Improving Thermoelectric Technology Performance and Durability with Aerogel

presented at the

Sol-Gel 2005 Conference

University of California, Los Angeles

August 2005

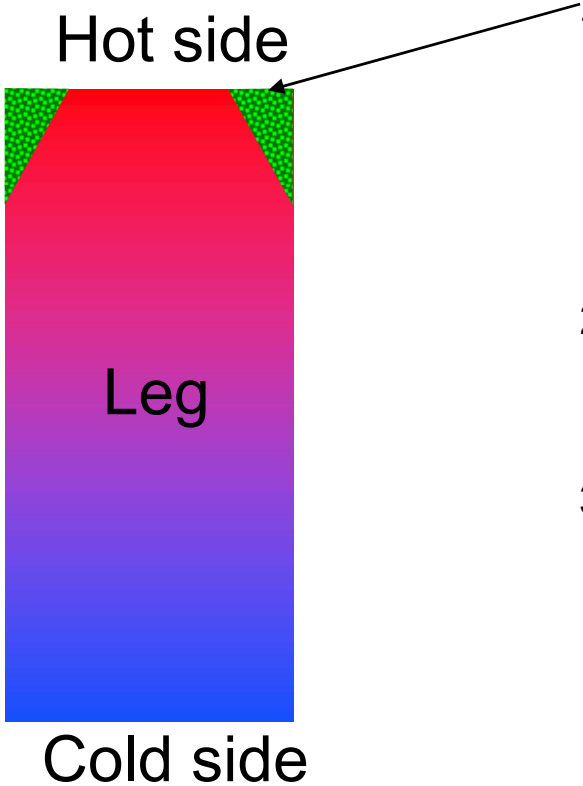
by

Jeff Sakamoto, Jay Paik, Steve Jones, Winny Dong, Thierry Caillat and Jean-Pierre Fleurial

Jet Propulsion Laboratory/California Institute of Technology

Pasadena, CA, USA

Sublimation Suppression Goals for Skutterudite-based Technology:



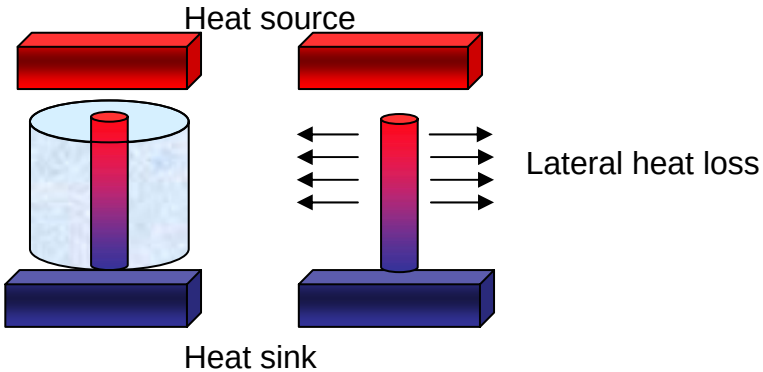
Goals:

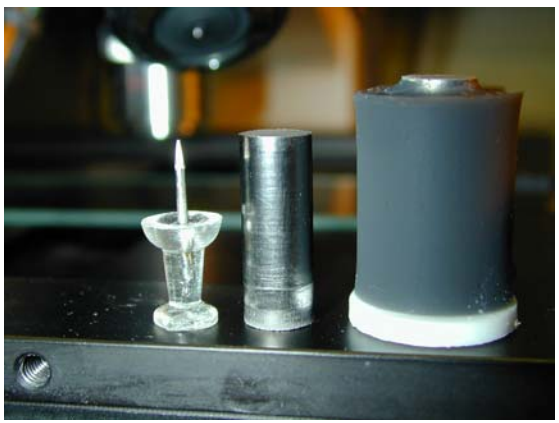
1) Suppress sublimation of antimony vapor to prevent the depletion band from decomposing 5% of the effective cross section after 10 years of operation.
   - Beginning of Life (BOL) <5.5 x 10^{-6} (g_{Sb}/cm^2·hours)
   - Or <2.3 x 10^{-7}cm/hr

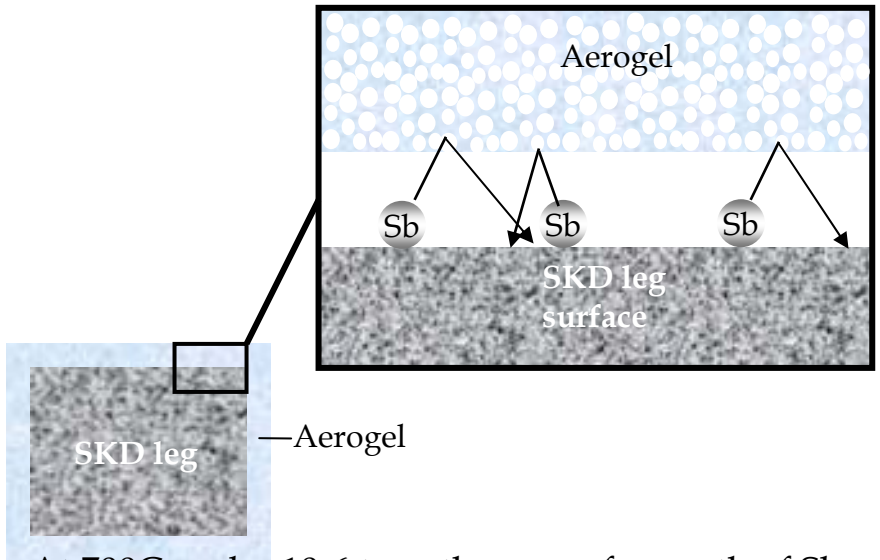
2) Contain metal vapor to prevent condensation, which can cause short circuiting on the cold side of the device

3) The method of suppression sublimation should not have a significant impact on the system performance

