance (QCMB) experiments can be used for mechanistical studies

Sample chamber of thin CH film on quartz crystal resonator

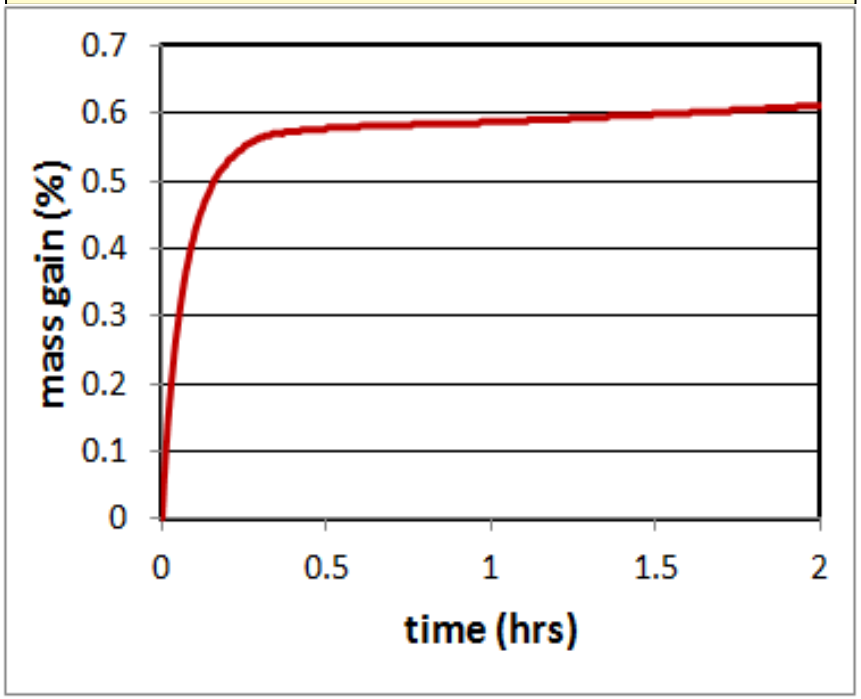


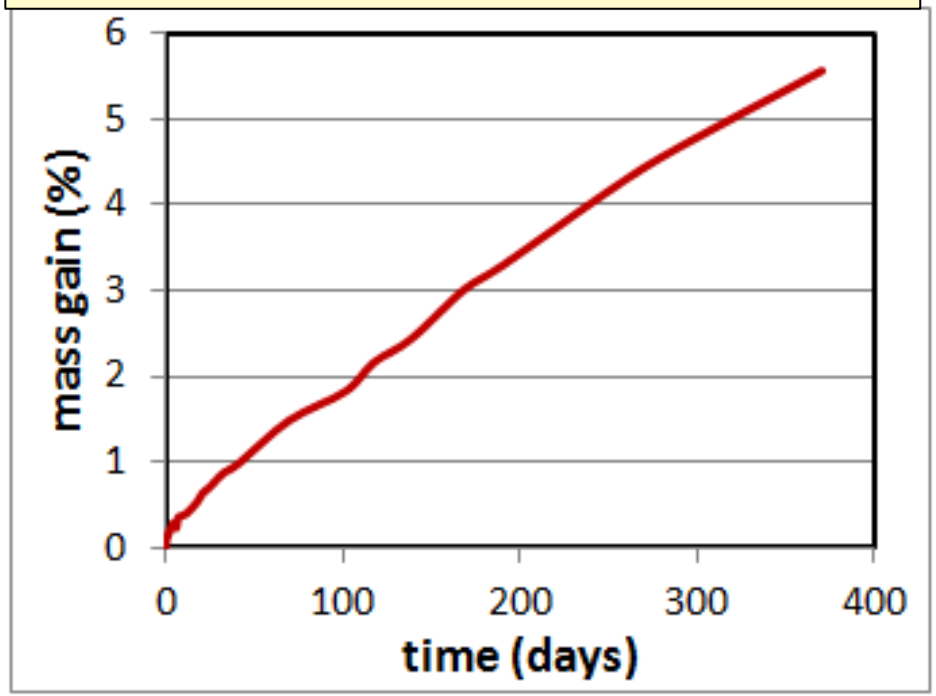
Data trace from QCMB experiment



Mass uptake studies have focused on two time scales

Short time scale – diffusion constants and environmental studies	Long time scale – reaction rates, oxygen profiles, and uptake model

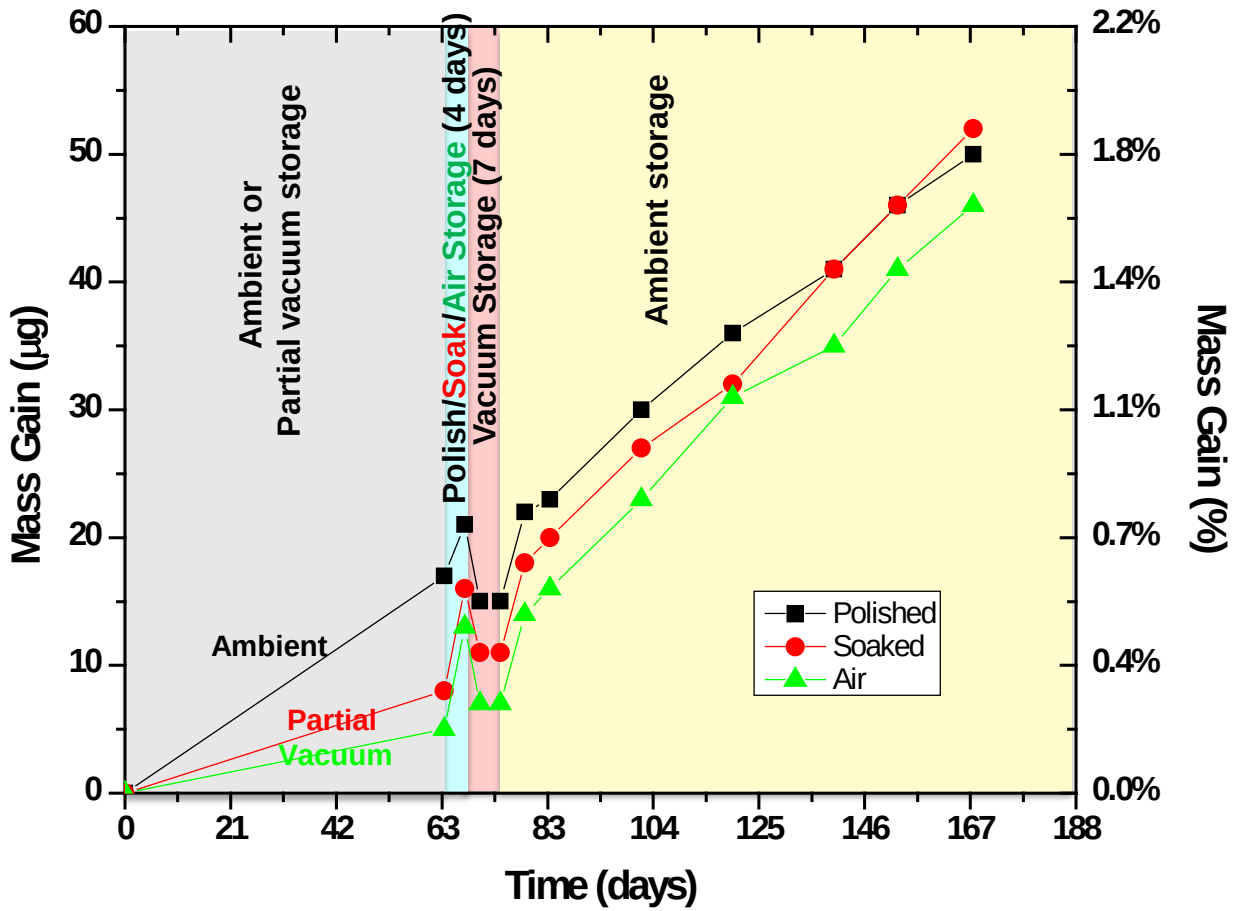




11:20 Thurs. AM2-4 **Measurement of Plasma Polymer Oxidation Using a Quartz Crystal Microbalance**
S.A. Letts

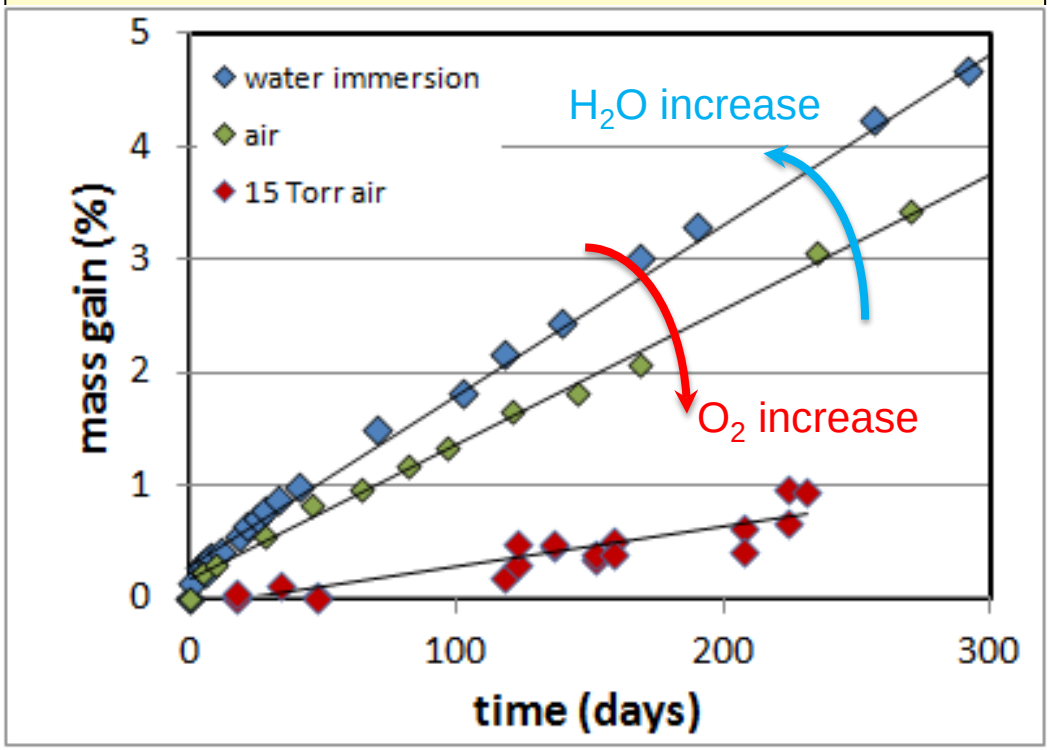
Capsule have gained ~1.8% in mass after ~6 months of ambient storage with no slow down in rate

Measured capsule weight as function of time and process



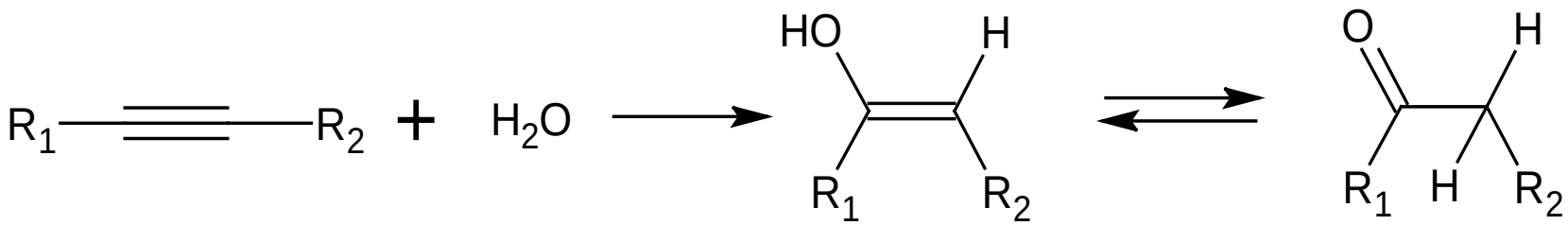
Weight data confirms that water concentration is more important than oxygen for mass uptake

Mass uptake in water is faster than in air

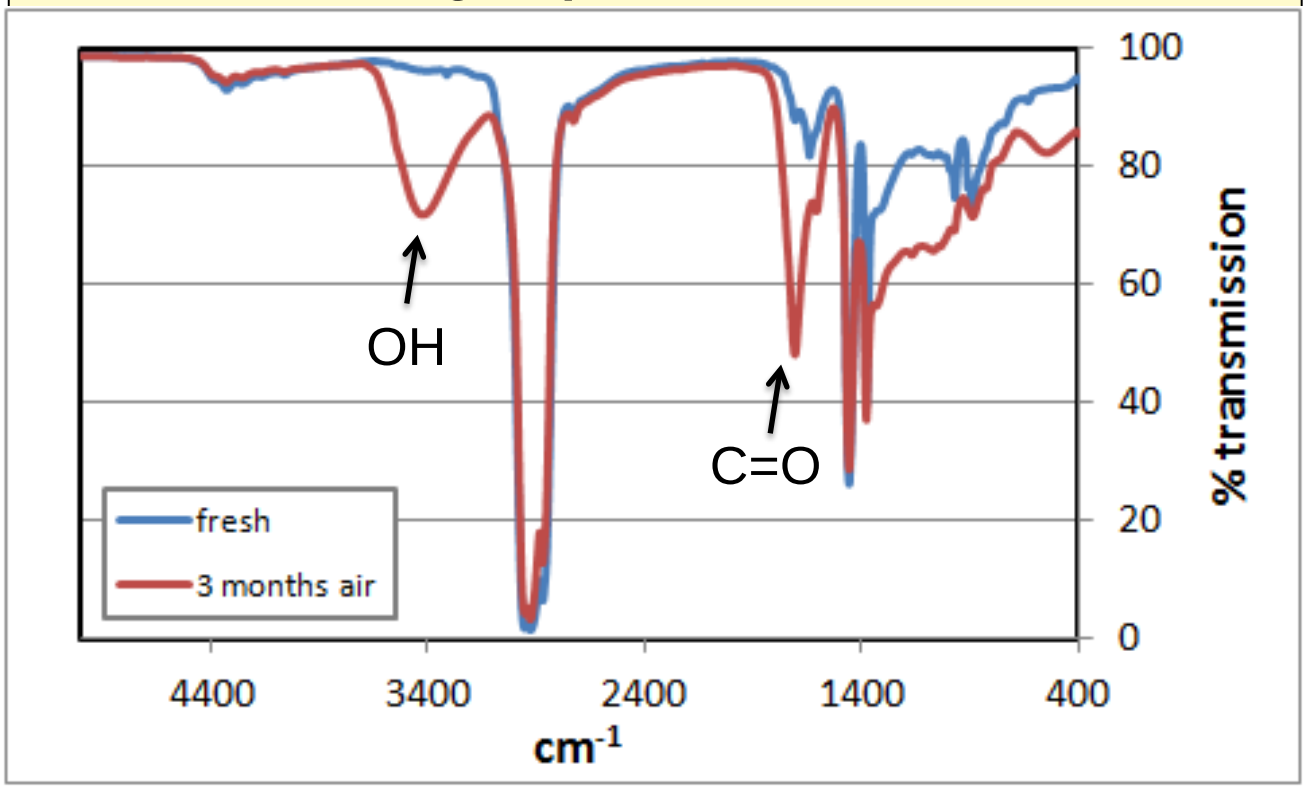


environment	c_{O2}	c_{H2O}	p_{H2O}	uptake rate
water	10 mg/l	10^6 mg /l	17.6 Torr	0.015 %/day
air	250 mg/l	6 mg/l	7.0 Torr	0.012 %/day
15 Torr air	5 mg/l	0.12 mg/l	0.14 Torr	0.004 %/day

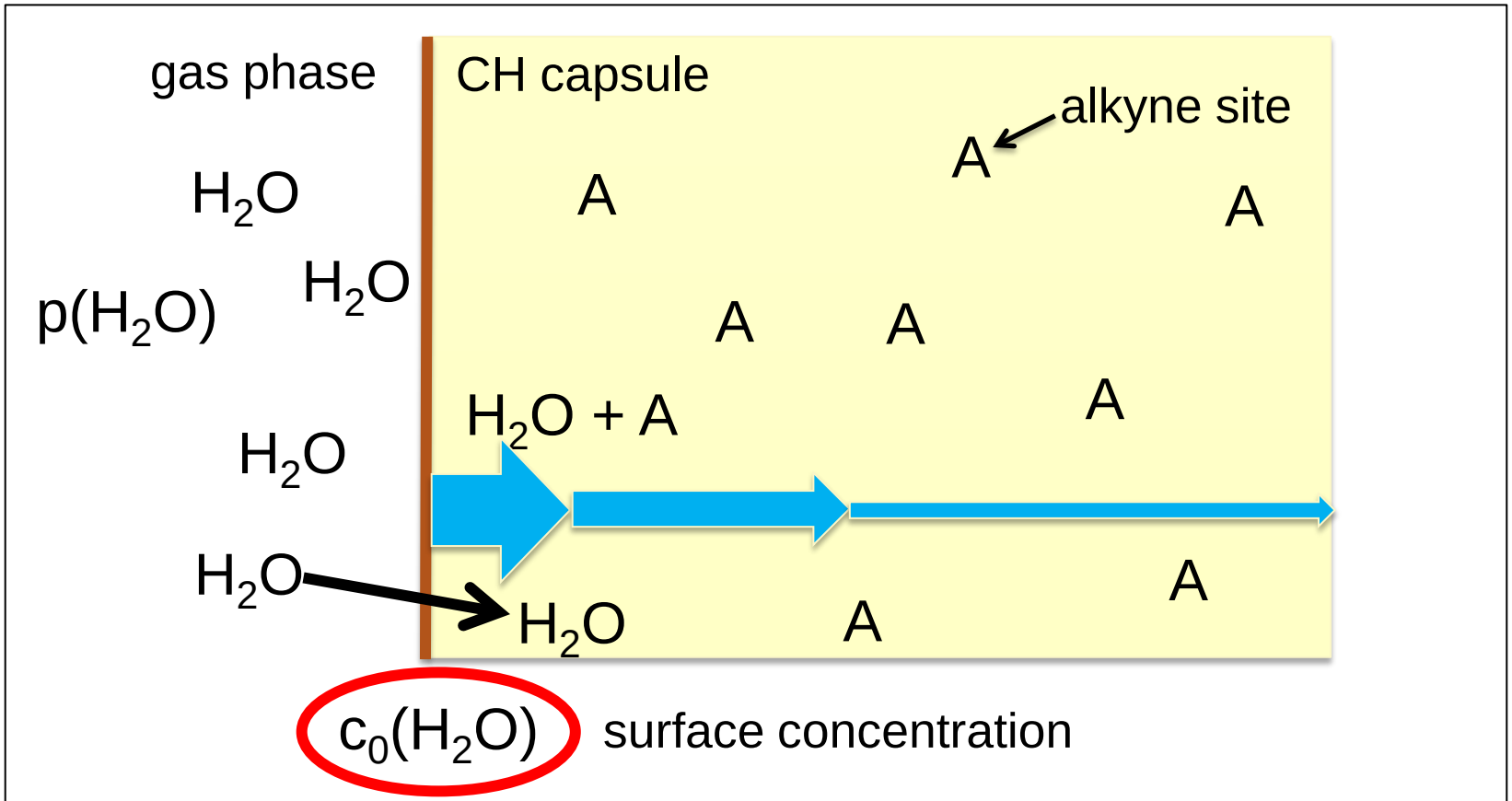
Water addition to alkyne bonds in the polymer is a potential mechanism for the mass uptake