Aerogel as a sublimation suppressing coating and insulation

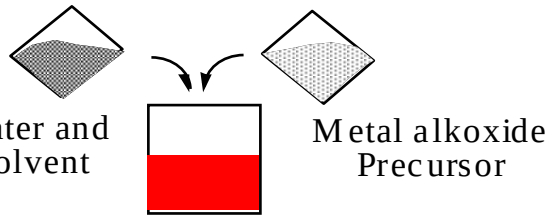






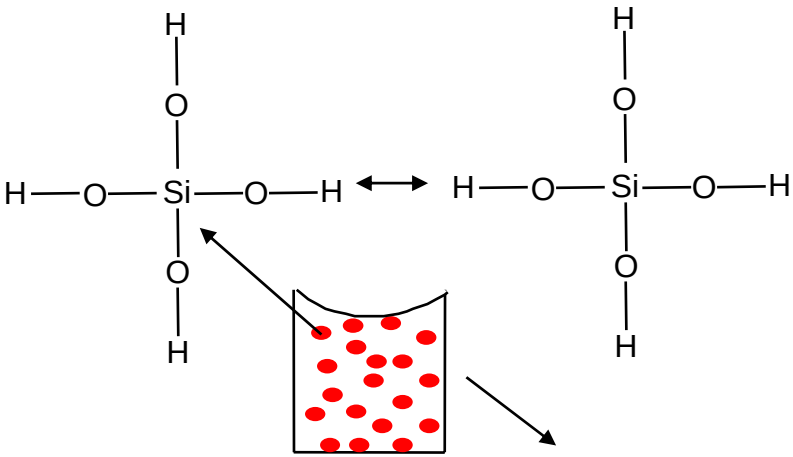
At 700C under 10-6 torr, the mean free path of Sb vapor is too long to penetrate the highly-tortuous, porous, aerogel network (not to scale). The Sb atoms are "re-directed" back to the SKD surface, thus establishing a highly-localized, equilibrium environment.