IR data shows an increase in –OH and C=O groups with time



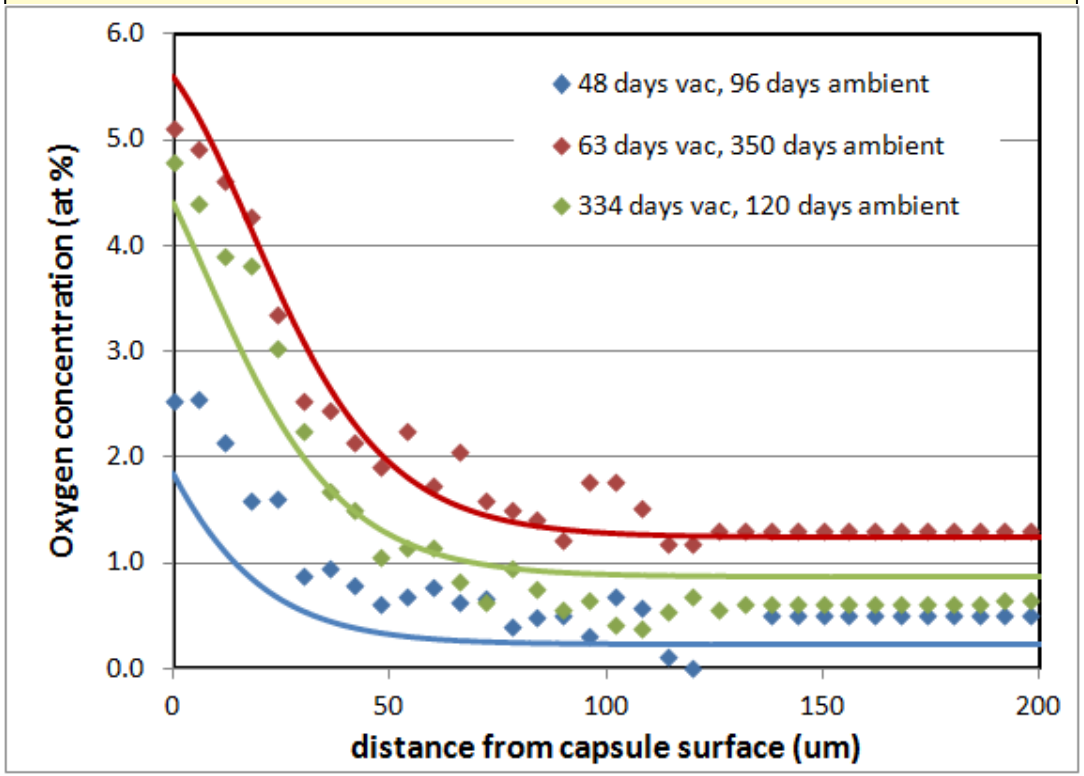
Mass gain can be modeled as simple diffusion/reaction process



$$\frac{\partial c(H_2O)}{\partial t} = \underbrace{D\frac{\partial^2 c(H_2O)}{\partial x^2}}_{\text{diffusion}} \underbrace{- r \cdot c(H_2O) \cdot c(A)}_{\text{reaction}}$$

The model fits well to long-term water uptake, underestimates short-term water

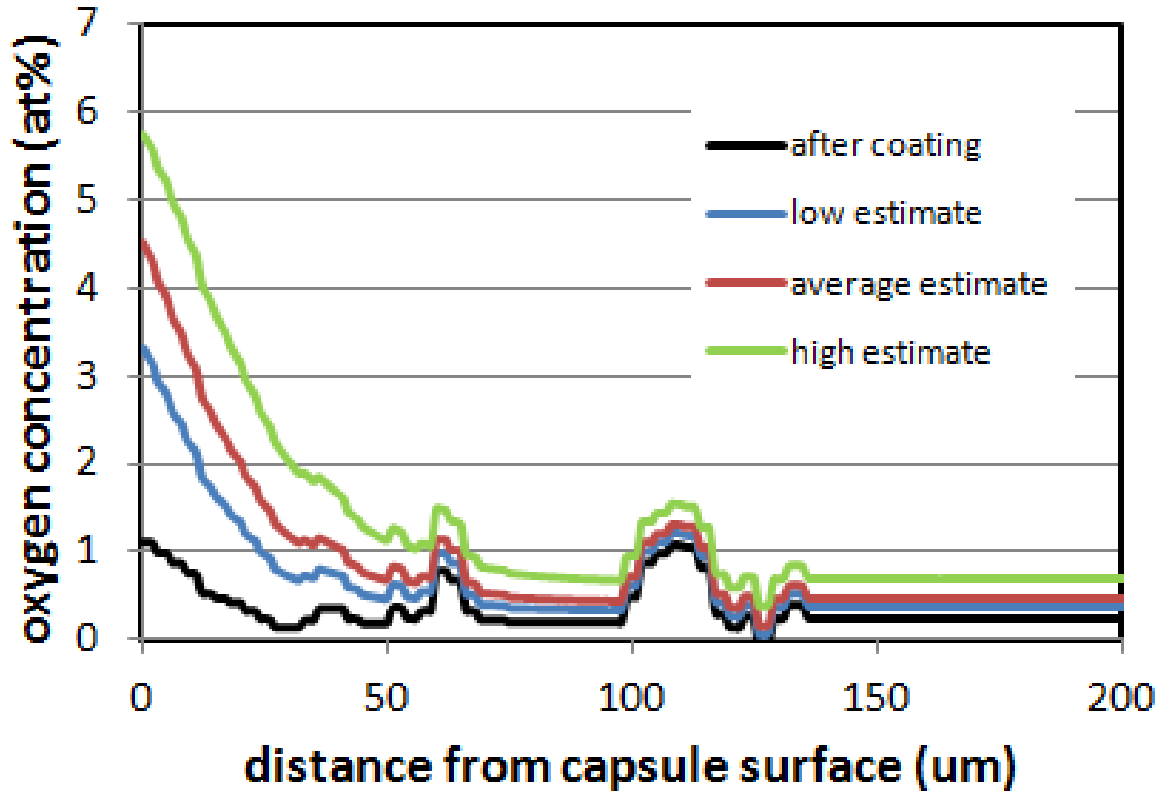
Model takes into account changing storage conditions



diffusion coefficient ($\mu m^2/hr$)	reaction constant (hr^{-1})	water solubility	reactive site concentration	baseline creep constant (hr^{-1})
25	1.6	$1.4 \cdot 10^{-4}$	0.055	$5 \cdot 10^{-7}$

The model can be used to predict oxygen profile ranges for shot capsules

Lower, average and upper uptake rates are modeled using the range of fit constants to exactly fit data



The model is the only source of information for oxygen distribution in target capsules

Mitigations for controlling the water uptake

- store capsules in dry nitrogen cabinets reduces partial pressure of water in storage environment by 90%+

- limit exposure of capsule to ambient to 60 days during processing

Stainless steel dry storage cabinets

Future work

- Validate the model through further experiments
  - — titrate alkyne amount and compared to amount predicted from the model
  - — measure long-term oxygen uptake of capsules
  - — measure permeability of pyrolyzed CH

- Improve the model:
  - — Diffusion constant dependent on degree of reaction
  - — water solubility dependent on degree of reaction
  - — better description of the baseline creep

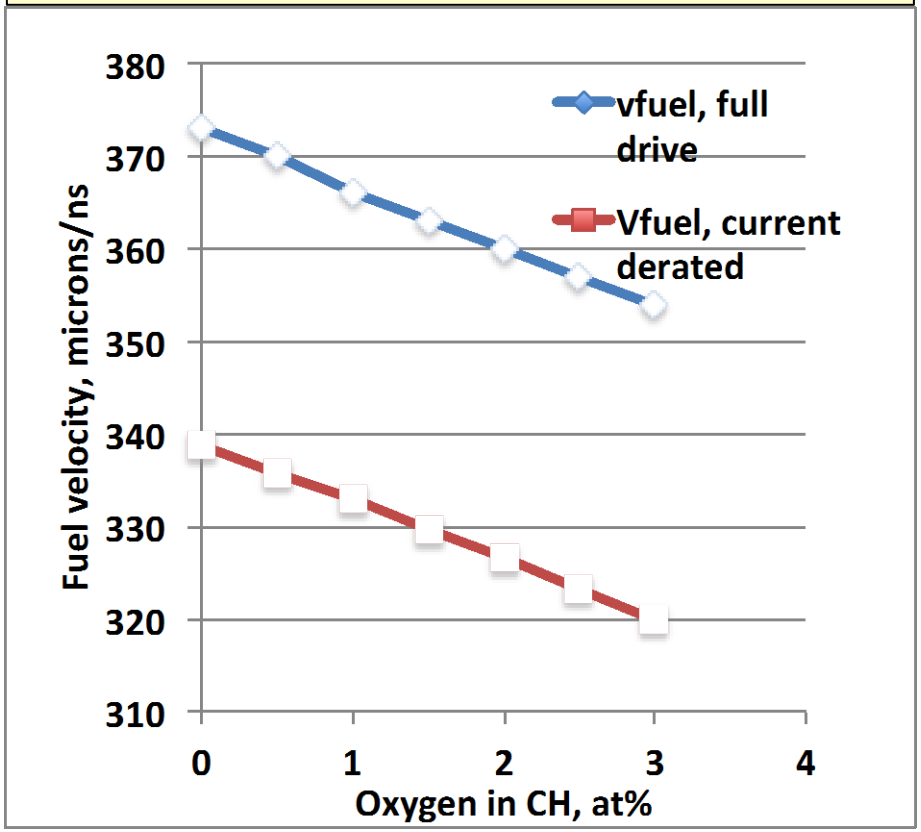
Conclusions

- Oxygen uptake of CH capsules during exposure to ambient affects the implosion
- Quartz crystal microbalance studies have identified water as the reactant
- An engineering model for simulating the oxygen profile has been successfully developed
- Mitigations have been put into place at LLNL to reduce water uptake during storage

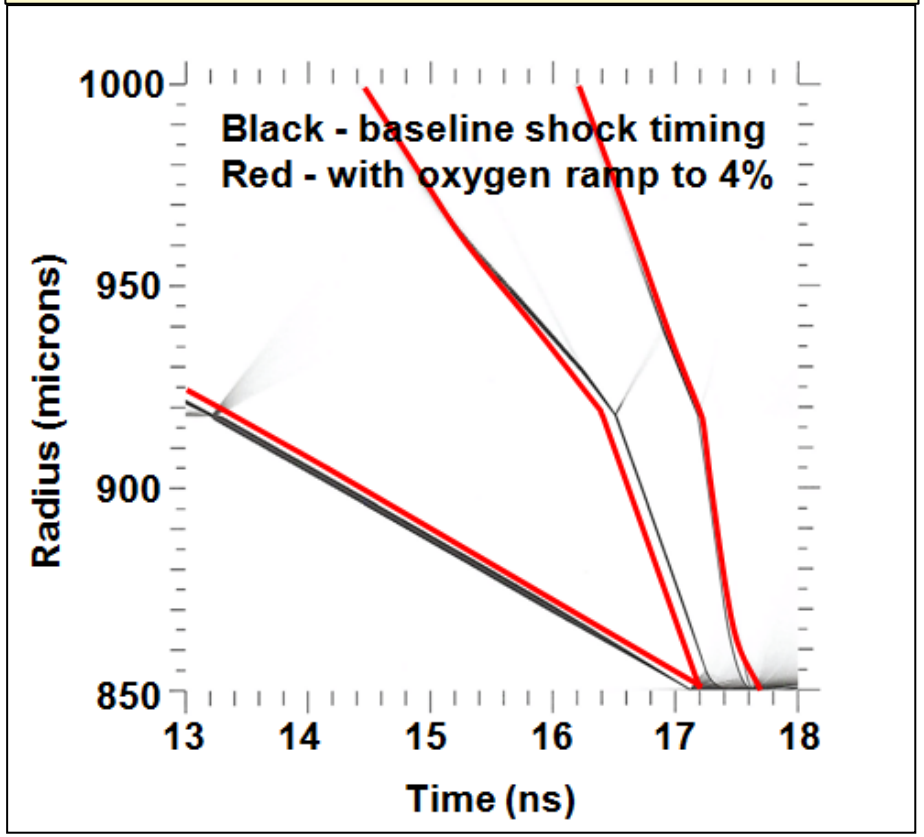
NIC

Oxygen in the ablator can reduce fuel velocity and change shock timing

O content greater than 1at% reduces fuel velocity below tolerable levels

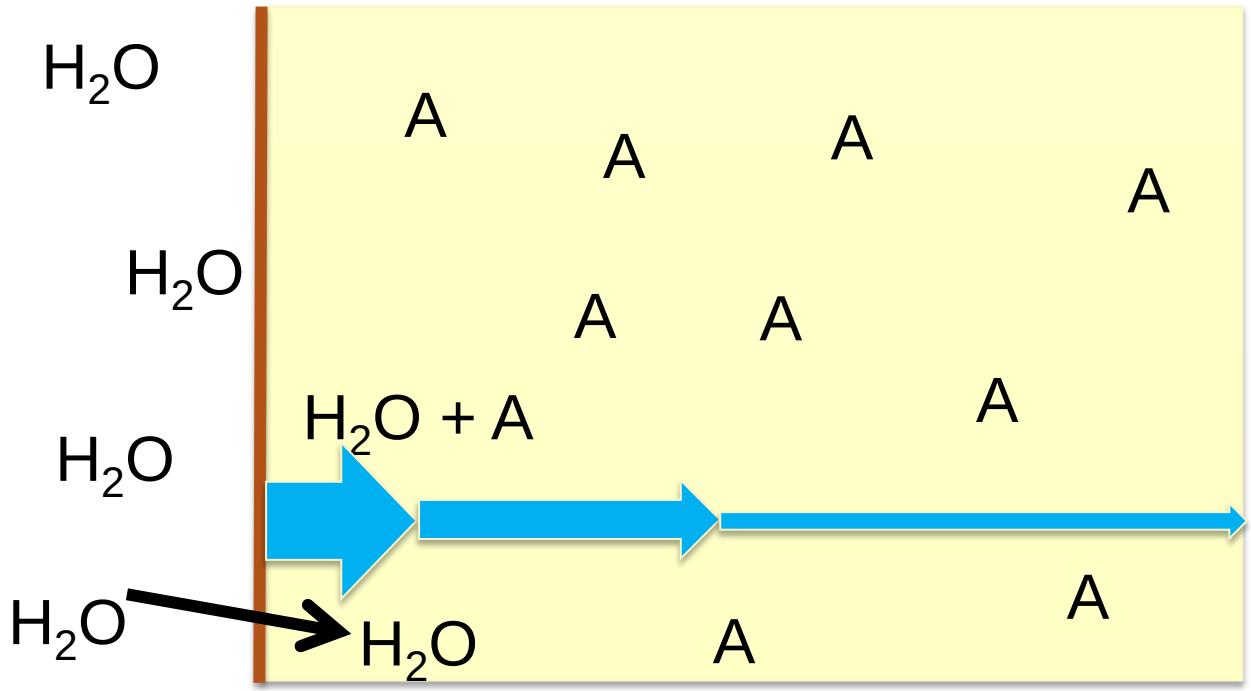


Non-uniform O distribution changes shock timing, decreasing likelihood of ignition



Oxygen concentration should be minimized if possible. Known oxygen distributions can be compensated for in shock timing.

Mass gain can be modeled as simple diffusion/reaction process

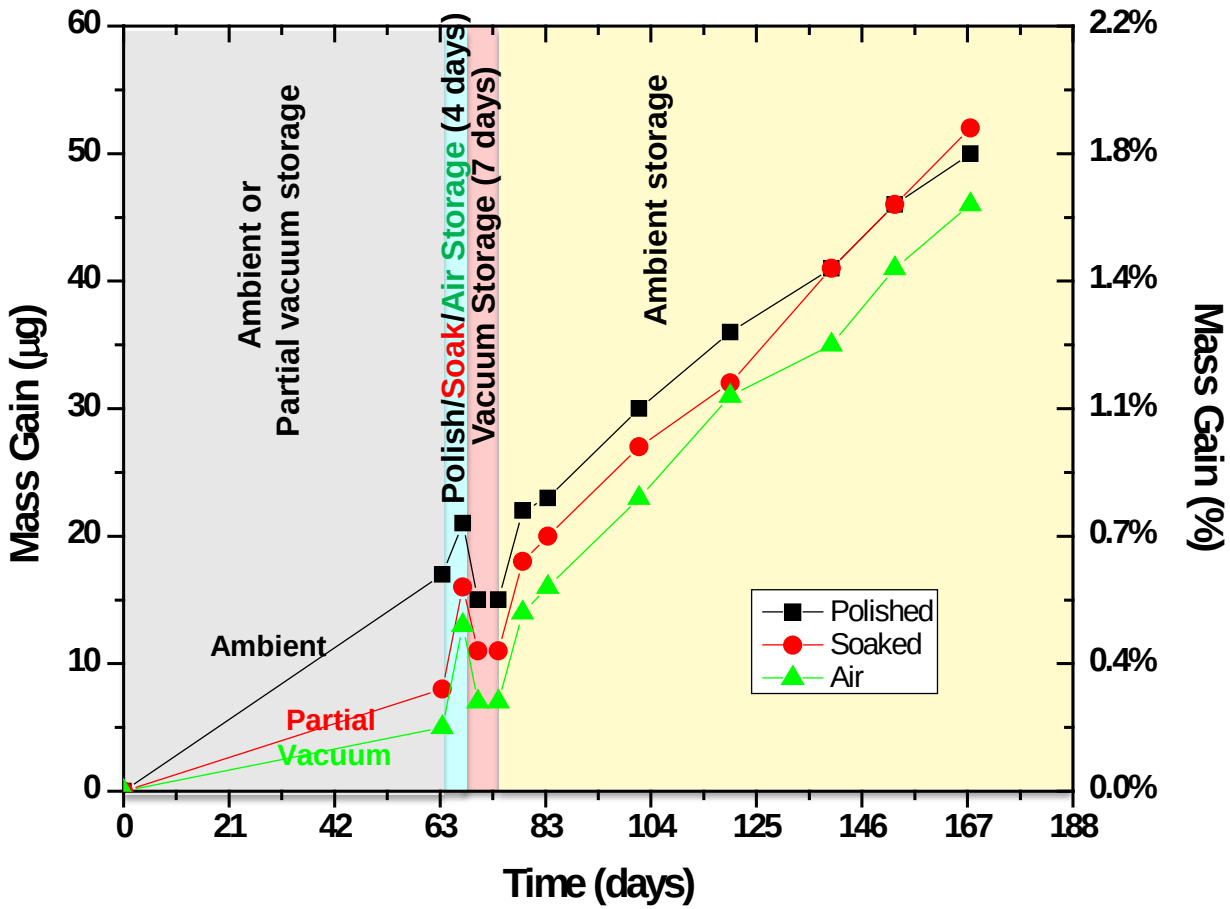


$p(H_2O)$ $c_0(H_2O)$

$$\frac{\partial c(H_2O)}{\partial t} = D\frac{\partial^2 c(H_2O)}{\partial x^2} - r \cdot c(H_2O) \cdot c(A) + k$$

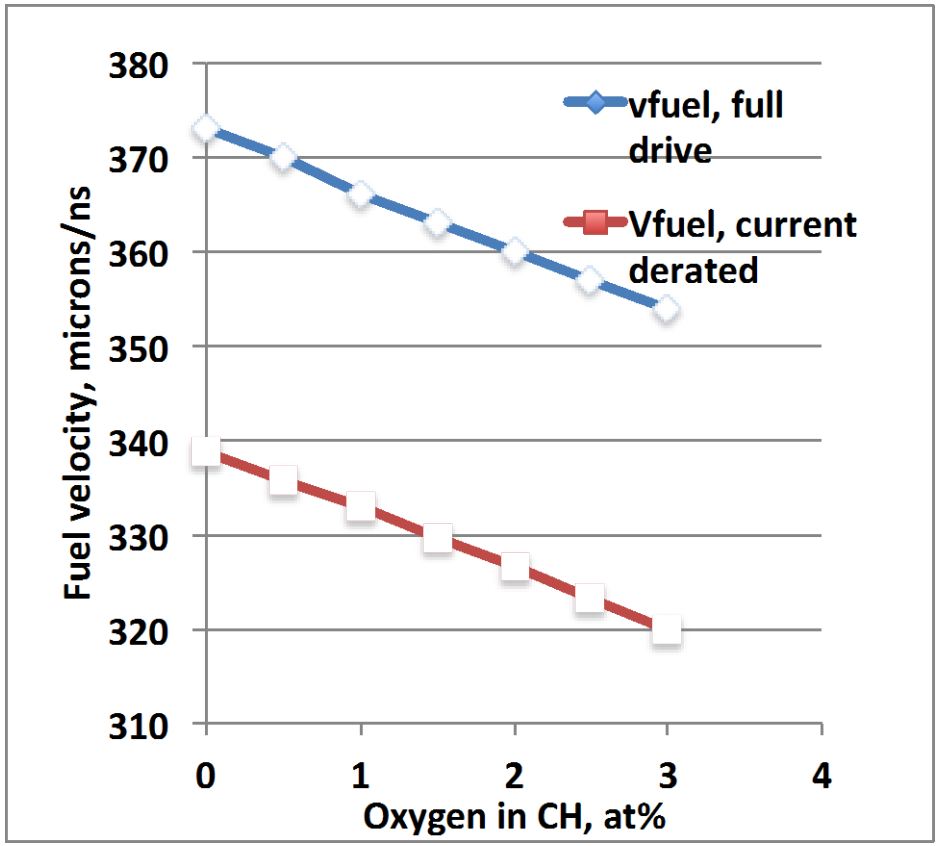
Capsule have gained ~1.8% in mass after ~6 months of ambient storage with no slow down in rate