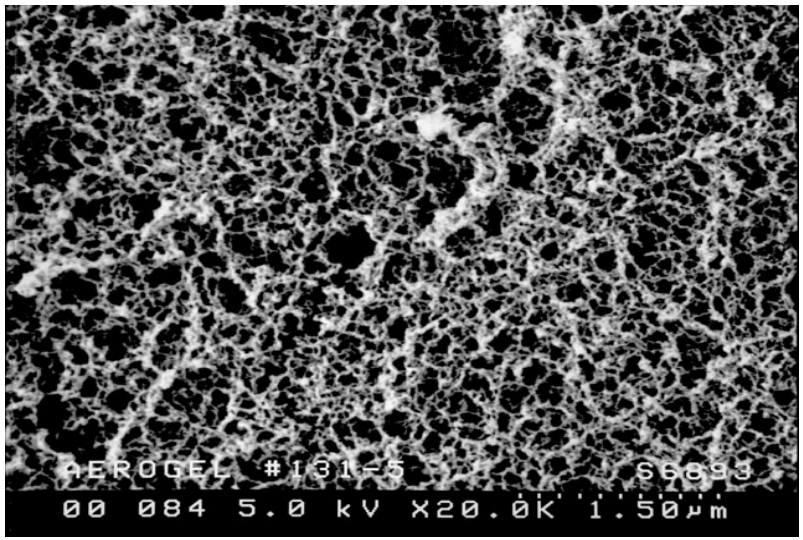
Sol-Gel Synthesis



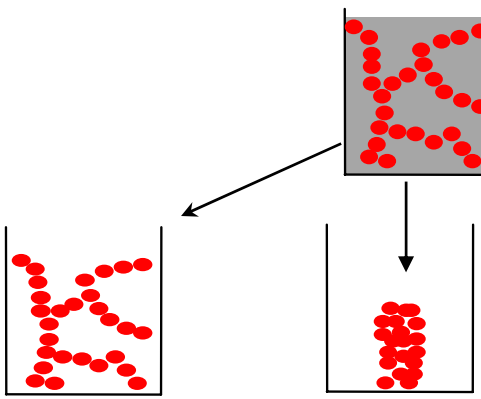
Sol

Sol contains Si-O-H molecules





Monolithic Wet Gel

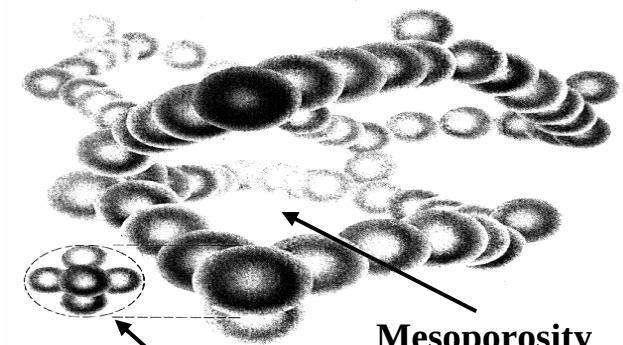


Aerogel

Supercritical extraction

Xerogel

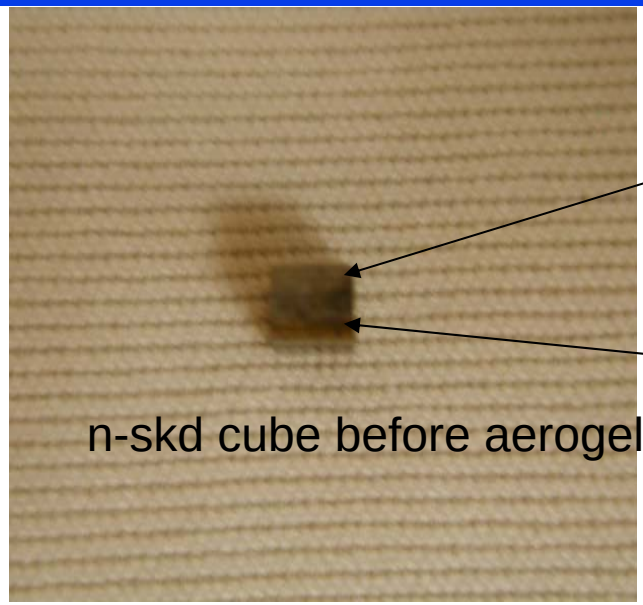
Air dry



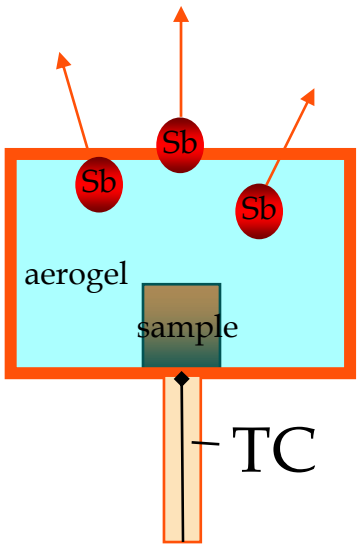
Mesoporosity
2 nm to 50 nm

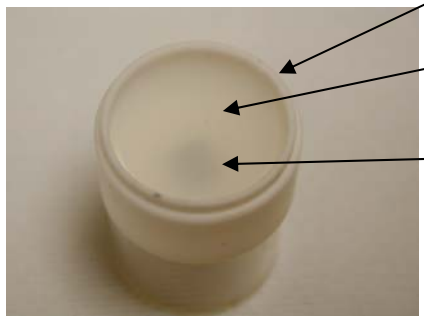
Microporosity