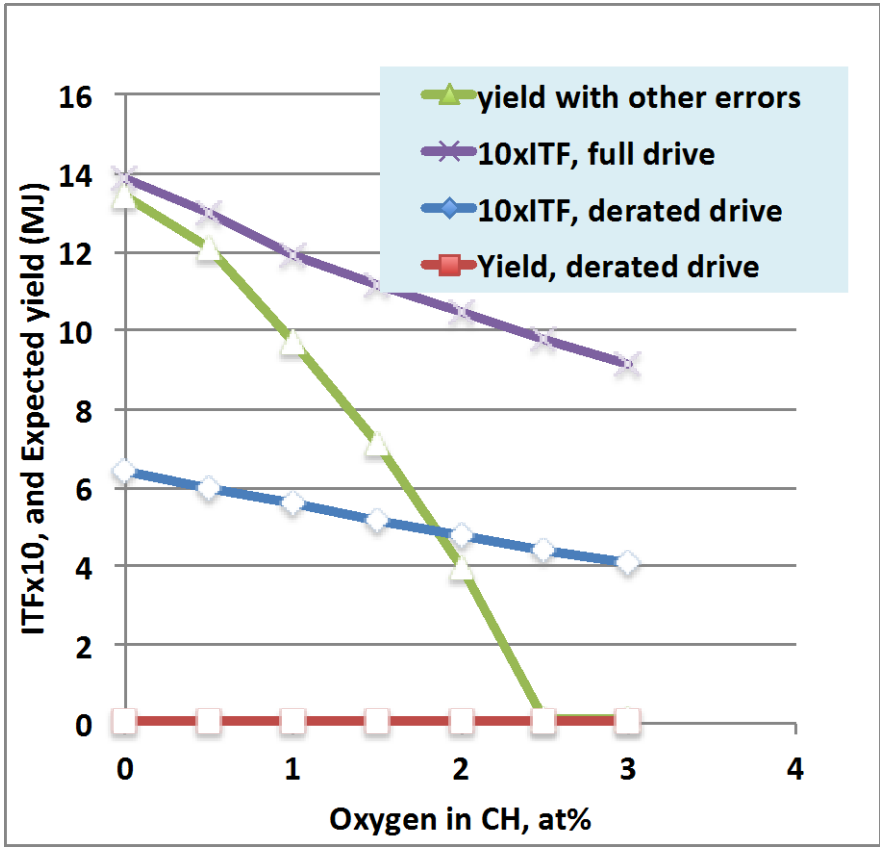
Measured capsule weight as function of time and process



- Weight gain is largely linear with time
- Solubility limit has not been reached in ~ 6 months
- Effect of polish, water soaking or air storage on weight gain is apparent, but it is a weaker effect than the long term ambient weight gain
- Partial Vacuum storage slows rate or only partially removes weight gain; subsequent ambient storage returns weight gain to nominal levels quickly
- **Hypothesis:** Capsule is taking up H_2O or O_2 which is only partially reversible

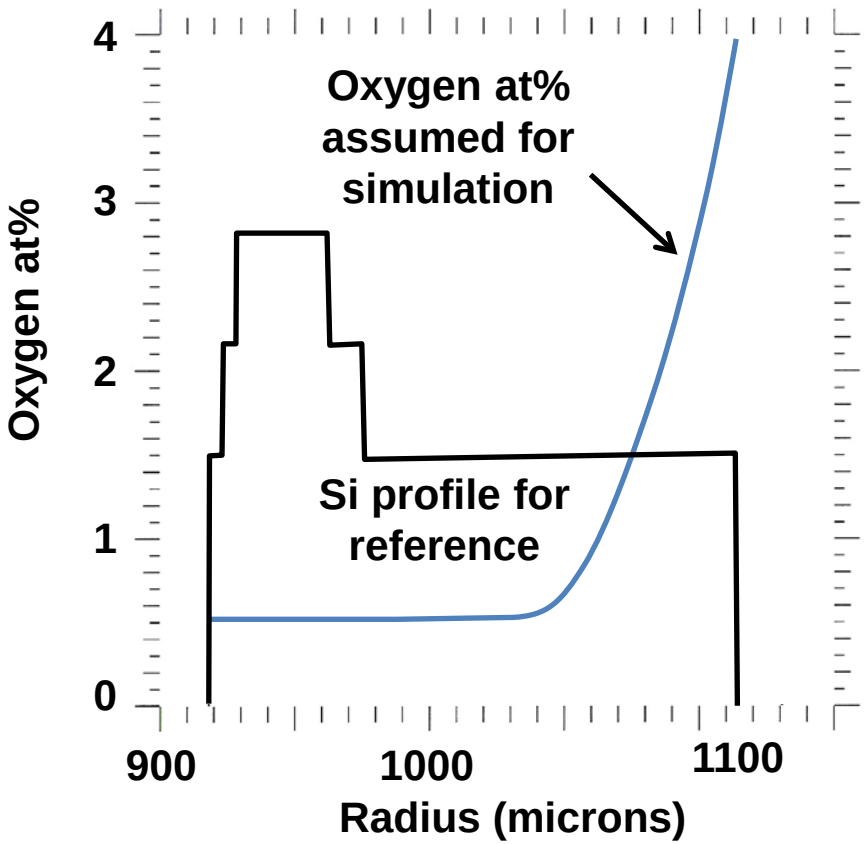
Average oxygen of 1at% or more affects implosion velocity unacceptably

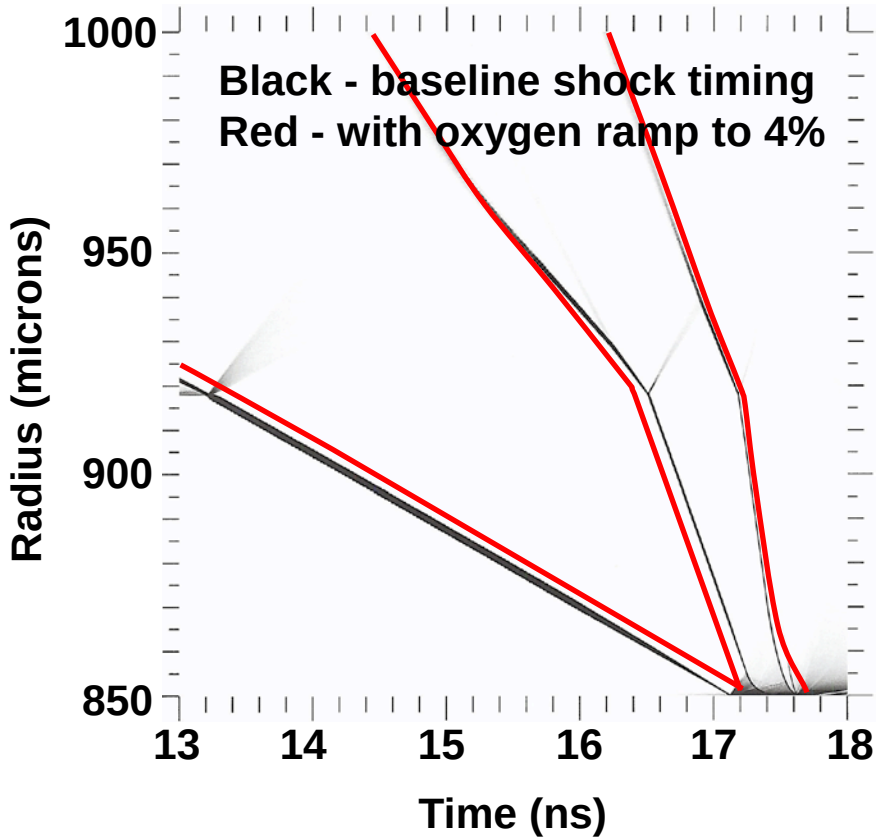




Requirement is "Average Oxygen < 1 at%"
Each 1 at% reduces velocity by 1.9%, we need implosion velocity within 3% of nominal for ignition

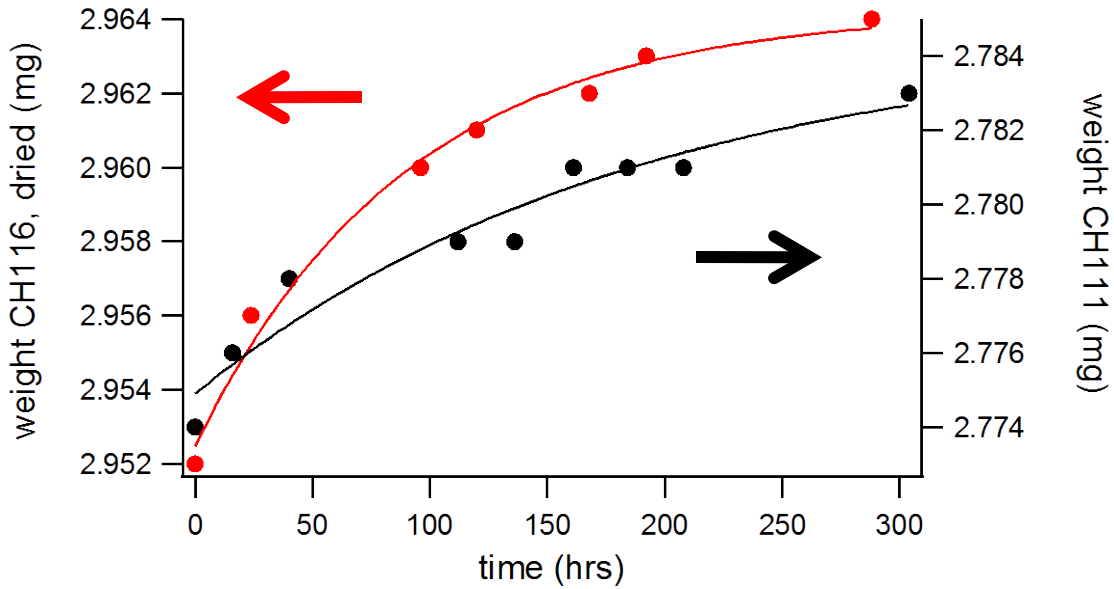
An oxygen ramp near the ablator surface changes the shock timing





- Oxygen profile ramping up to 4% over 50 microns changes shock timing by 50 ps, which is 1x spec for Keyhole shock timing
- Because it changes several shocks, changes adiabat from 1.44 to 1.472, loss of 8.5% in ITF
- If Keyholes set timing with this ramp, and this is reproducible for Keyholes and THD/DTs, it doesn't matter

Time constants of water uptake

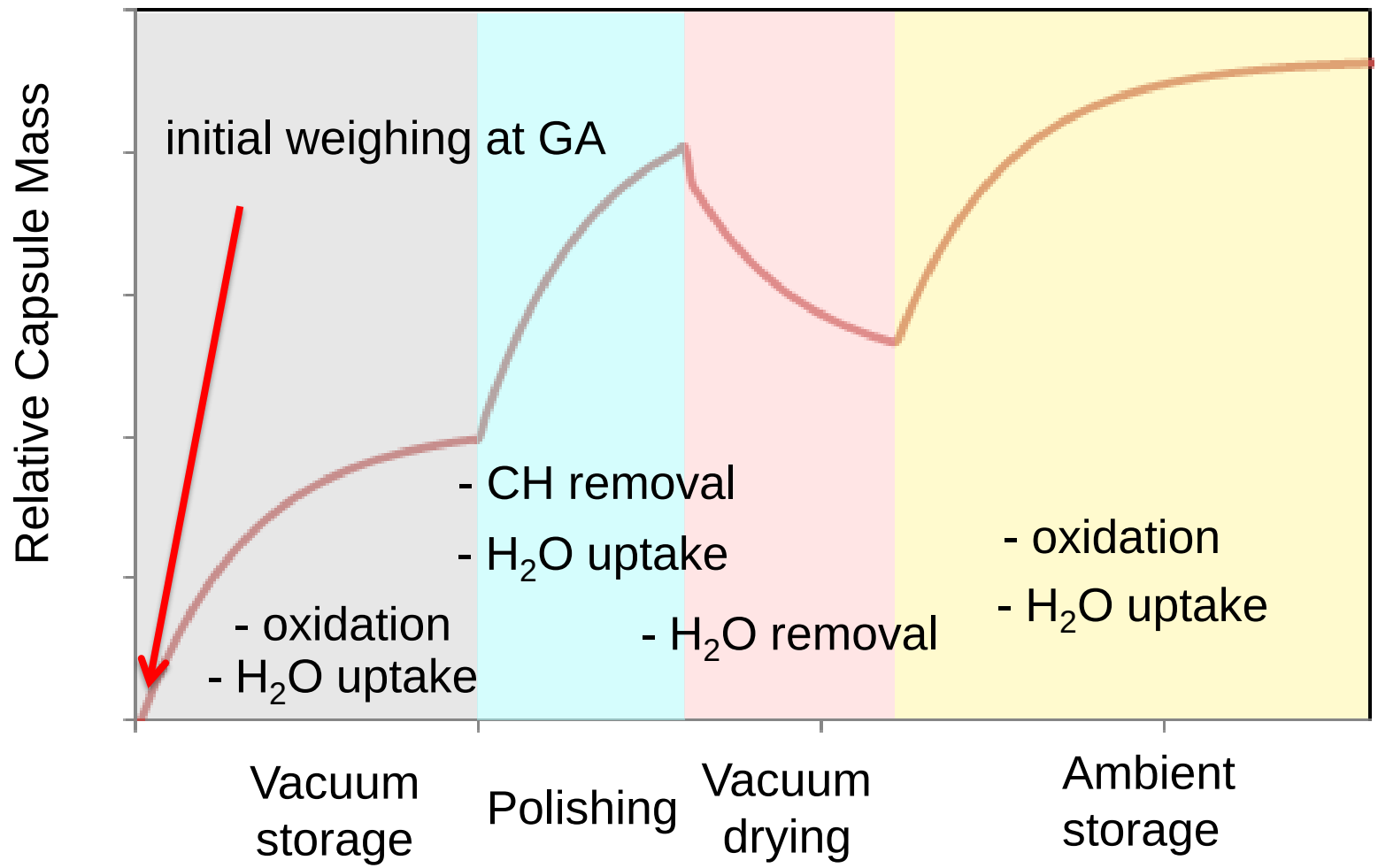


- both sets of data (dried and non-dried) can be fit with exponentials
- the time constants are 90 hrs and 190 hrs
- starting points are different, as expected; CH 111 is assumed to have some water contents at the beginning of the experiment

The mass change rate of the capsule is dependent on capsule history.

We designed an experiment to quantify capsule mass change due to O_2 & H_2O exposure and CH removal during polishing

Schematic of hypothesized changes in capsule mass

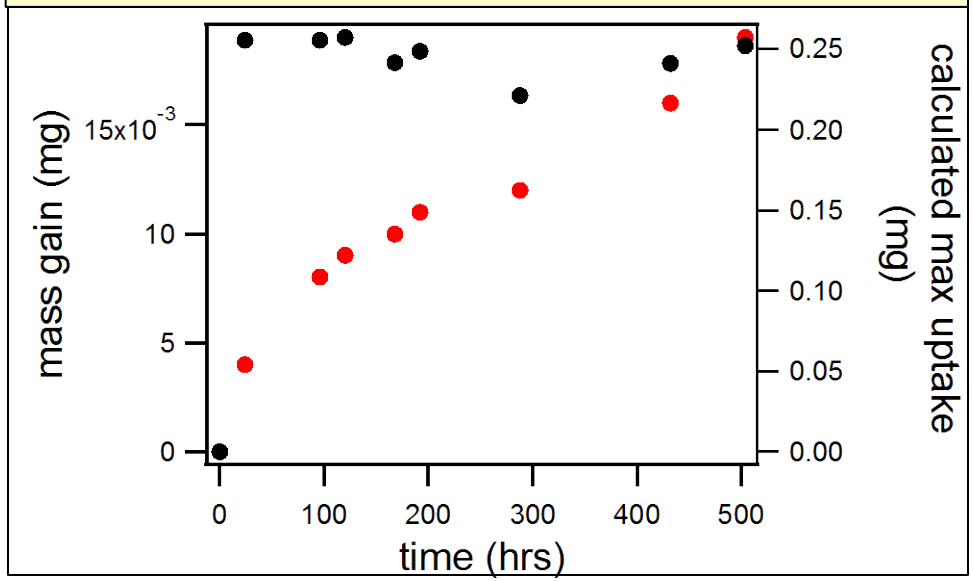


Not to scale

Predicted mass gains and times

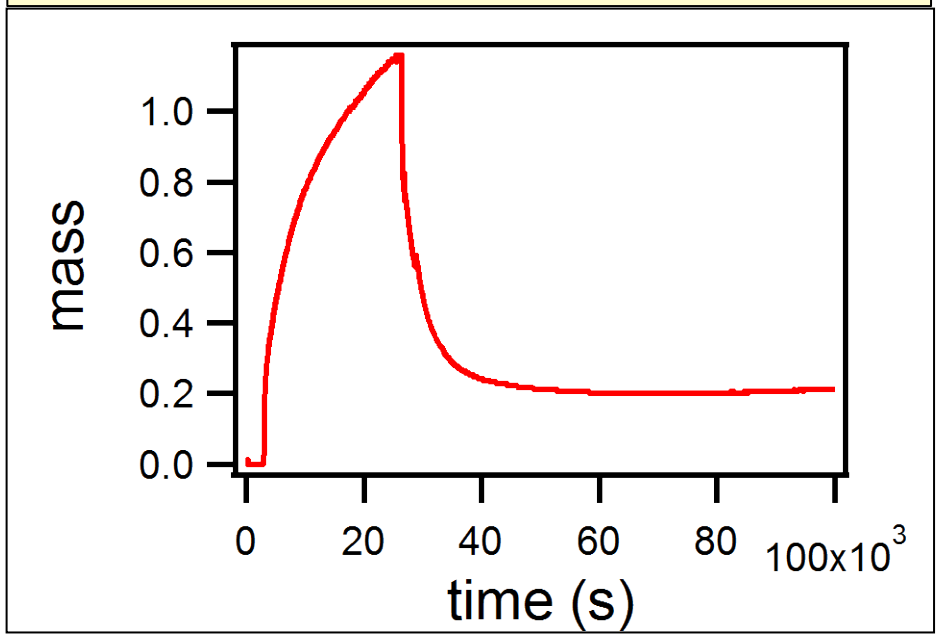
- maximum water uptake for capsules can be estimated from thickness, diffusion coefficient, and the immersion data
- average predicted mass gain is 0.246 mg, or 8.3% (largest total mass gain observed in QCMB so far is 3.5%)
- estimated time to total soak for capsules is more than 30 years!!

Max mass gain for capsules from immersion data

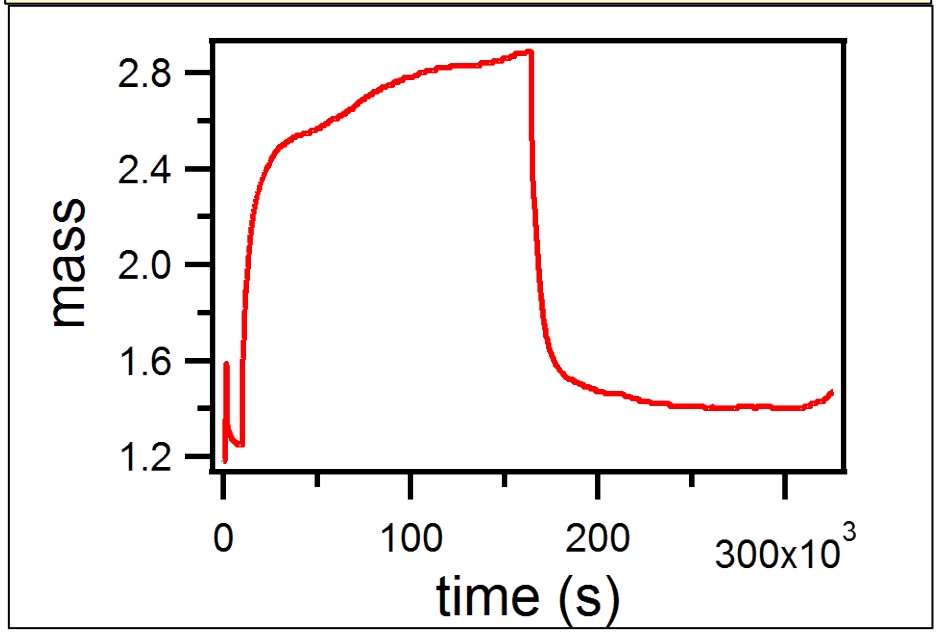


Some of the mass uptake is irreversible- water or oxygen?

1st QCMB run



2nd QCMB run

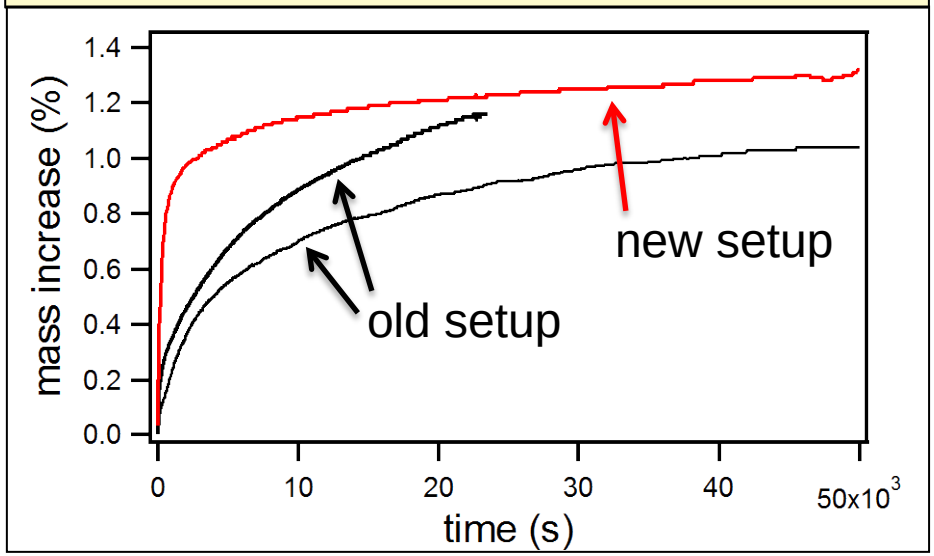


- after every exposure, some of the mass remains in the CH film
- film was exposed to ambient air between the two runs

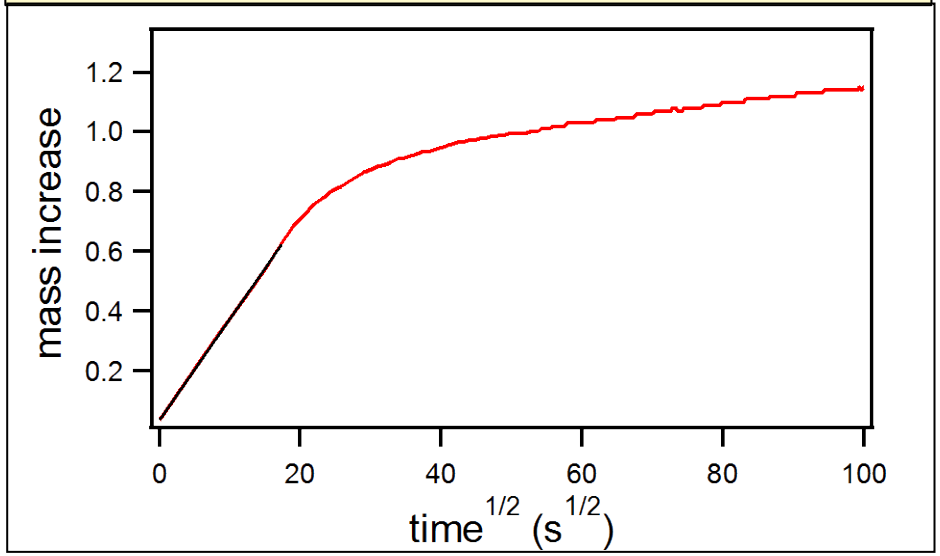
- first run with dry air on new pyrolyzed film showed no weight increase

New setup shows previous measurements were gas-diffusion limited

Comparison between data from old and new setup



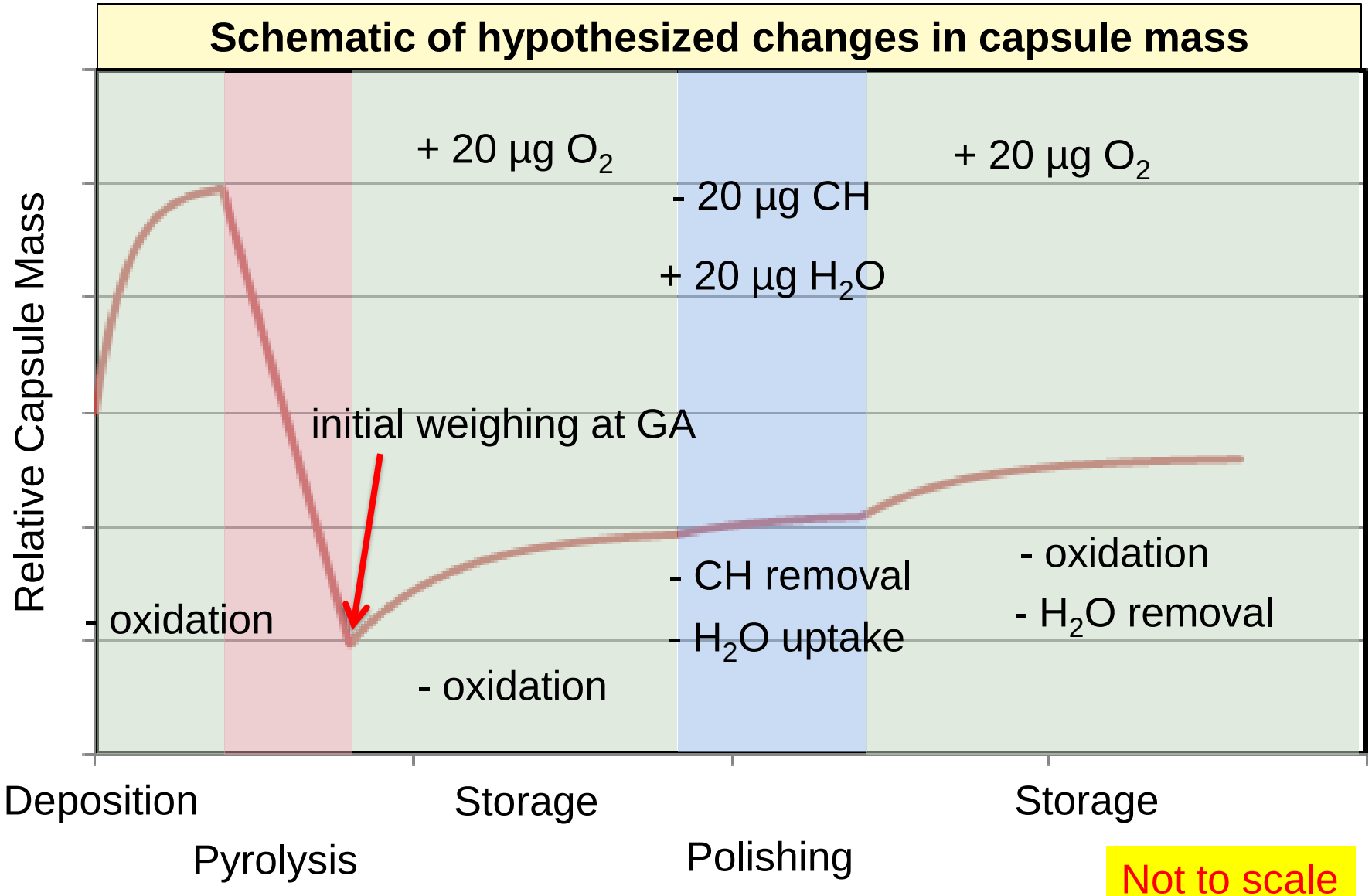
Plot vs time$^{0.5}$ gives good linear fit in the initial curve



- smaller chamber with gas flow directed straight at the film reduces concentration equilibration time

- measured diffusion constant is $2.02 \cdot 10^{-12}$ cm^2/s

The mass and thickness of the capsule changes with time due to O_2 uptake, H_2O uptake, and CH removal during polishing



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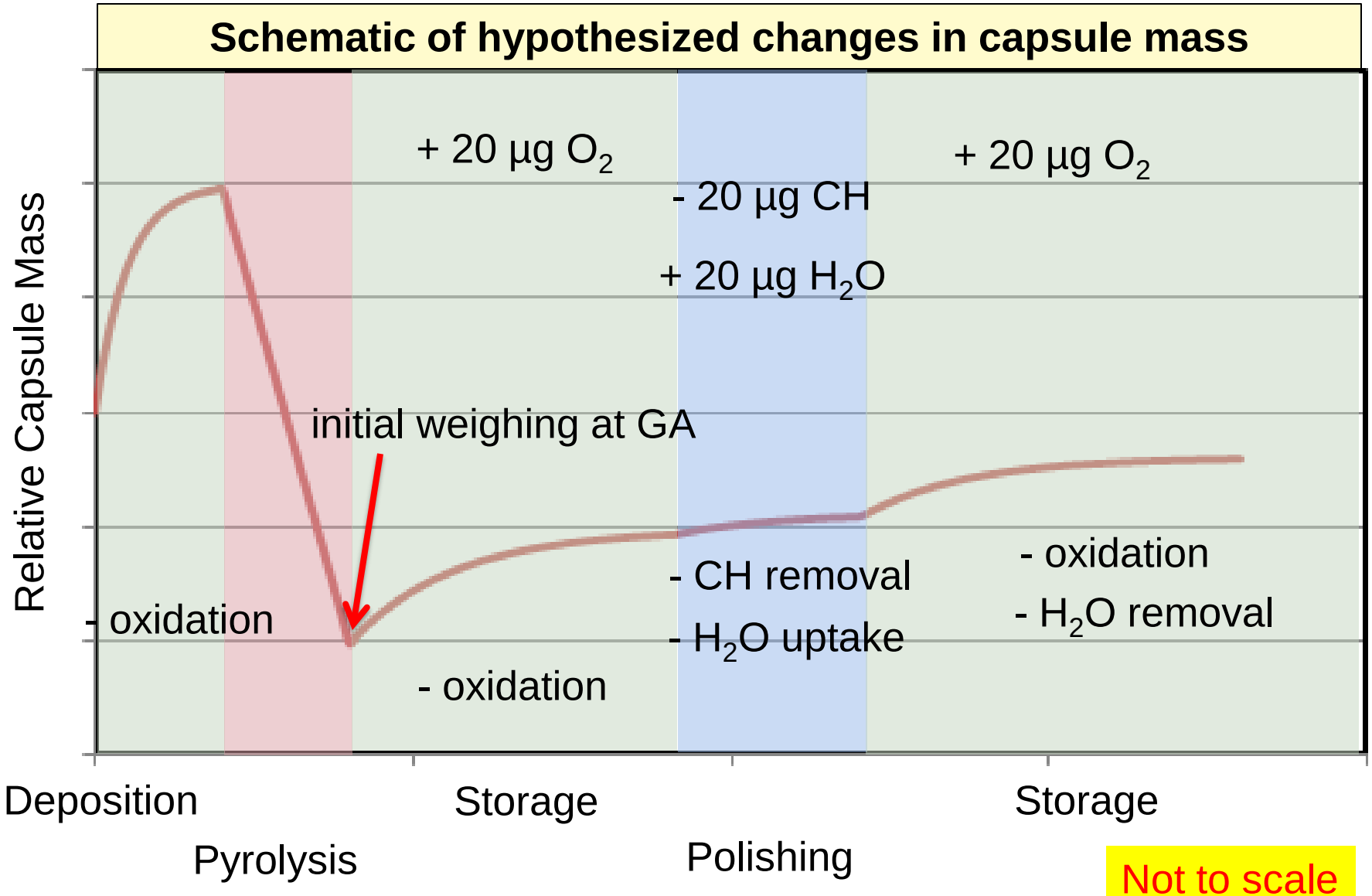

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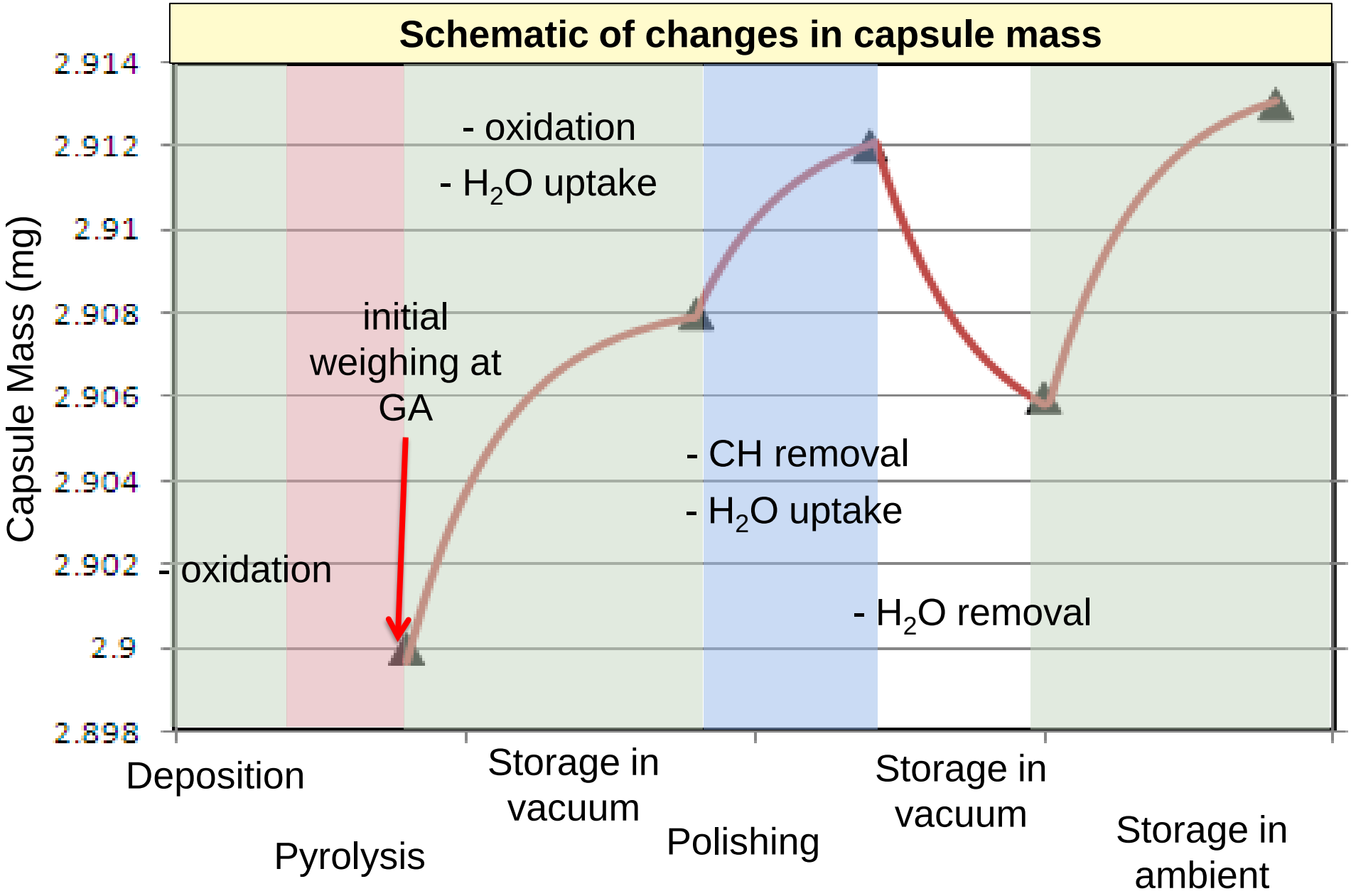
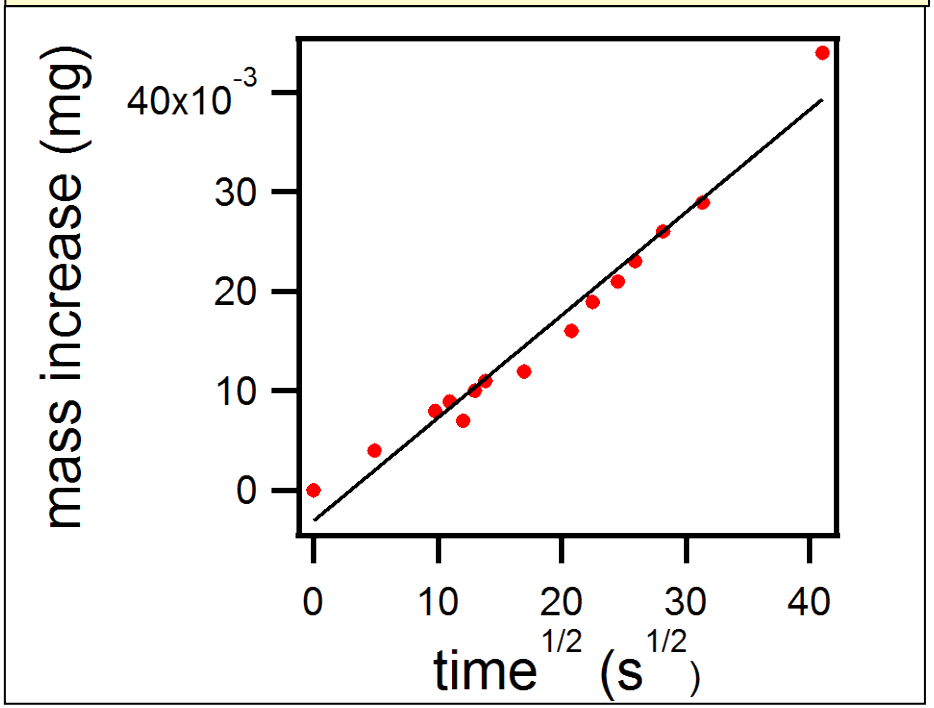
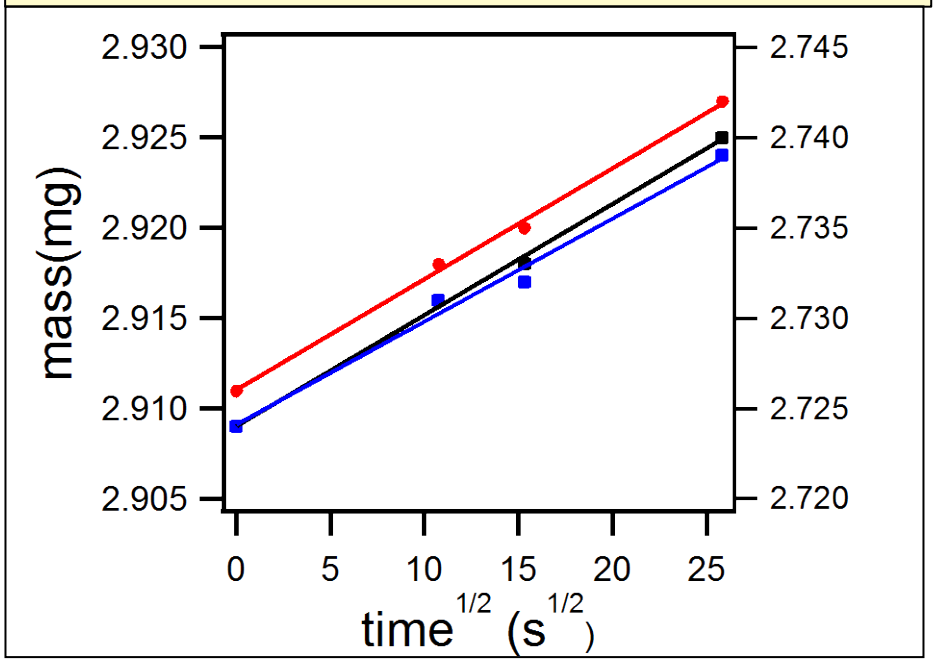