< 2 nm

Characterizing Sublimation Suppression of Aerogel Coatings

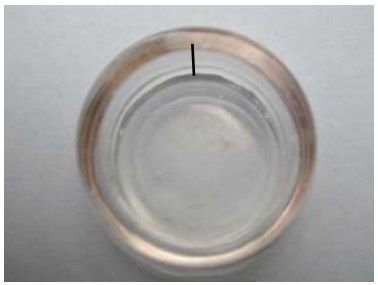


Aerogel encapsulation



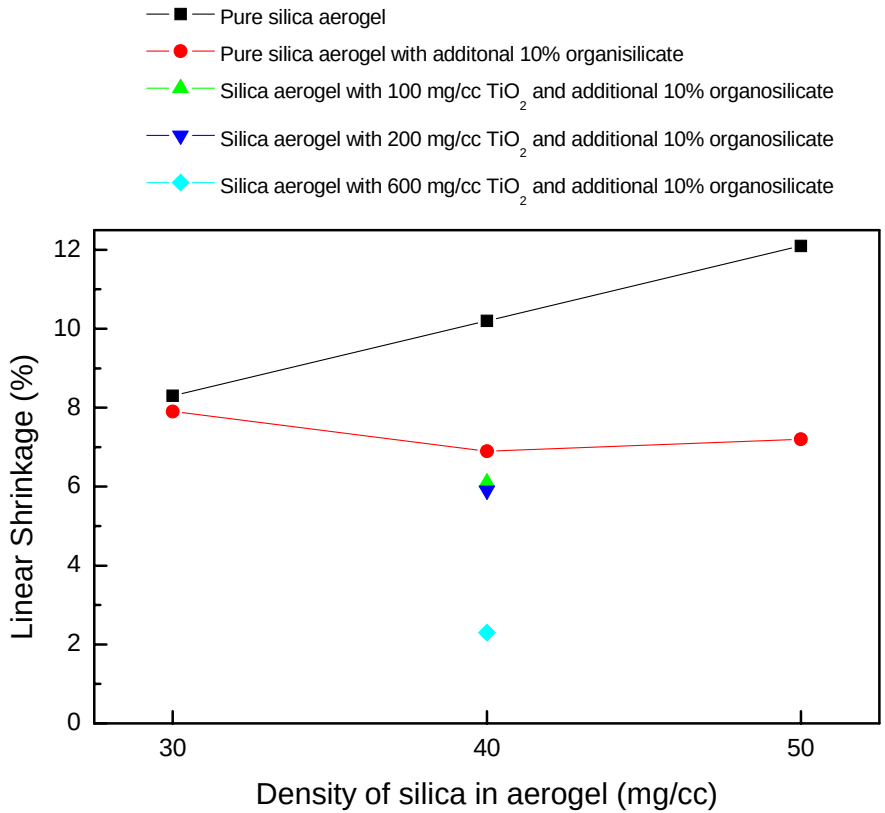


Controlling Shrinkage of Aerogel to provide crack-free coatings

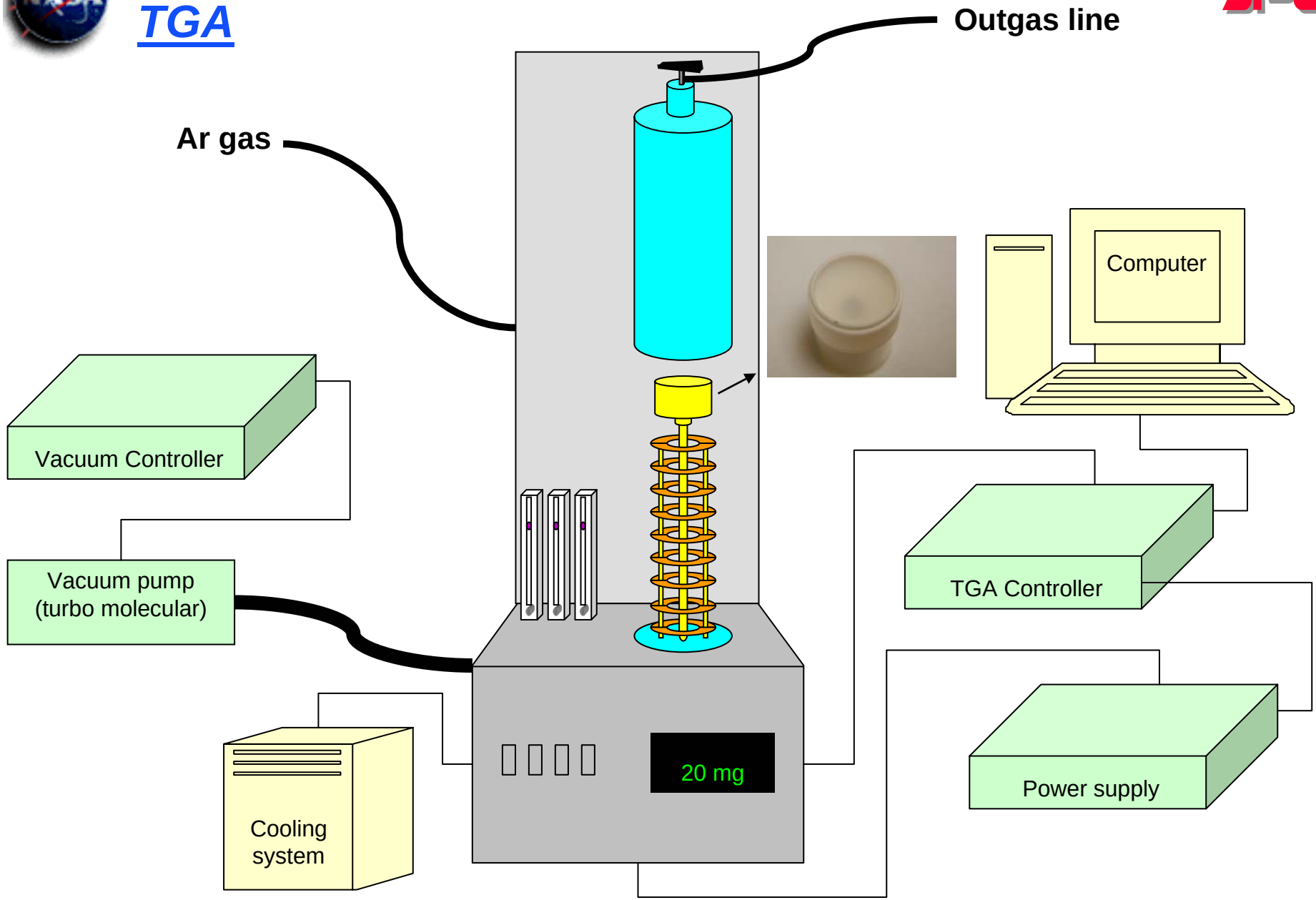


Plain silica ~10% shrinkage

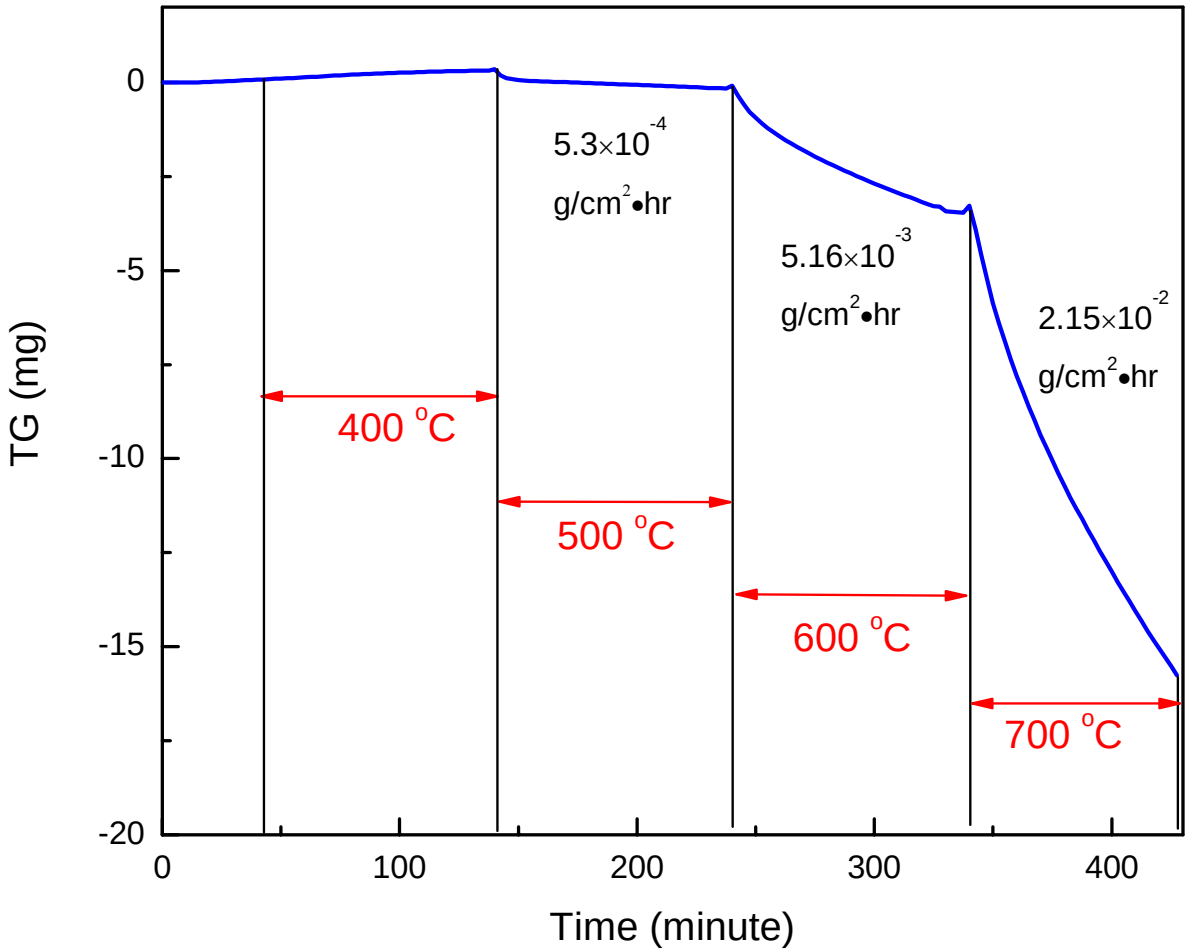
Adding extra organosilicate and TiO_2 significantly reduces shrinkage



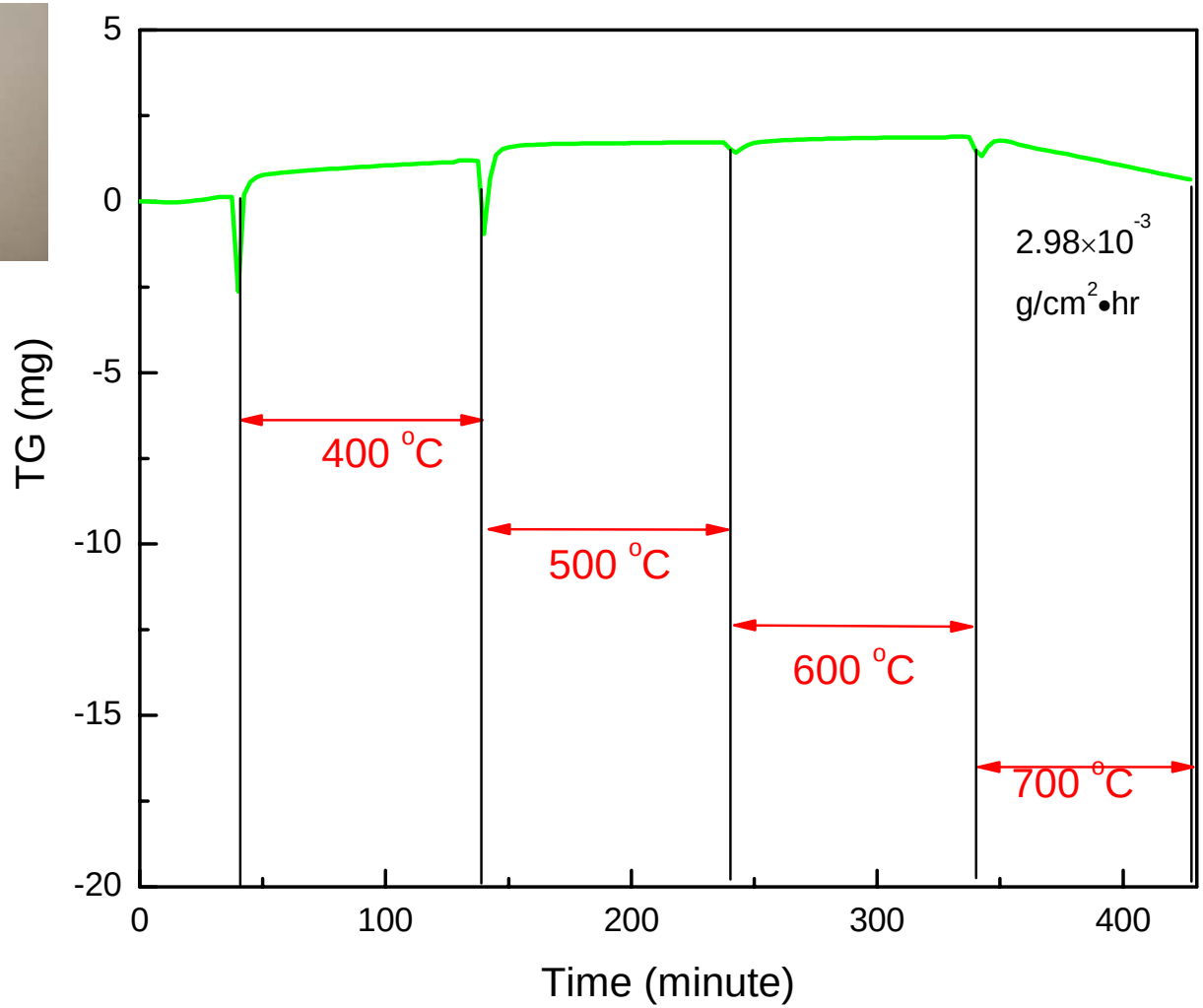
TGA


Outgas line
Ar gas
Computer
Vacuum Controller
Vacuum pump
(turbo molecular)
TGA Controller
20 mg
Power supply
Cooling
system

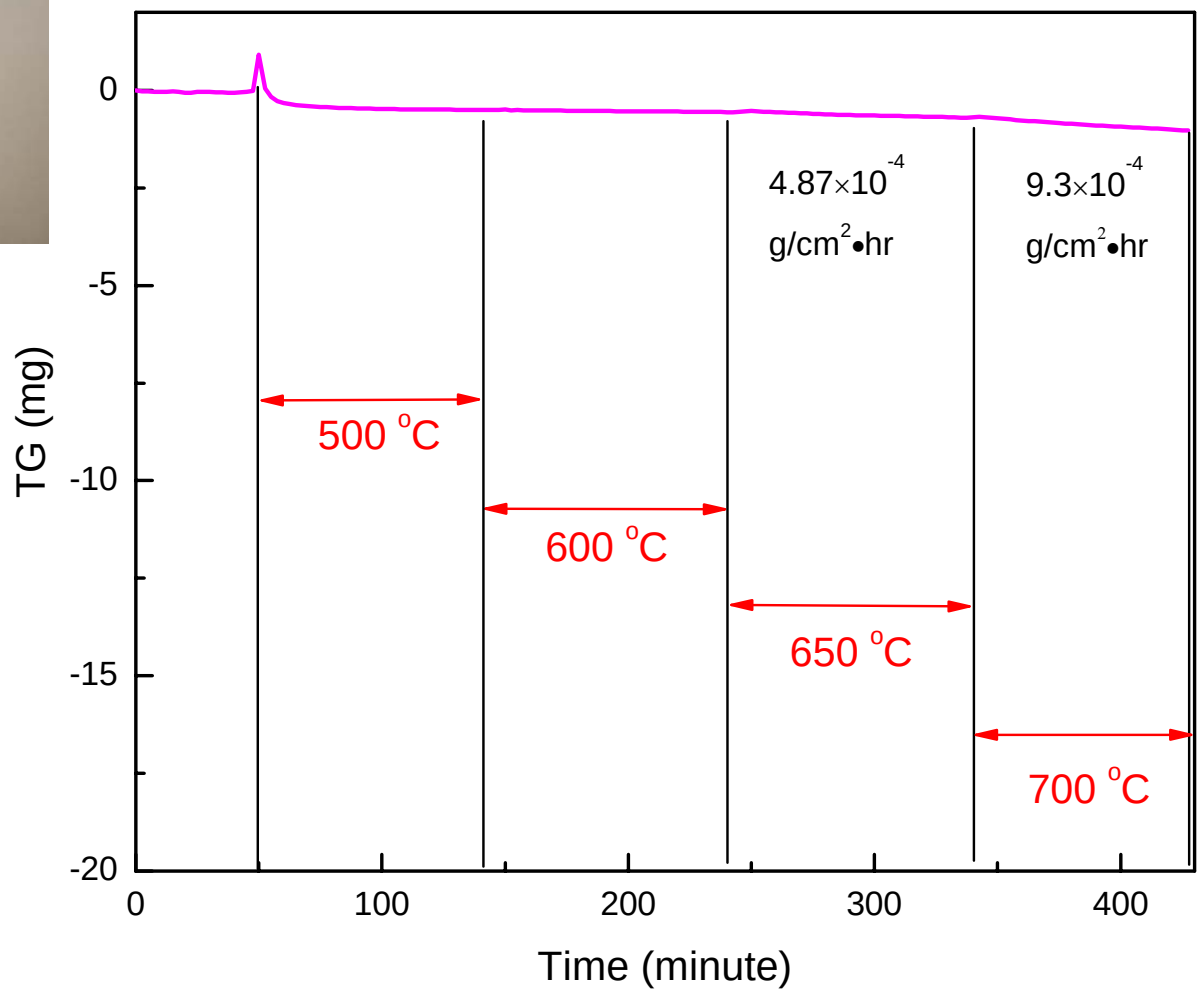
Baseline, BOL n-type SKD Uncoated Coupon (10^{-6} torr)