Water uptake on capsules as of 11/04/10

CH 116 – full water immersion



polishing test – ambient air

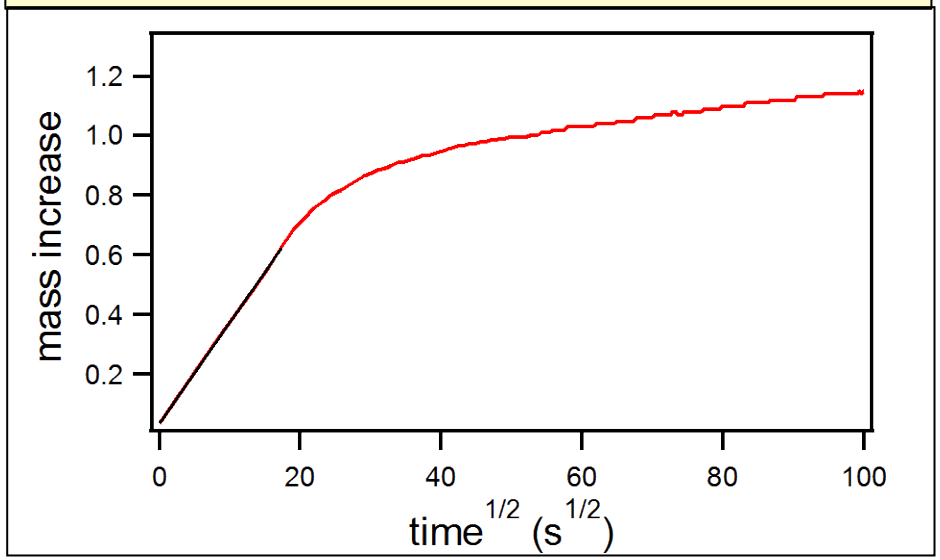


- slope of CH116 is 0.0010 mg/hr$^{0.5}$
- slope of polishing experiment is 0.0006 mg/hr$^{0.5}$

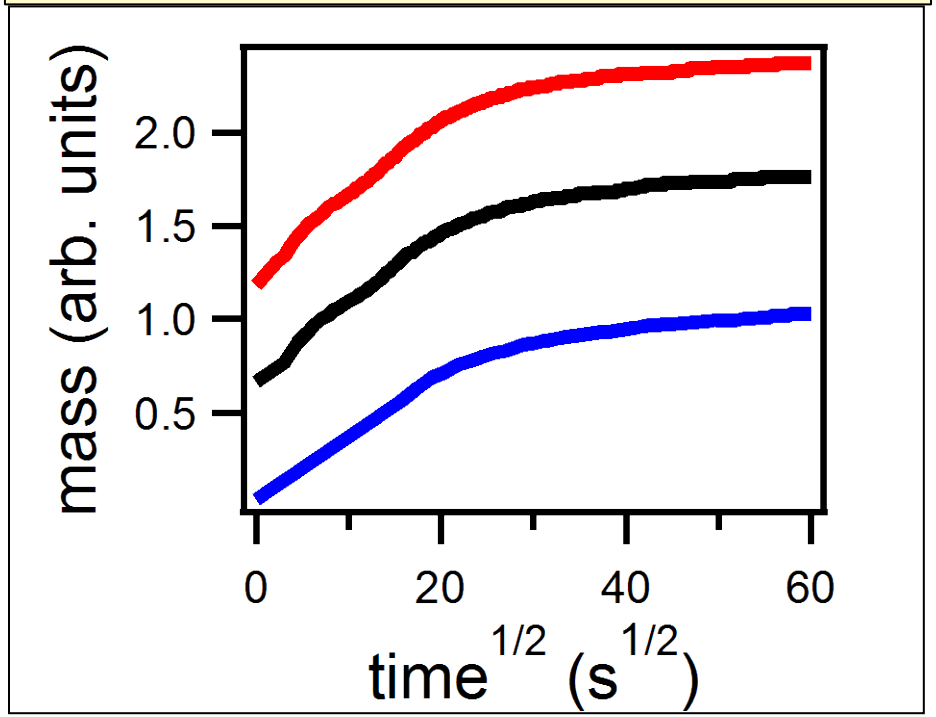
- if CH116 is fit in the same time range as the polishing experiment, slope becomes 0.0008 mg/hr$^{0.5}$

Mass does not return to baseline after load/unload cycle; diffusion constant increases

Plot vs time$^{0.5}$ gives good linear fit in the initial curve



Subsequent uptakes have higher slopes



- total uptake stays about the same (~1.2)
- uptake is not fully reversible
- slope increases by 24% -> D increases by 50%

Short term water uptake follows Fick's Law well for QCMB measurement

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2}$$ Fick's 2nd Law

- for our boundary conditions,

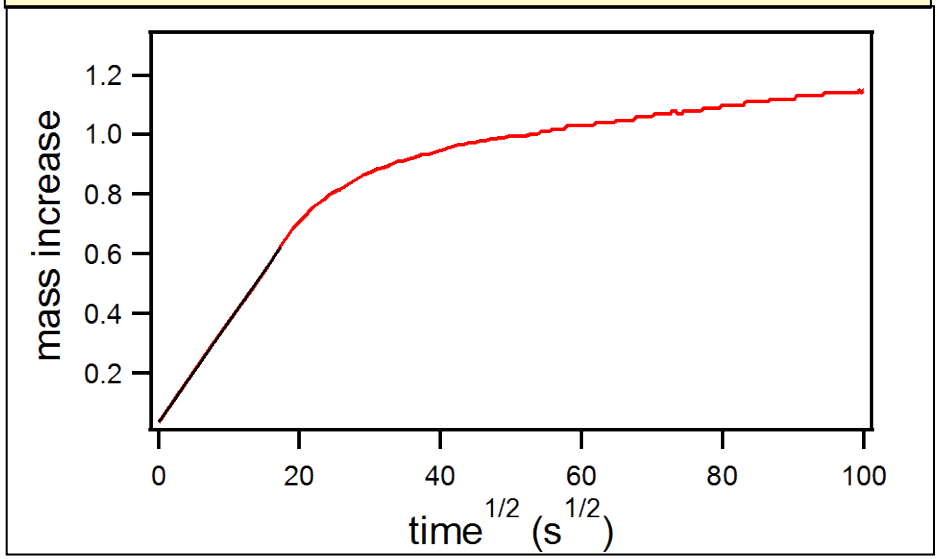
$$\frac{M_t}{M_\infty} = \frac{4\sqrt{Dt}}{d}\cdot\left\{\frac{1}{\sqrt{\pi}} + 2\sum_{n=0}^{\infty}(-1)^n ierfc\frac{nd}{2\sqrt{Dt}}\right\}$$

In the initial part of the curve

$$\frac{M_t}{M_\infty} \approx \frac{2}{d}\sqrt{\frac{D}{\pi}}\sqrt{t} = I\sqrt{t}$$, so

$$\boxed{D = \frac{\pi}{4}I^2 d^2}$$

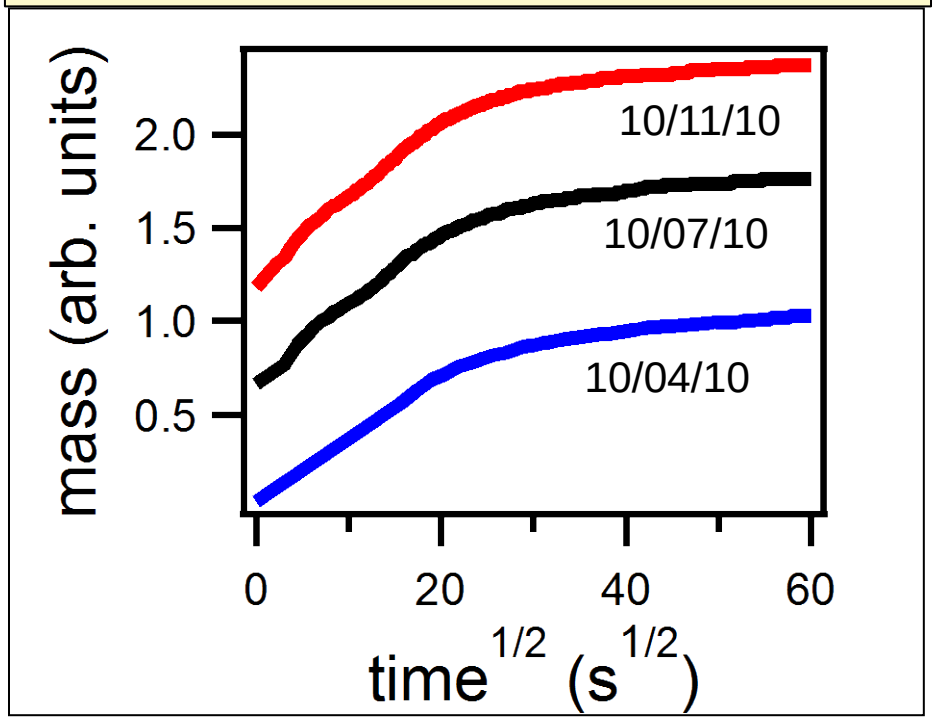
Plot vs time$^{0.5}$ gives good linear fit in the initial curve



Mass does not return to baseline after load/unload cycle; diffusion constant increases

date	process	slope (a.u.)	total mass change (a.u.)	D (10^{-12} cm^2/s)
10/04/10	soak	0.034	1.17	2.92
10/05/10	dry	-0.039	1.07	4.45
10/07/10	soak	0.040	1.18	3.89
10/08/10	dry	-0.042	1.17	4.47
10/11/10	soak	0.042	1.16	4.52
10/11/10	dry	-0.045	1.14	5.28

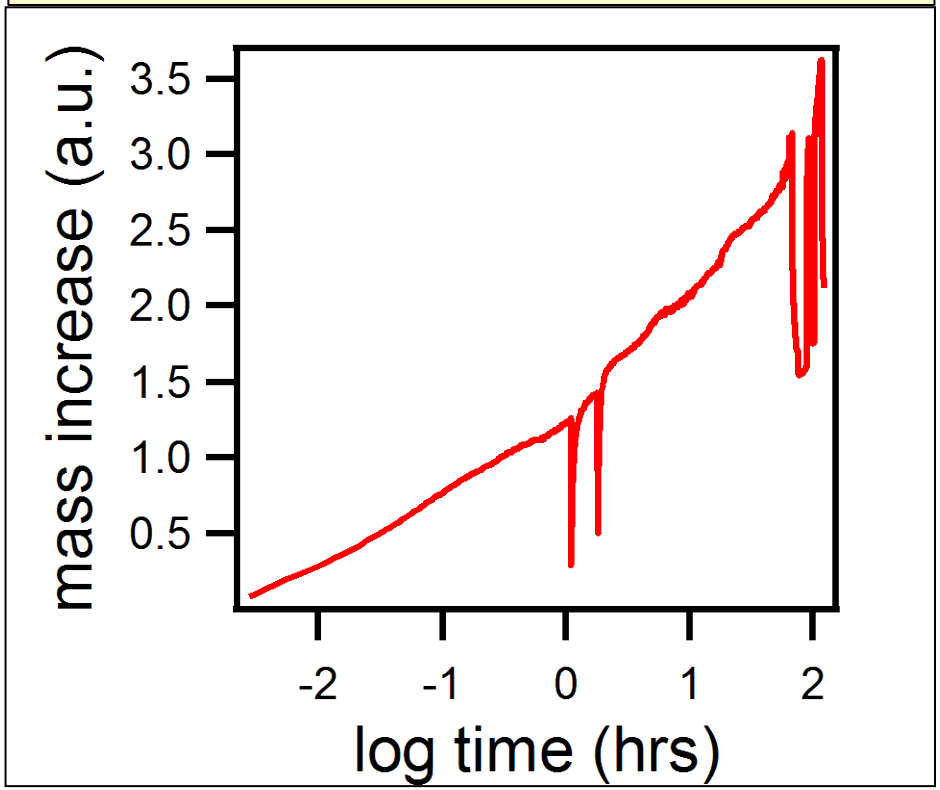
Subsequent uptakes have higher slopes



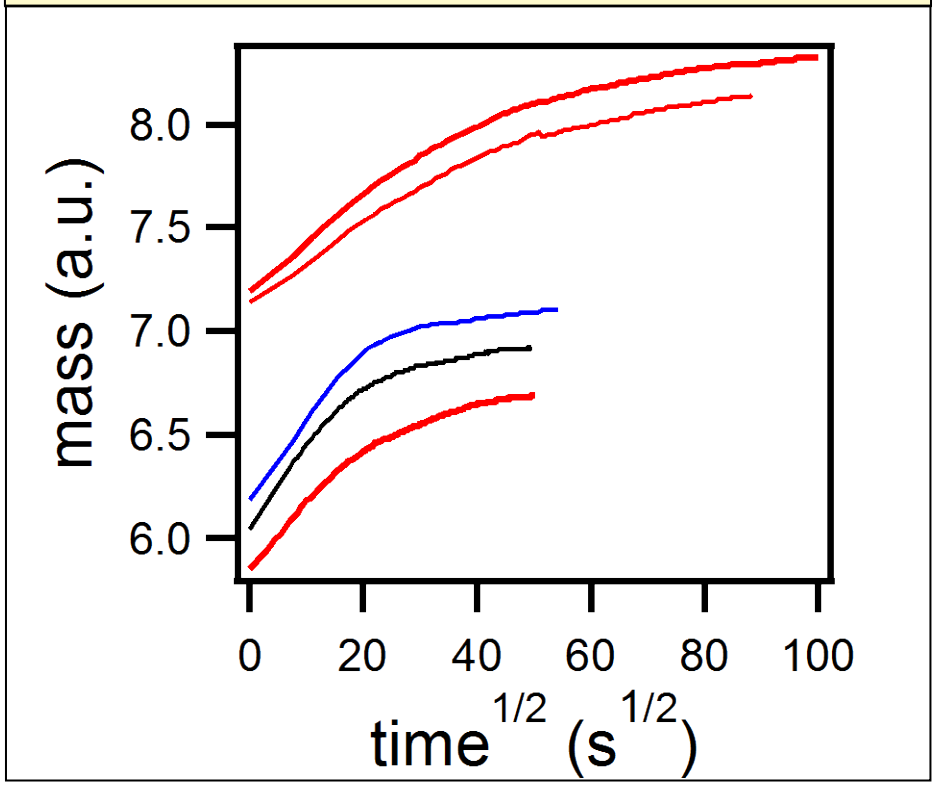
- drying typically shows a higher D than soaking
- total uptake stays about the same (~1.2 a.u.)
- water uptake continues beyond initial soak
- diffusion constant increases with every soak/dry cycle

Long term measurements show irreversible uptake is linear with log t

Irreversible uptake scales with log t



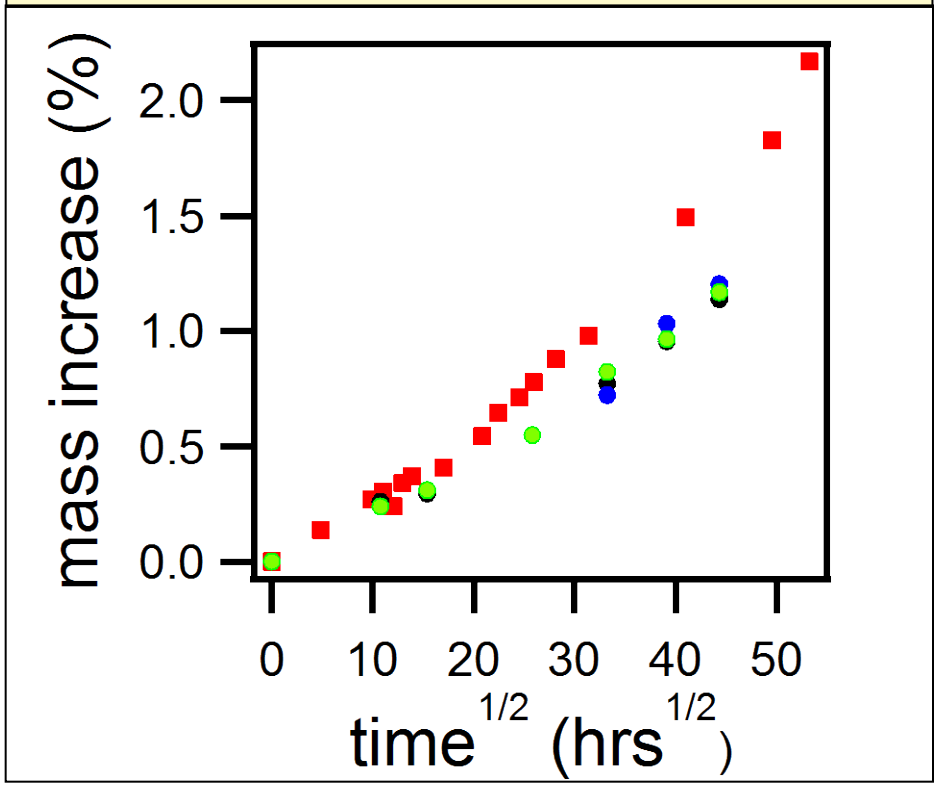
D no longer increases monotonically



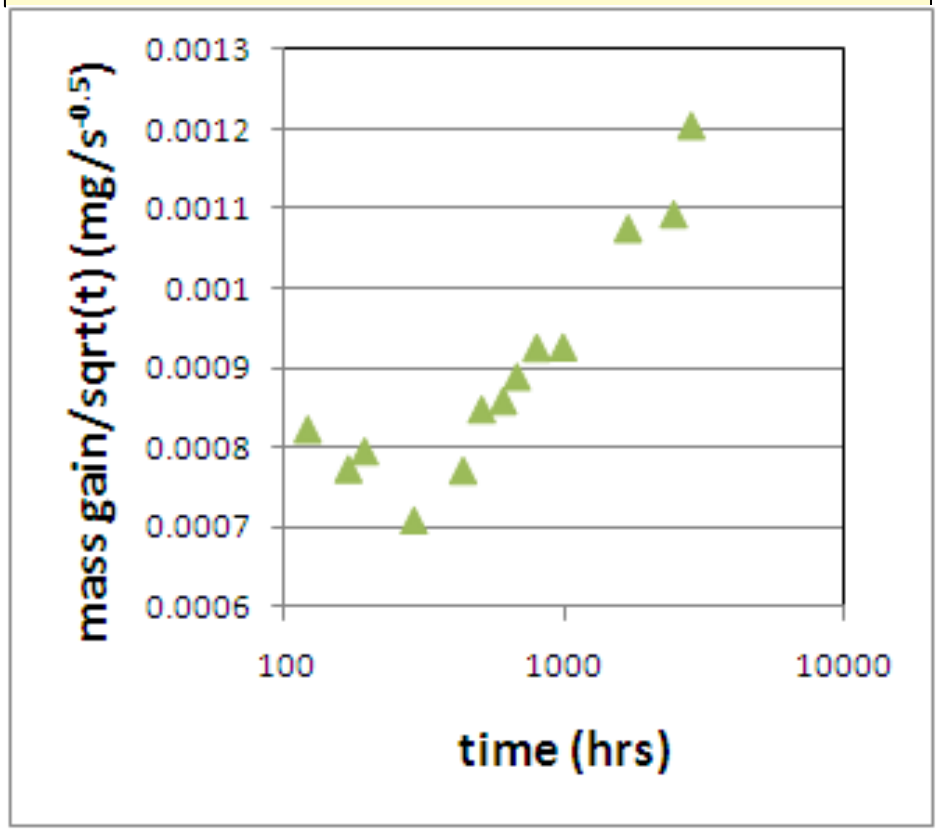
- total uptake increases with time
- around 1 hr, slope increases from 0.49 to 0.88

Capsule mass is linear with $t^{0.5}$, but slope changes after ~550 hrs

Capsule mass gain is linear with $t^{0.5}$, but the slope is not constant



Change in slope appears to be linear with log t



- behavior is different from thin film
- change in slope could mean either D or total mass uptake (or both) are increasing with time