Low density (50 mg/cc) encapsulation decreased sublimation by a factor of 7 at BOL (10^{-6} torr)

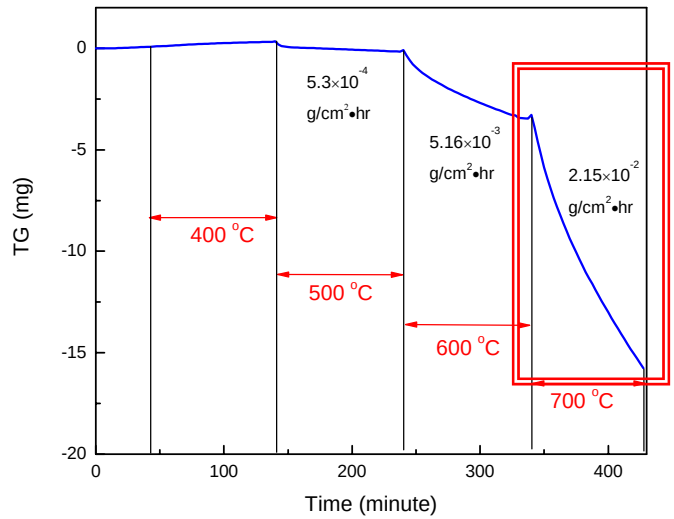


Higher density (100 mg/cc) aerogel encapsulation decreased sublimation by a factor of >20 at BOL (10^{-6} torr)

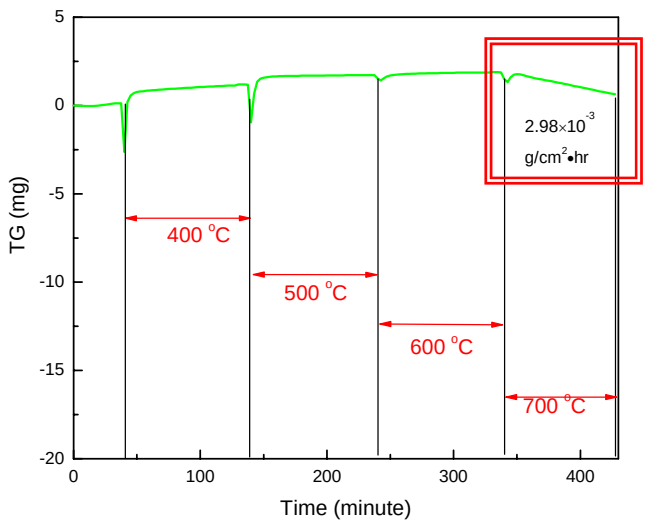


Demonstrated that Aerogel Coatings Significantly Reduce Sublimation BOL

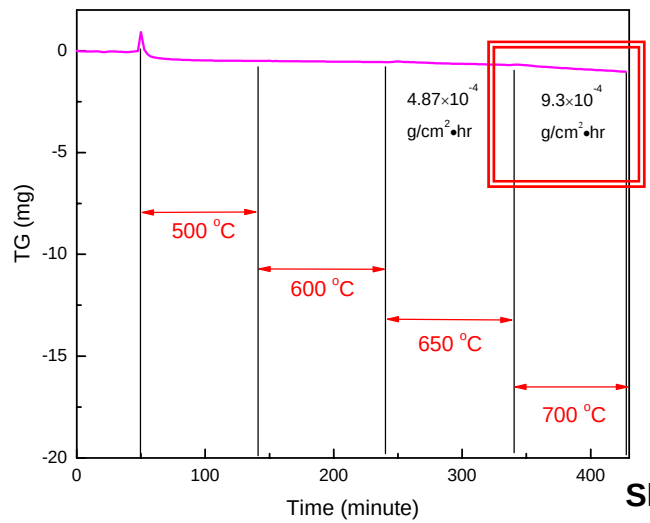
Uncoated



Low Density Aerogel (50 mg/cm^3)



Higher Density Aerogel (100 mg/cm^3)