Short term water uptake follows Fick's Law well for QCMB measurement

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2}$$ Fick's 2nd Law

- for our boundary conditions,

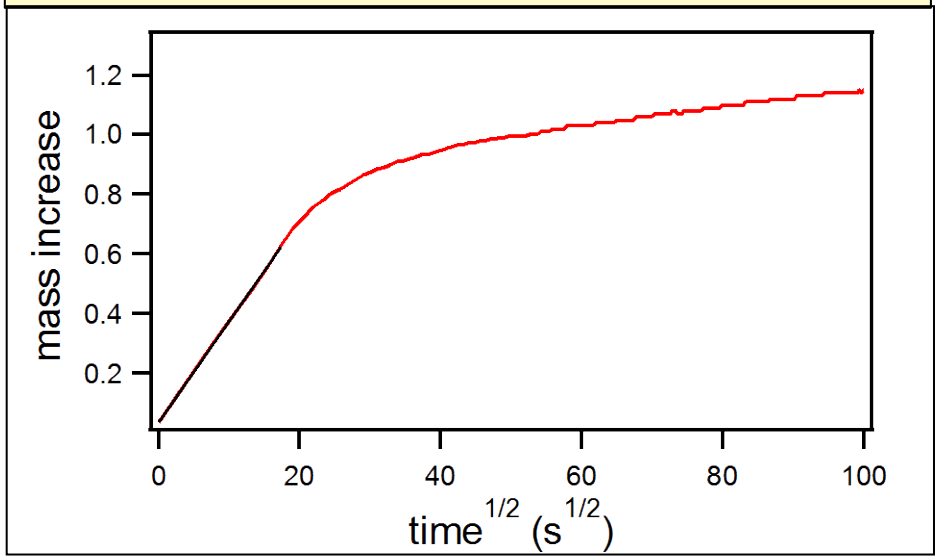
$$\frac{M_t}{M_\infty} = \frac{4\sqrt{Dt}}{d}\cdot\left\{\frac{1}{\sqrt{\pi}} + 2\sum_{n=0}^{\infty}(-1)^n ierfc\frac{nd}{2\sqrt{Dt}}\right\}$$

In the initial part of the curve

$$\frac{M_t}{M_\infty} \approx \frac{2}{d}\sqrt{\frac{D}{\pi}}\sqrt{t} = I\sqrt{t}$$, so

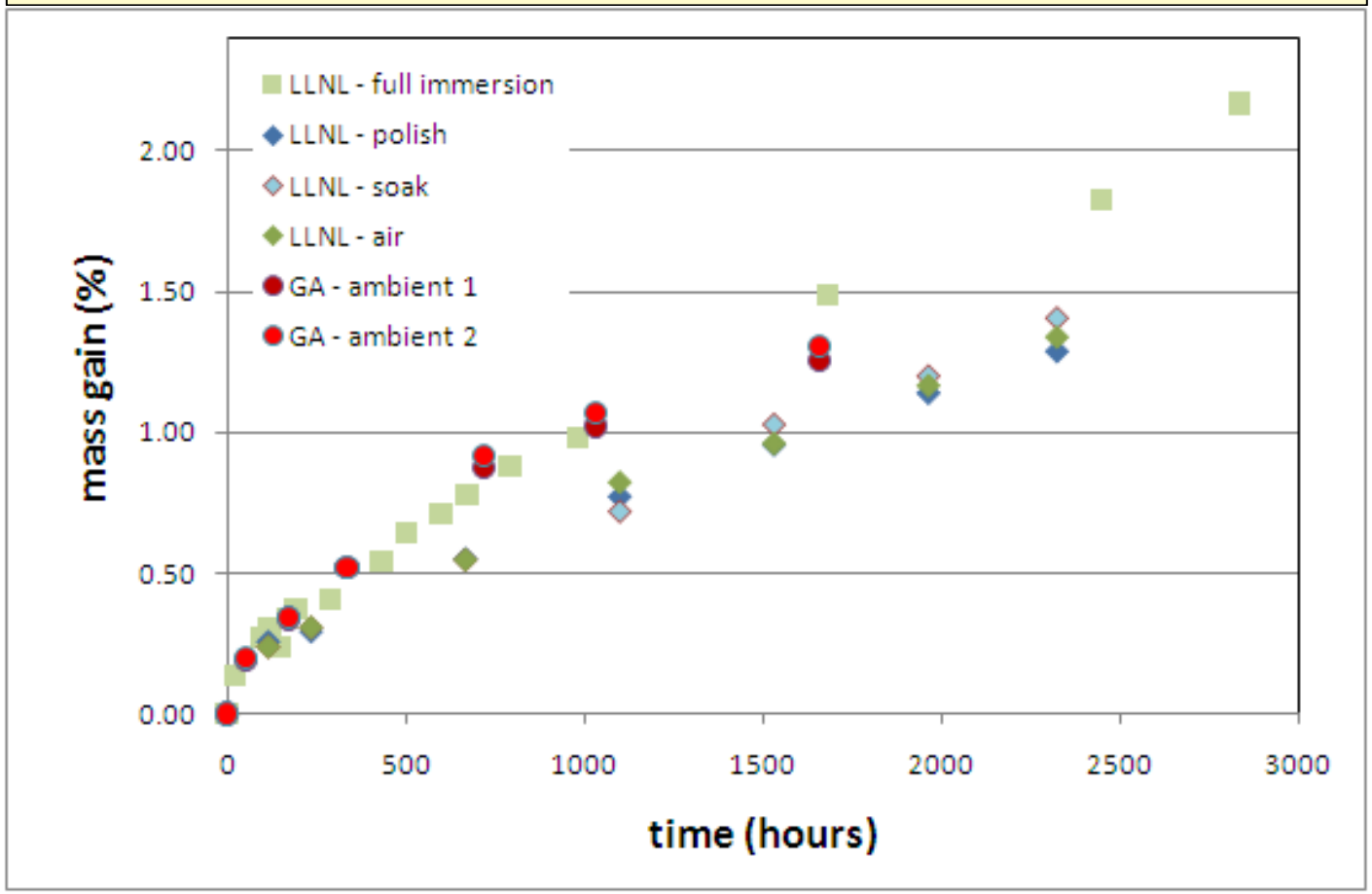
$$\boxed{D = \frac{\pi}{4}I^2 d^2}$$

Plot vs time$^{0.5}$ gives good linear fit in the initial curve



Recent data is consistent with data measured by GA on equivalent capsules; recent data has been measured for longer times

Relative mass gains of LLNL measurements are comparable to GA measurements



- **Magnitude of weight gain is comparable for all measurements**
- **Capsules have different initial exposures at t = 0, which may explain the varying slopes**

Path forward

- To what level do we need to track the mass at shot time?
- Is there a maximum O_2 at% that may not be exceeded?
- Current Physics assumption: 0-1%at, evenly distributed in the shell

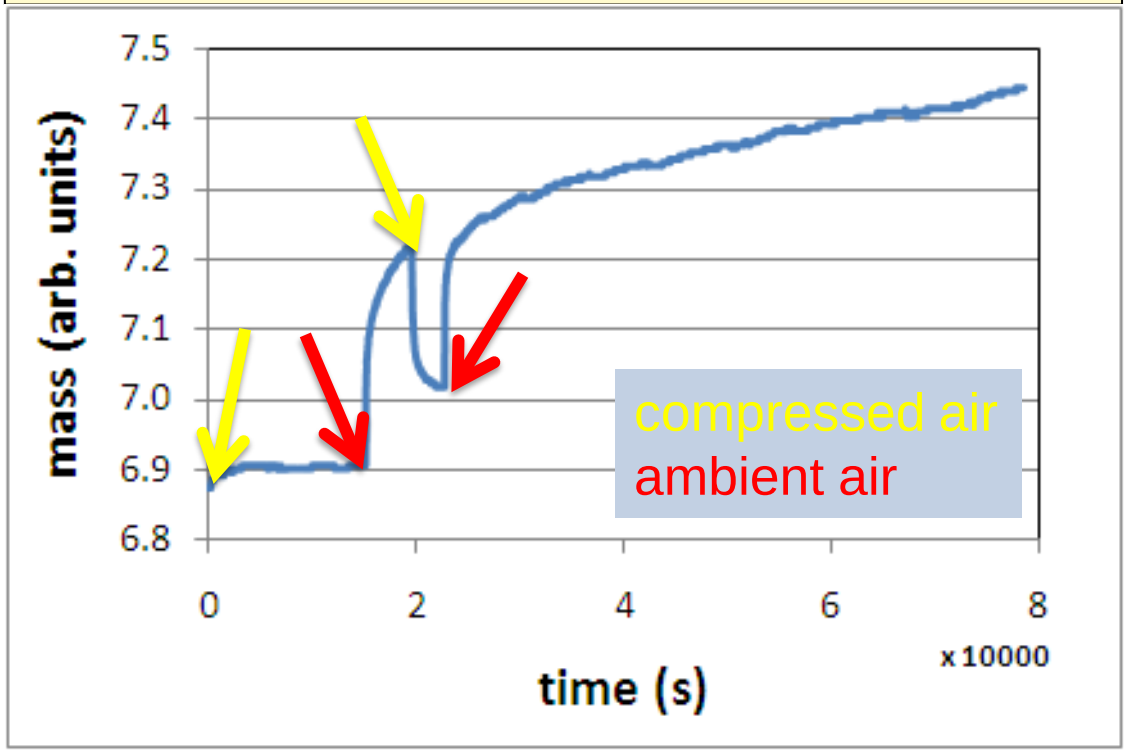
- Internal plan
  — List of experiments (S&T driven and Production driven)

  Questions to answer with experiments:
  - What is causing the mass gain (O_2, H_2O, other)?
  - What is the mass gain at shot time?
  - How does the mass gain depend on partial pressure?
  - How is the absorbed species distributed in the shell?
  - What is the uptake mechanism?

  Experiments:
  - Track weight gain of capsule in vacuum, dry air, wet nitrogen.
  - Use QCMB to observe mass uptake at varying humidity (oxygen levels).
  - Ge vs non-Ge capsule mass gain
  - Dry water-exposed capsule

Pyrolyzed CH QCMB experiment shows that water uptake is most likely cause of mass gain

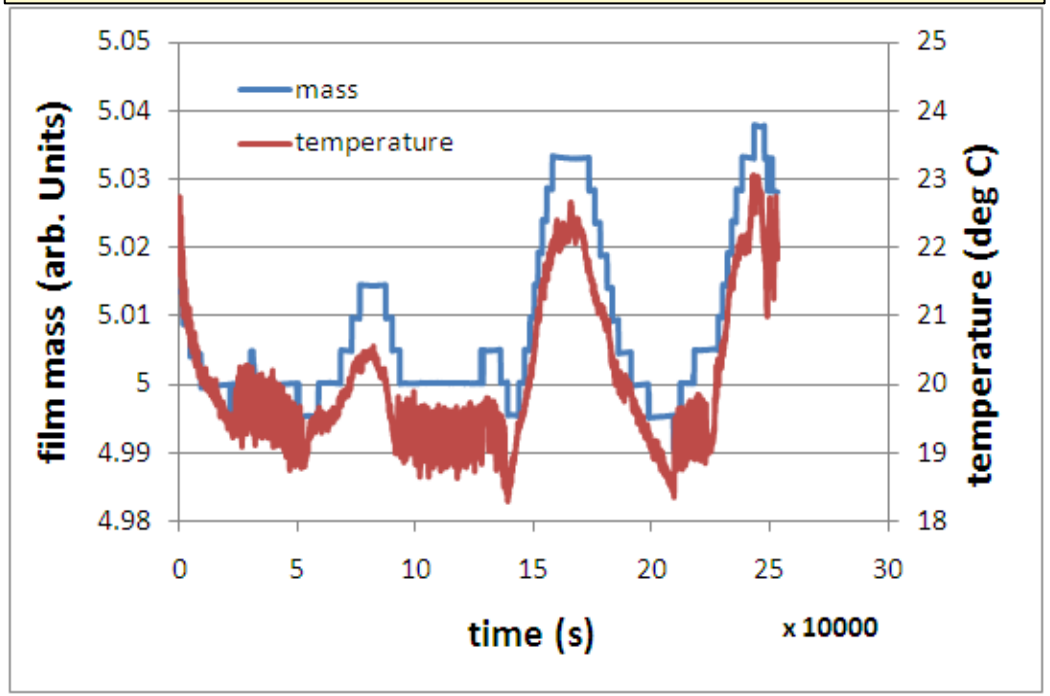
Compressed air does not give mass gain, but ambient air does



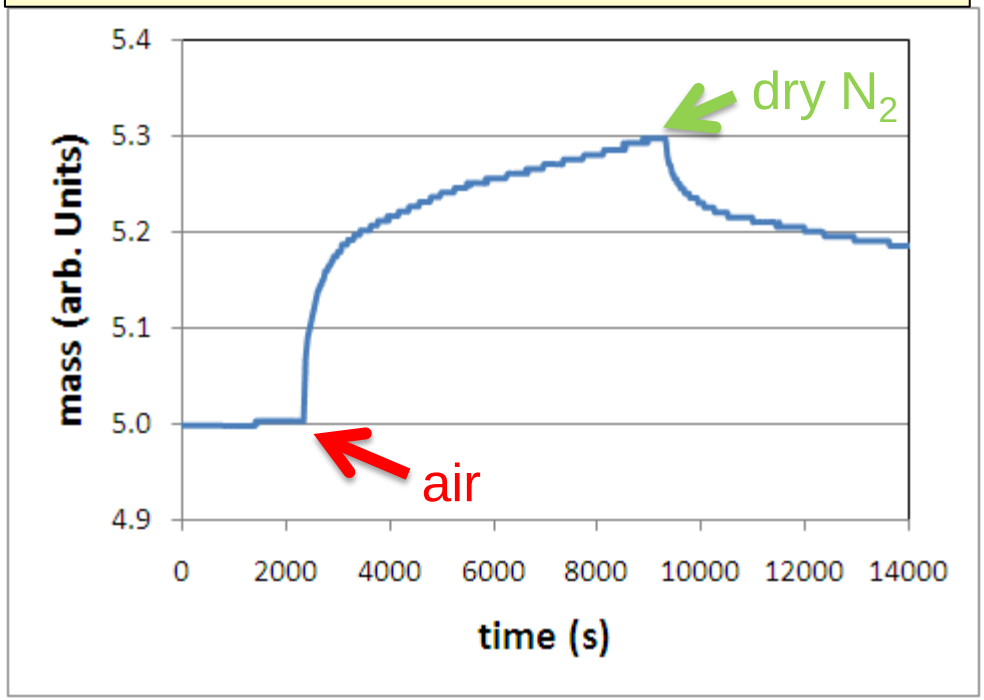
- deposition thickness ~ 1500 nm
- 5 hrs of exposure to compressed air show no noticeable mass uptake
- 4200 s produce a jump of 4 nm CH equivalent (0.27% mass increase)
- mass gain continues at a rate of ~1 nm/ 15000 s CH equivalent
- purging with compressed air seems to reverse uptake as well as purging with dry N_2

First QCMB experiment with unpyrolyzed films show that dry N_2 does not contain enough O_2 or H_2O to produce mass gain

Only mass changes over 3 days in dry N2 caused by QCMB thermal response



On air exposure, sample quickly gains 6 % mass, some of which is reversible

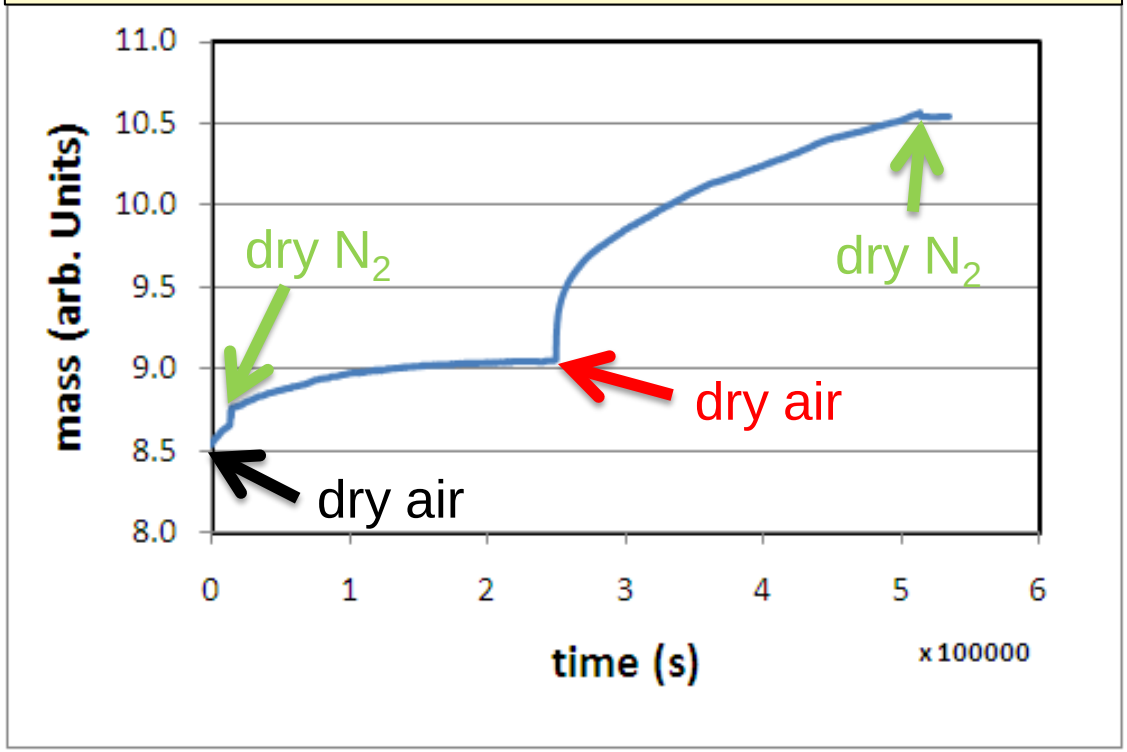


- deposition thickness ~ 100 nm
- mass reading change with temperature is <1%

- 7000 s of ambient air exposure give 6% weight increase, or 6 nm CH equivalent
- initial weight gain is rapid, drops to 1%/ 4000s later (1 nm/ 4000s CH equivalent)
- purging with N_2 reverses some of the uptake

Unpyrolyzed CH QCMB experiment shows that oxygen uptake is irreversible

Exposure to dry air produces a noticeable, irreversible mass increase

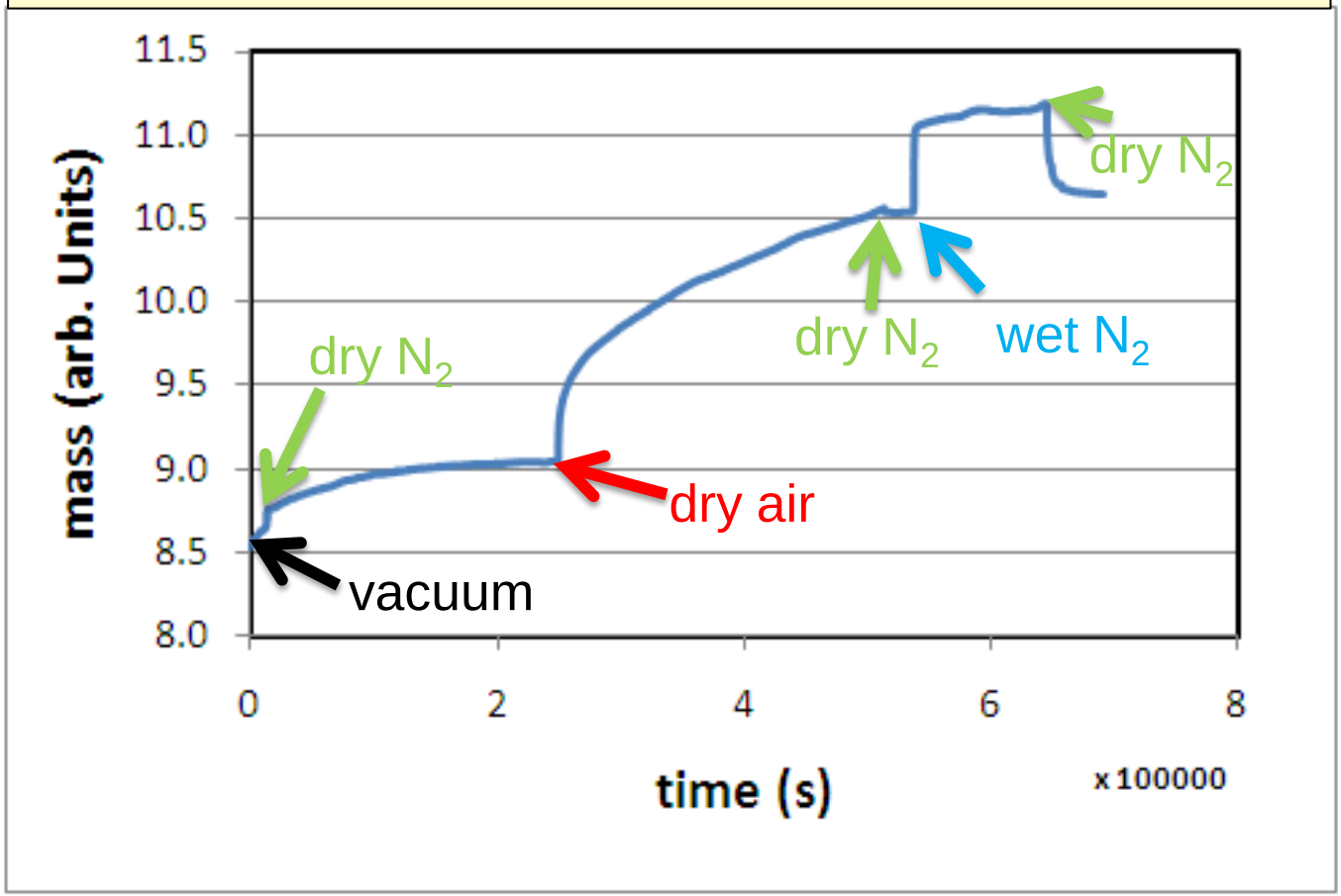


- deposition thickness ~ 1350 nm
- ~ 3 days of exposure to dry N2 give a 10 nm CH equivalent increase (~0.7% mass increase)
- ~ 3 days of CDA produce a gain of 30 nm CH equivalent (2.22% mass increase)