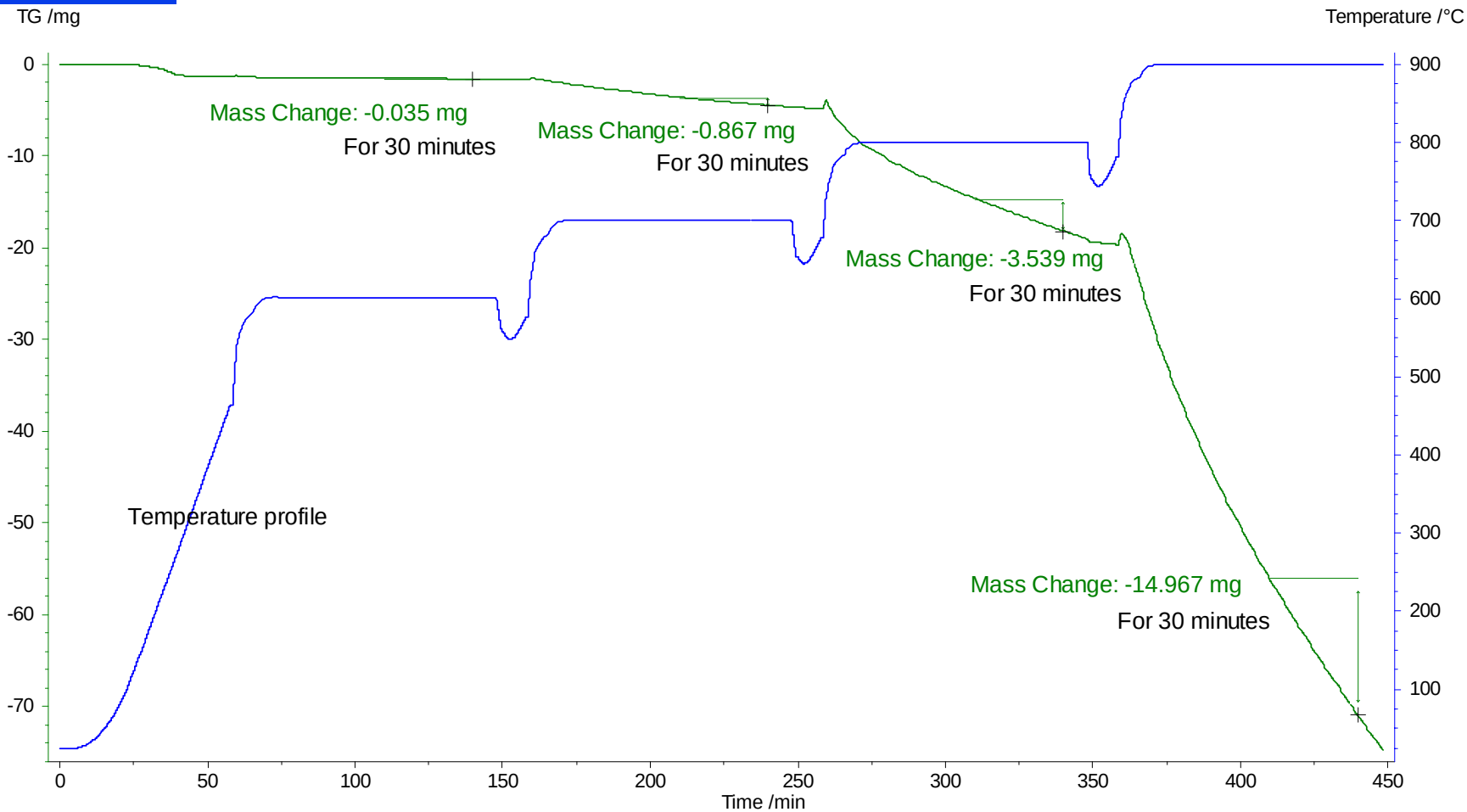
These are Preliminary results:

- n-type: 2×10^{-2} g/cm^{2}·hr (or 8.33×10^{-4} cm/hr)
- From BOL – 10 years must be $<5.5 \times 10^{-6}$ g/cm^{2}·hr (or 2.27×10^{-7} cm/hr)
- Requires a factor of 3500 reduction from uncoated n-type SKD
- Preliminary results with 100 mg/cc aerogel retards sublimation by a factor of >20 over the uncoated sample.

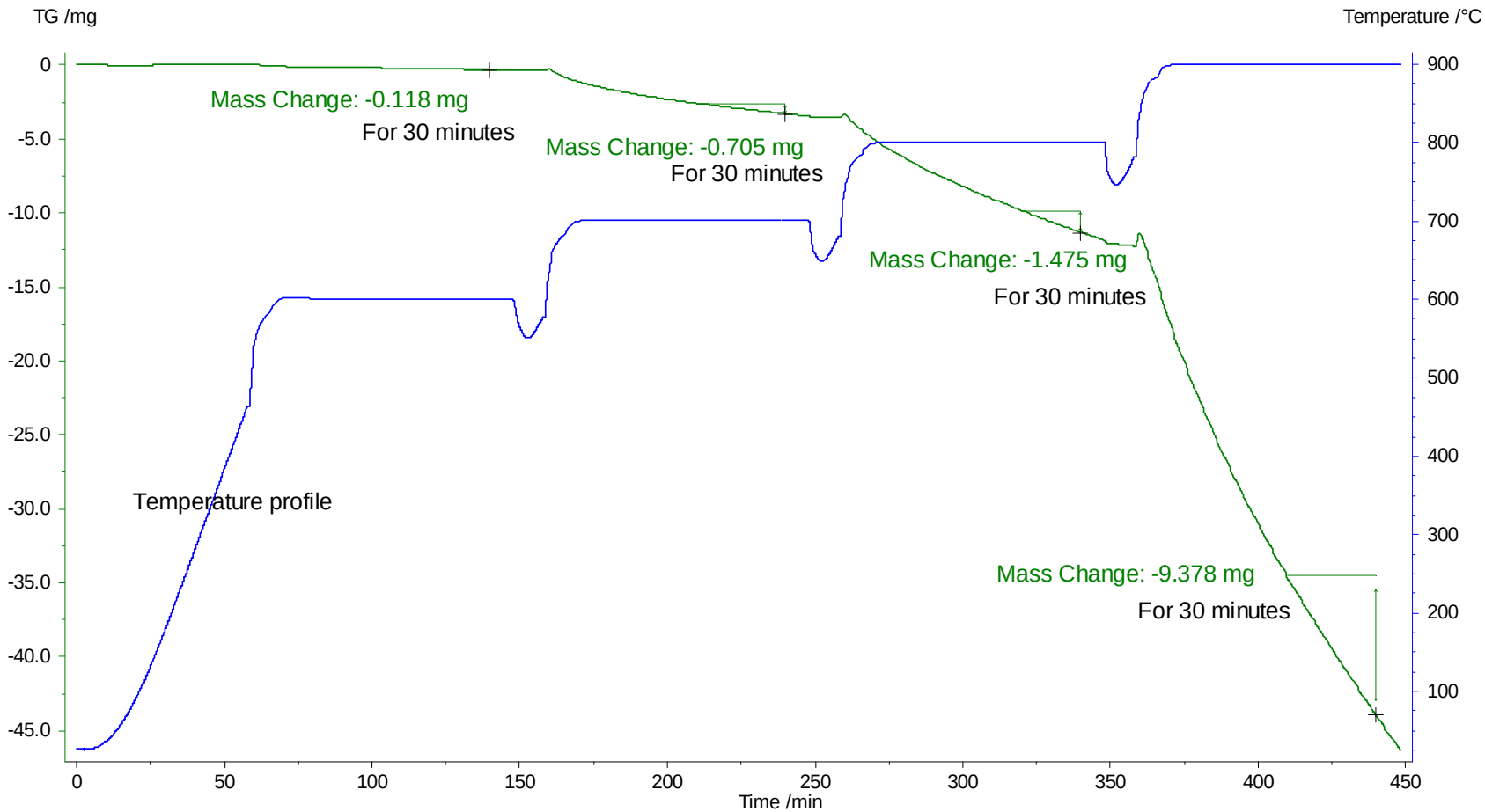
- Approach to Improved Sublimation Suppression
  1. Improve the intrinsic stability of the (add refractory elements)
  2. Further increase the density of aerogel and test in-gradient