- mass gain through oxygen appears to be almost completely irreversible
- mass gain from dry air is much slower than that from humid air (6% gain in 2 hrs)
- humid air uptake should be redone to see how the initial jump scales with total mass

For unpyrolyzed CH, water uptake is slower than oxygen uptake

Exposure to dry air produces a noticeable, irreversible mass increase



- water uptake is mostly reversible, oxygen uptake is irrversible
- initial water uptake is faster than initial oxygen uptake, but long term uptake of water is slower than that of oxygen
- water uptake amount of unpyrolyzed CH looks comparable to that of pyrolyzed CH

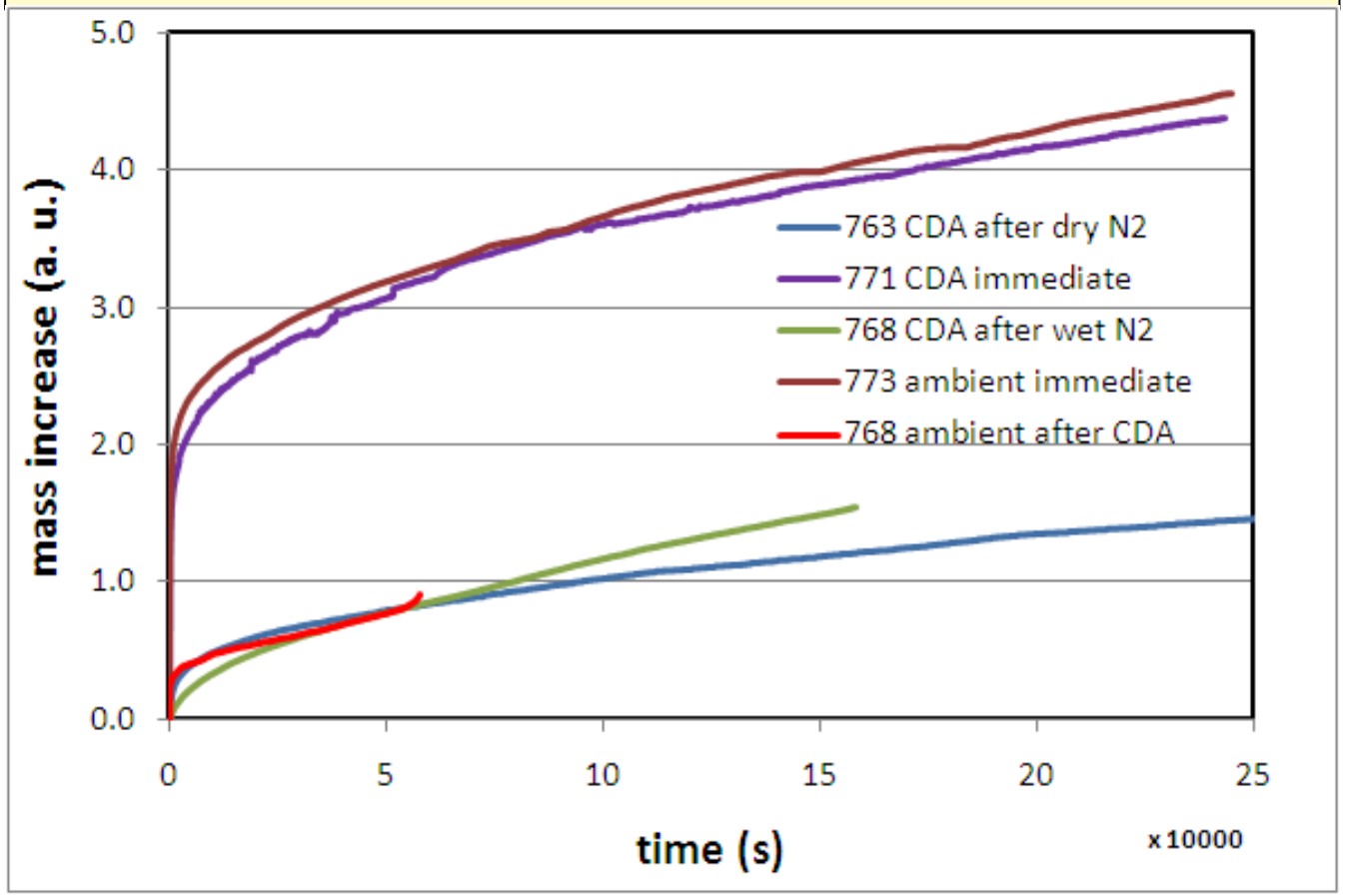
Unpyrolized QCMB experiment results: exposure history

sample	thickness	first exposure	second exposure	third exposure
763	1.35 µm	dry N_2	CDA	30% RH N_2
768	1.7 µm	30% RH N_2	dry N_2	CDA
771	1.66 µm	CDA	ambient/dry N_2	CDA
773	1.66 µm	ambient	dry N_2/ambient	CDA/ambient

- **exposures are typically done for 2-3 days**
- **two gas types in the exposure column means that the flow was switched between those two gases on a shorter time scale**

Unpyrolized QCMB experiment results: Exposure history affects uptake rate

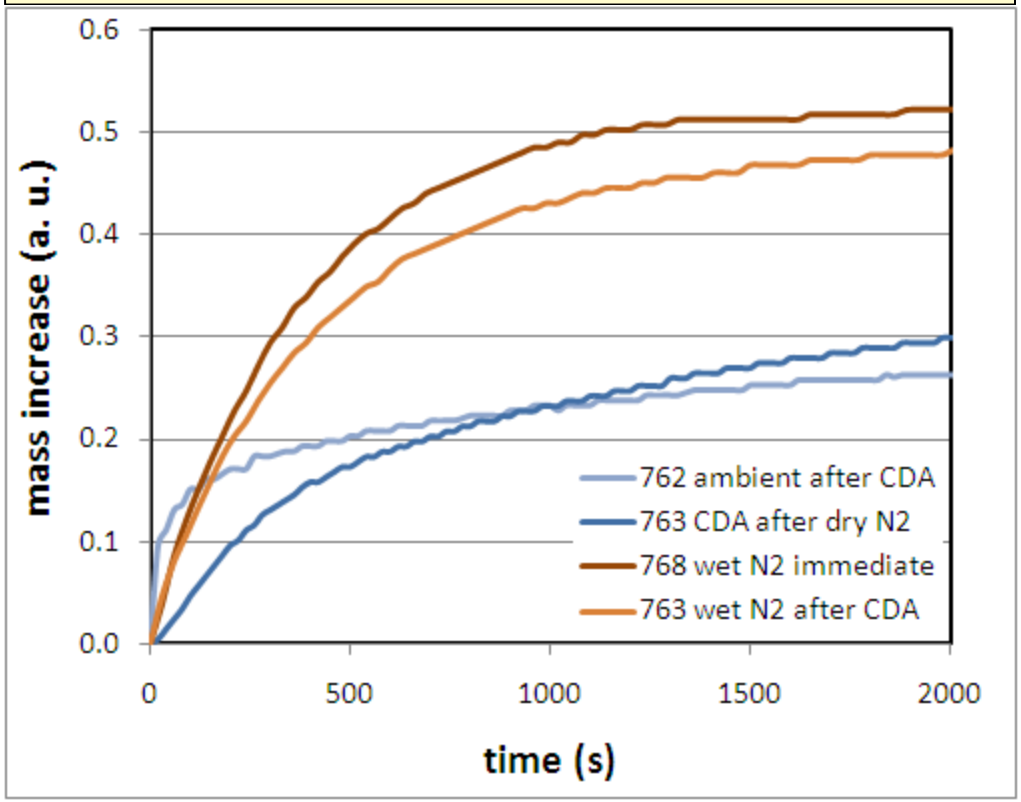
Exposure to O_2 immediately after coating results in substantially higher uptake rates



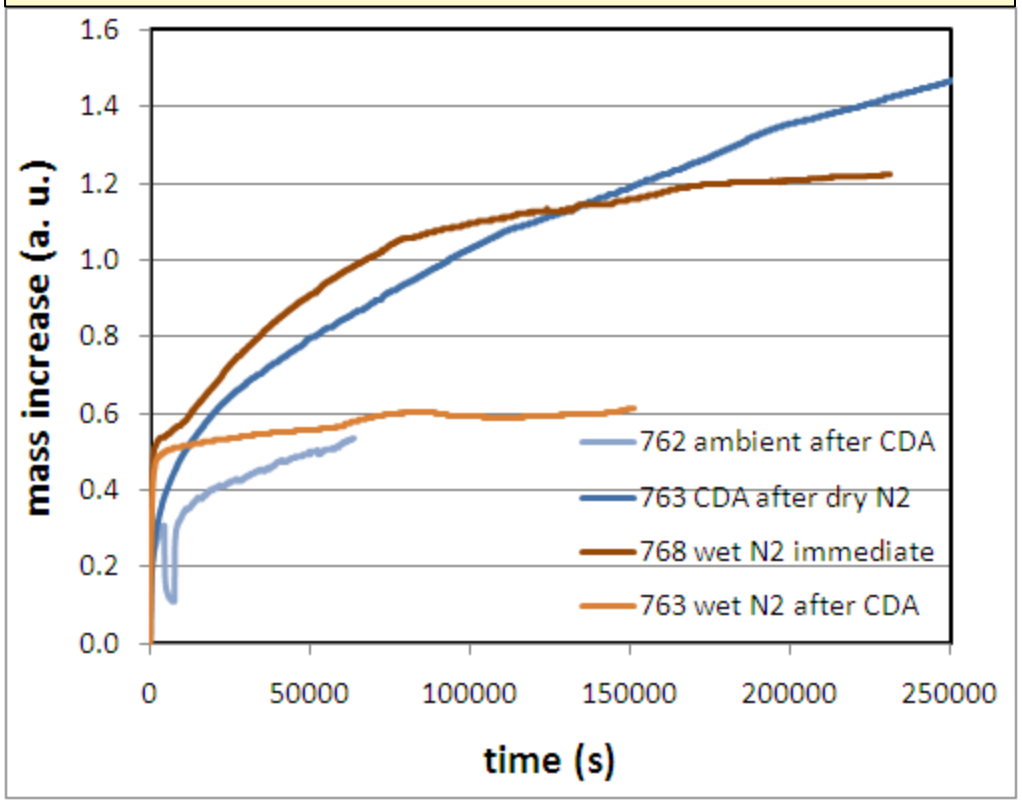
- large uptake rate immediately after coating indicates there may be more leftover radicals that recombine if not exposed to oxygen
- difference between O_2 + H_2O vs dry O_2 is small
- all O_2 uptake curves follow $t^{1/2}$ reasonably well -> diffusive process?

Unpyrolized QCMB experiment results: water uptake behaves differently from O_2 uptake

Initial mass increase is faster for wet exposures than for dry exposures



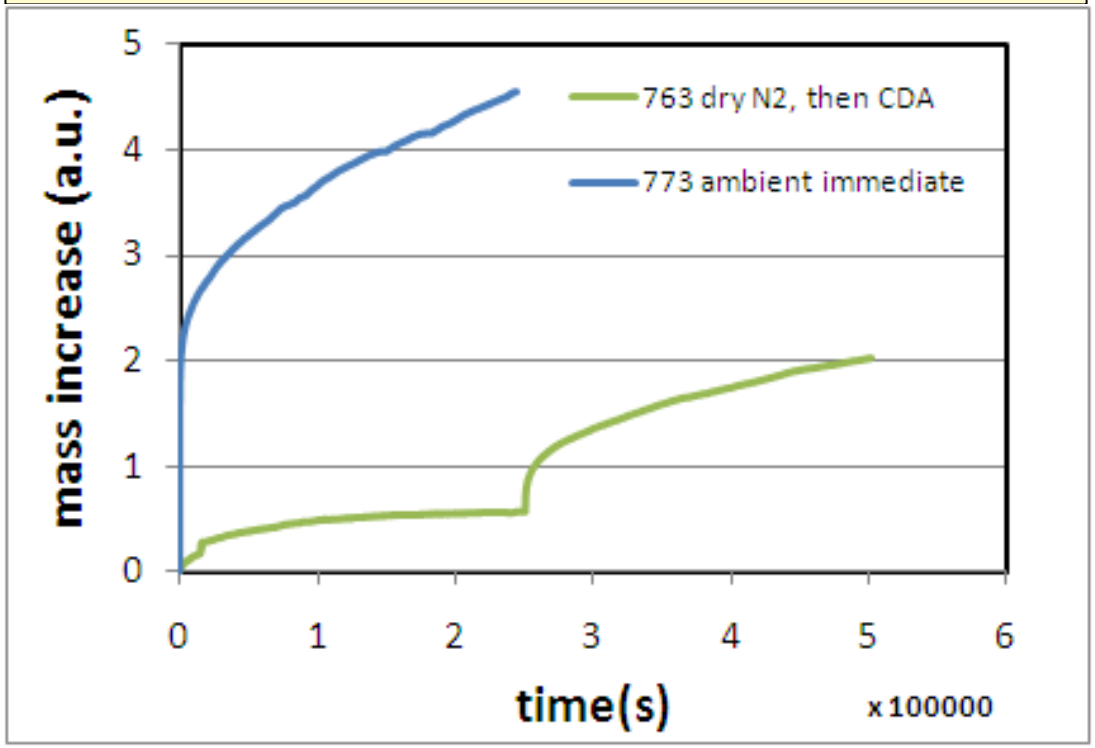
Water uptake is slower in the long run than O_2 uptake



- immediate water exposure leads to larger mass gains than water uptake after delay or O_2 uptake -> can water react with radical similarly to O_2?
- mass gain from water either does not follow $t^{1/2}$, or the amount is too small to clearly discern the curve
- the early mass gain during water uptake is reversible

Storing the capsule in an unreactive environment after deposition reduces mass uptake significantly

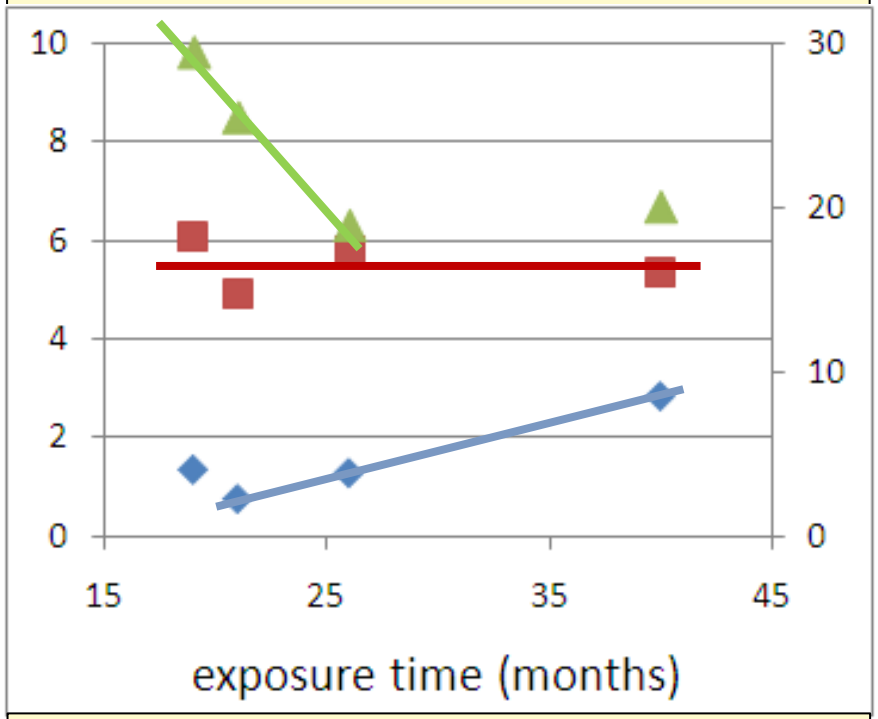
Uptake rate and total uptake after are reduced N_2 exposure for 3 days



- **radicals may be quenched by chain gyration if not given the opportunity to react after deposition**

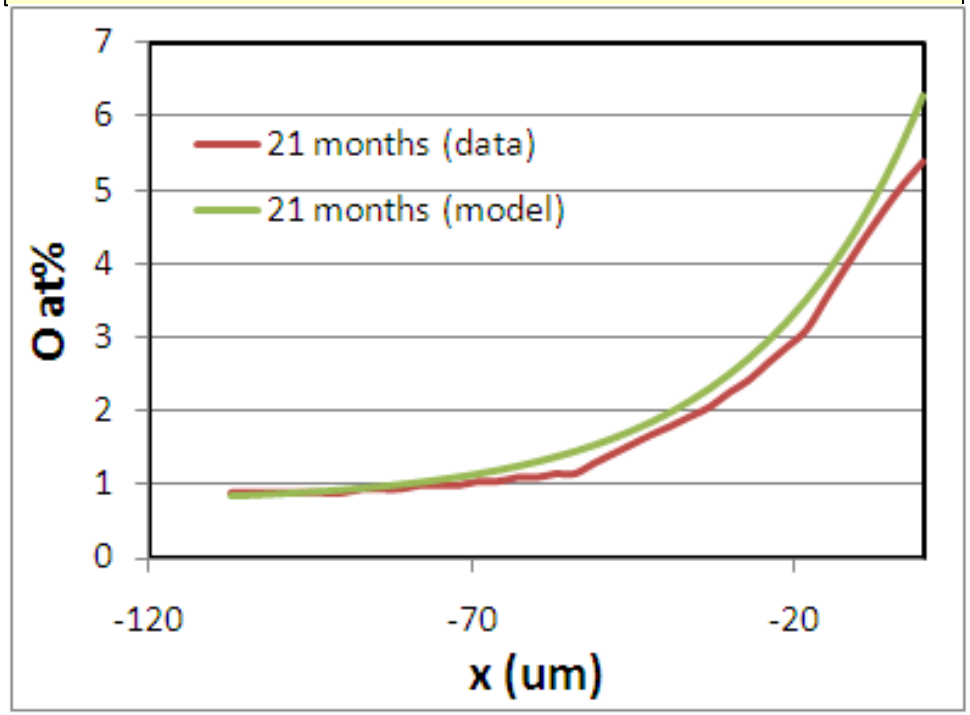
Engineering model for water uptake: Not enough data for a meaningful model

$$c(x,t) = y_0 + A\, e^{x/x0}$$



$$c(x,t) = 0.11t - 1.6 + 5.5\, e^{x/(57-1.5t)}$$

Comparison between model and data shows good agreement

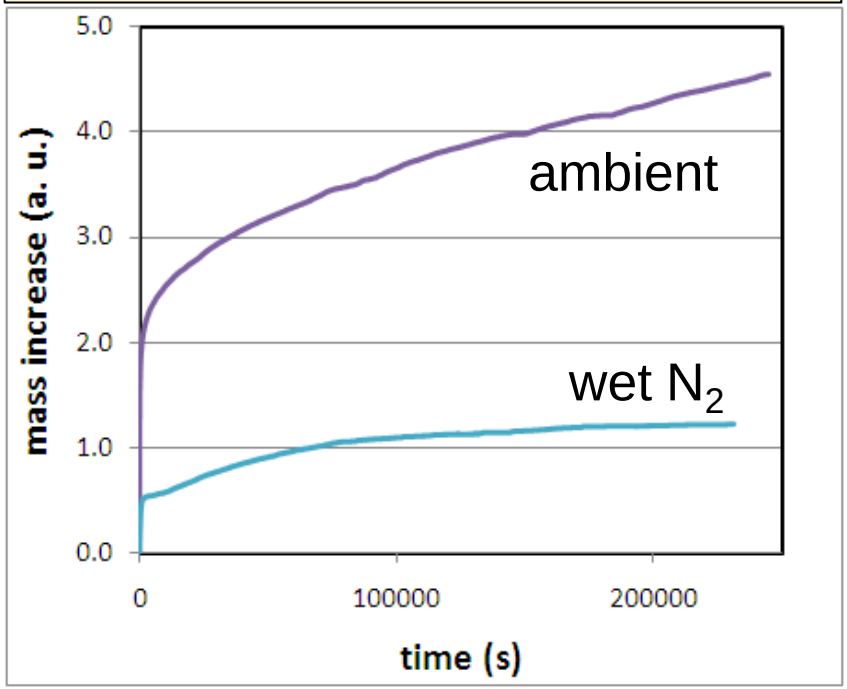


However:

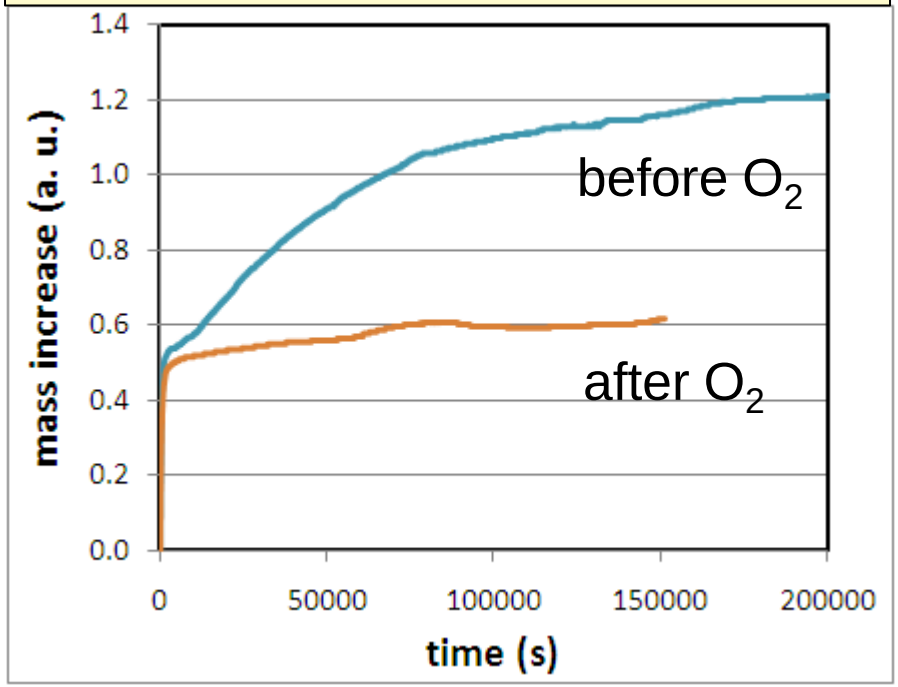
- the model breaks down for both edge cases
- there are only two points in between, so naturally the data in that region should fit the model well
- more data is needed to create a meaningful model

Reactions of H_2O and O_2 with unpyrolyzed CH

Unpyrolyzed CH: O_2 and H_2O reaction



Unpyrolyzed CH: H_2O before and after O_2 exposure



- A + A → self-termination?
- A + O_2 → R1
- A + H_2O → R2
- B + O_2 → R3
- B + H_2O → R4

R1 > R2 > R4 >> R3

- Unpyrolyzed CH contains two reactive sites: A and B
- Sites A scavenged by O_2 can no longer react with H_2O

Reactions with site A roughly look ~$t^{0.5}$ → diffusion limited, fast reaction

Next steps 6/10/11

1. Confirm mass uptake rates at various humidities
2. Gather contact radiography data with only one exposure condition (ambient only, vacuum only) to get a baseline for uptake
3. Deconvolve polishing water uptake from data using single exposure condition data
4. Attempt to measure the fitting constants independently
   - permeability
   - diffusion constant
   - solubility
   - reaction rate

Water uptake and environment

environment	c (water)	uptake (10^{-2} %/day)	uptake (µg/day)
water immersion	1 kg /l	1.5 - 1.7	0.45-0.53
ambient air	6 mg/l	1.0 - 1.2	0.28-0.35
15 Torr air (vacuum)	0.12 mg/l		

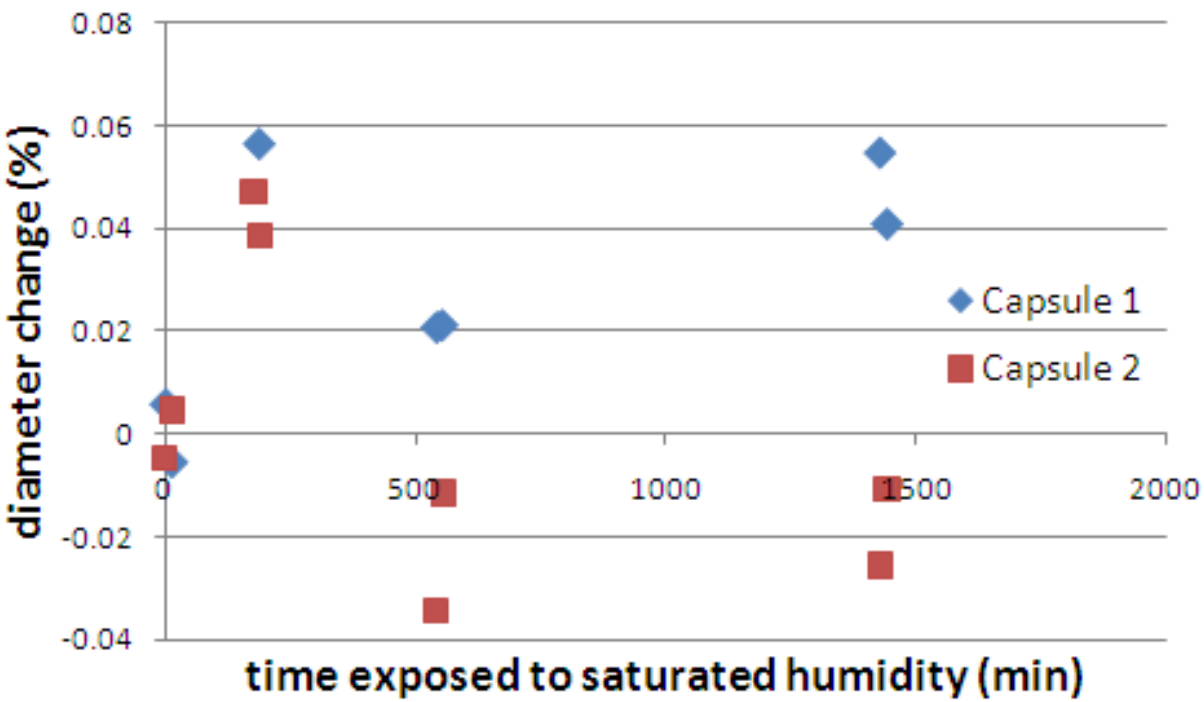
- uptake in water is 30% faster than in air, air is 300% faster than 15 Torr vacuum
- uptake is not expected to increase further once saturation concentration is reached
- existing data shows faster uptake in water than in air -> water must play a role in mass gain

Diameter measurements and changes

Capsule	after pyrolysis		before polish		after polish		after polish	
(all in µm)	diameter	thickness	diameter	thickness	diameter	thickness	diameter	thickness
10CH76-02	2245.1	201.4	2250.2		2247.9		2246	201.4
10CH76-03	2288.2	206	2292.4		2291.5		2288.9	205.7
10CH76-05	2300.1	206.1	2304.6		2304.1		2300.4	206.4

GA measurement (contact radiography) LLNL measurement (interferometer)

- measurements are not reproducible between methods, even differences are not consistent
- diameter change after polish does not behave as expected (especially for CR)
- Does water uptake/oxygen uptake cause swelling? What is the impact of CTE?



Weight measurements and changes

capsule histories			
	CH111	CH116	CH118
GA	2.731	2.913	2.943
LLNL before polish	2.746	2.928	
LLNL after polish	2.746	2.930	
after 45 days storage			
33% RH (NaCl, sat)	2.774		2.951
100% (over dist H2O)		2.954	
after drying (3 day, 90C)		2.950	

- capsules gain 40 µg of weight just sitting in air/saturated humidity
- polishing should remove 20 µg of material, yet capsules don't lose weight or even gain weight during polishing
- water accounts for very little of that mass: 4 µg lost after drying
- oxygen uptake estimated to be up to 0.5at% (38 µg)

Outline

- Water and oxygen uptake during capsule processing
- Experiments in progress:
  - Capsule soak/dry
  - Quartz crystal microbalance experiments
- Planned work (water/oxygen uptake)
- Potential mitigation measures

Planned work

1. Repeat QCMB experiment for different thicknesses, oxygen uptake (dry air)
2. Mass increase during and after polish
   - 3 fresh capsules, 1 steel ball (reference)
   - polish 2
   - dry 1 polished and unpolished in oven at 90°C for a day (?)
   - store all three capsules in ambient and track weight gain over time
3. Accelerated oxygen uptake
   - two fresh capsules
   - expose both capsules to air at 90°C, track weight gain (TGA?)

Mitigation

Procedures that could be implemented to reduce mass/dimension change during the processing:

- pretreat capsule to do most oxygen uptake before other processing
- dry capsules after polish

- others?

Measuring changing capsule properties

• capsule properties (weight, diameter, wall thickness, composition) need to be known to within tight tolerances

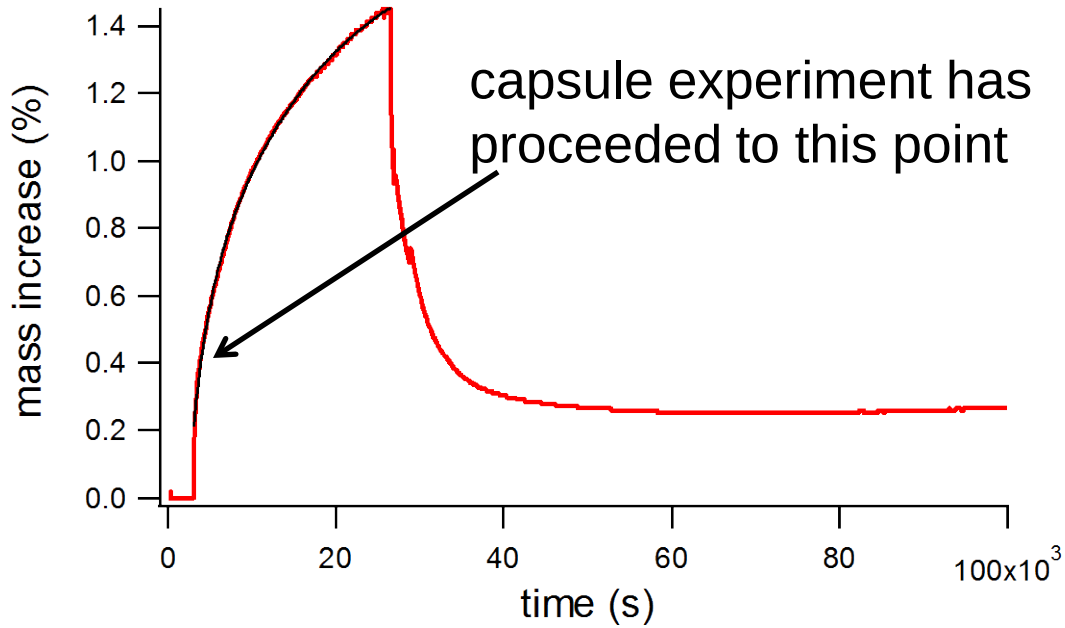
OD tolerance: ±10 µm (known to ±1 µm)
O_2 uptake: <0.5 at%
currently no specs for weight, water uptake, other elements

• capsule are subjected to processes and conditions which can change a property (ambient oxygen, polishing, temperature changes)

• some of the changes (water uptake, oxygen uptake, mass change during polishing, CTE?) are not well understood

Determining exact capsule properties is important. Some properties change during processing, and measurements can be influenced by ambient conditions.

Water uptake: QCMB initial data



Double exponential fit coefficients

	Uptake	Dry
y0	1.69	0.26
A1	-0.33	0.31
t1 (s)	1820	46
A2	-1.15	0.78
t2 (s)	14800	4150

- mass increase is around 1.4%
- uptake is not fully reversible (H_2O or trace O_2 reacting with CH)
- curve fits double exponential
- extrapolated time constant for full thickness shell is estimated to be 90 hrs (720 hrs) (time constant scales with thickness)

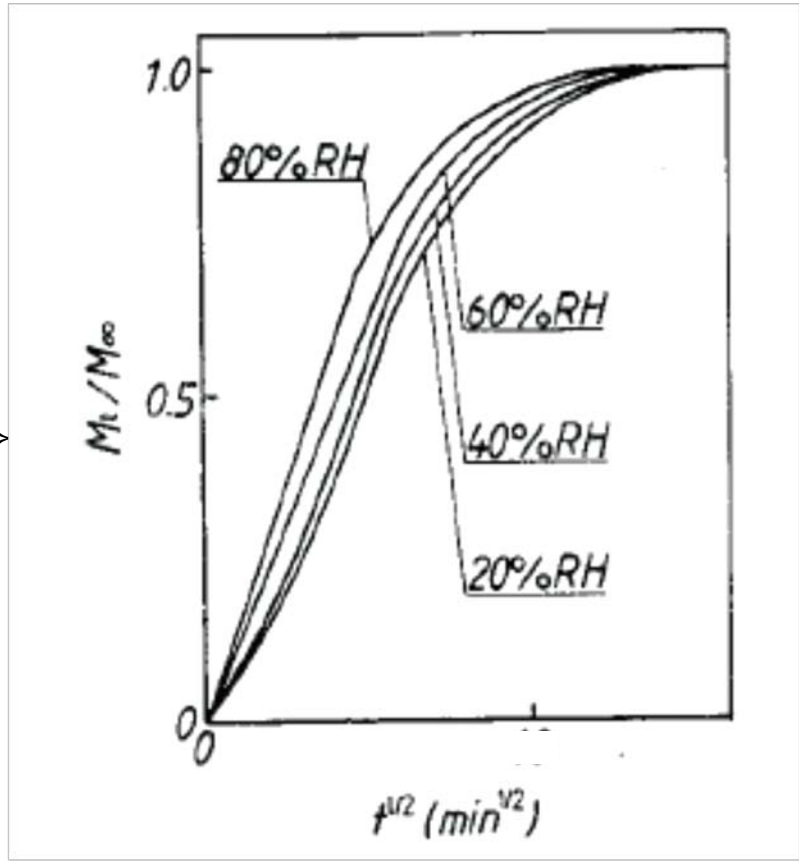
  → close to time constant measured with capsules

Capsule water uptake follows Fickian diffusion

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2}$$

- for our boundary conditions,

$$\frac{M_t}{M_\infty} = \frac{4\sqrt{Dt}}{d}\cdot\left\{\frac{1}{\sqrt{\pi}} + 2\sum_{n=0}^{\infty}(-1)^n ierfc\frac{nd}{2\sqrt{Dt}}\right\}$$



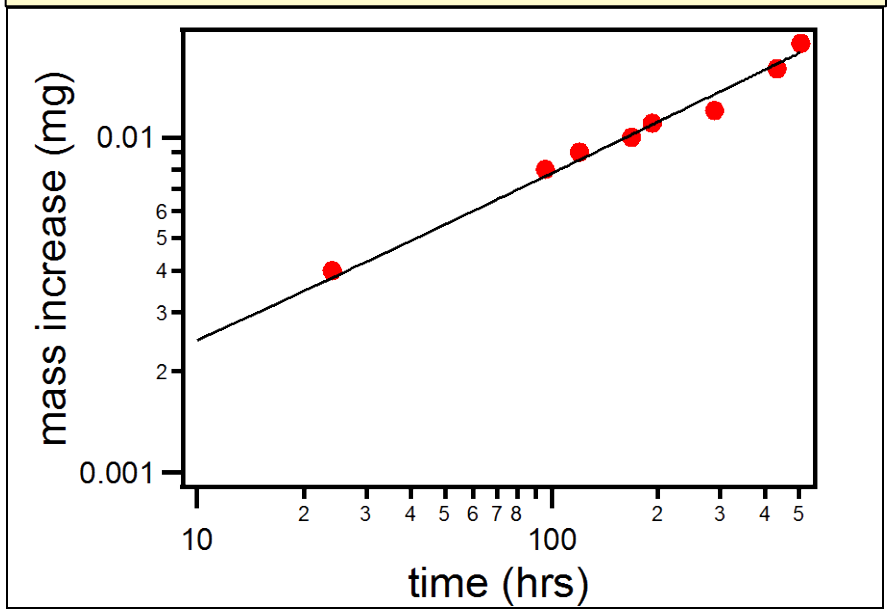
In the initial part of the curve

$$\frac{M_t}{M_\infty} \approx \frac{2}{d}\sqrt{\frac{D}{\pi}}\sqrt{t} = I\sqrt{t}$$, so

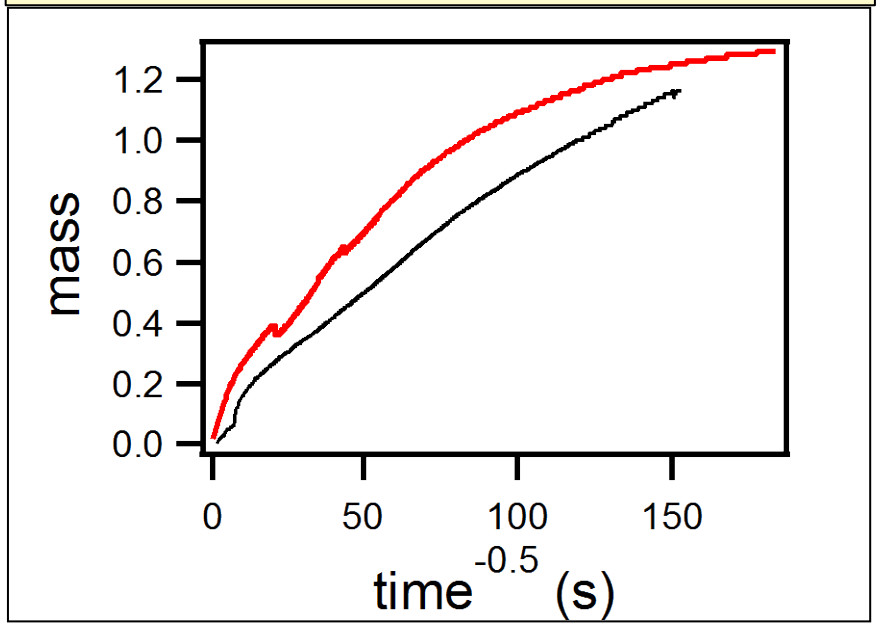
$$\boxed{D = \frac{\pi}{4}I^2 d^2}$$

Water uptake behavior is Fickian

Uptake from full immersion



Uptake from QCMB



- initial part of the QCMB curve is not clean because of gas diffusion limitation (chamber size: 1L, flow rate: 0.2L/min)
- estimated M_∞ for QCMB curves is 1.34

→ first estimate of diffusion coefficient for water in CH is

$$D = 2.3 \cdot 10^{-13}\ cm^2/s$$