Improving High Temperature Stability of n & p type Skutterudite

TGA: High-Temperature n-type Skutterudite (Iridium-doped) (10^{-6} Torr)



TGA: High Temperature p-type Skutterudite (Ruthenium-doped)(10^{-6} Torr)



Sublimation rates

High temperature skutterudite
(Maximum operation temperature : 900 ºC)

	Sublimation rate of n-SKD (ISN03)	Sublimation rate of p-SKD (NSKP16)
600 ºC	3.88×10^{-5} (g/cm²·hr)	1.32×10^{-4} (g/cm²·hr)
700 ºC	9.61×10^{-4} (g/cm²·hr)	7.91×10^{-4} (g/cm²·hr)
800 ºC	3.92×10^{-3} (g/cm²·hr)	1.65×10^{-3} (g/cm²·hr)
900 ºC	1.66×10^{-2} (g/cm²·hr)	1.05×10^{-2} (g/cm²·hr)

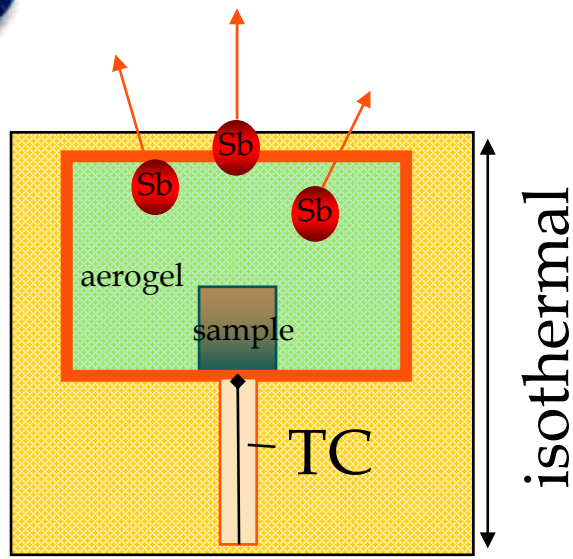
Skutterudite
(Maximum operation temperature : 700 ºC)

	Sublimation rate of n-SKD	Sublimation rate of p-SKD
500 ºC	5.31×10^{-4} (g/cm²·hr)	7.40×10^{-4} (g/cm²·hr)
600 ºC	5.16×10^{-3} (g/cm²·hr)	6.78×10^{-3} (g/cm²·hr)
700 ºC	2.15×10^{-2} (g/cm²·hr)	2.80×10^{-2} (g/cm²·hr)

- Reduced coating goal requirements from a factor of 3500 down to 1450!

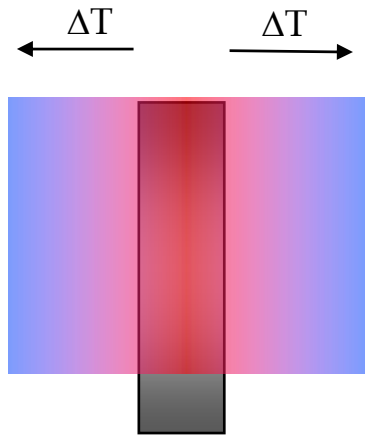
Increasing aerogel coating density and testing in-gradient

In-gradient Tests of Aerogel coatings



In TGA

vs.



Aerogel In-gradient

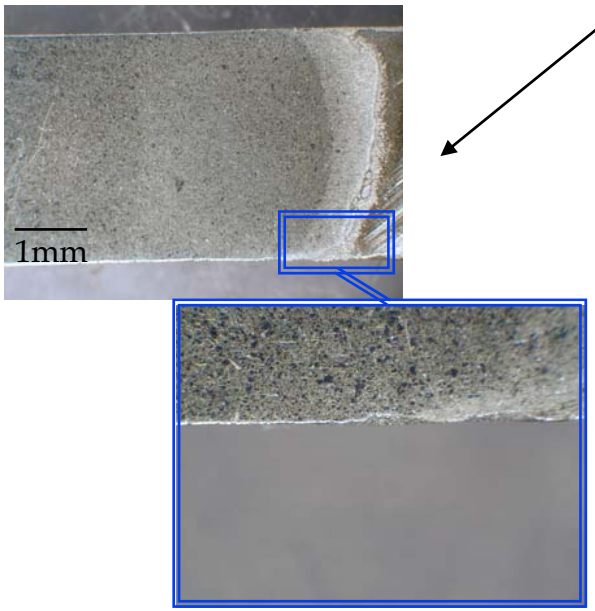
- **In-gradient tests are more accurately simulate operation**

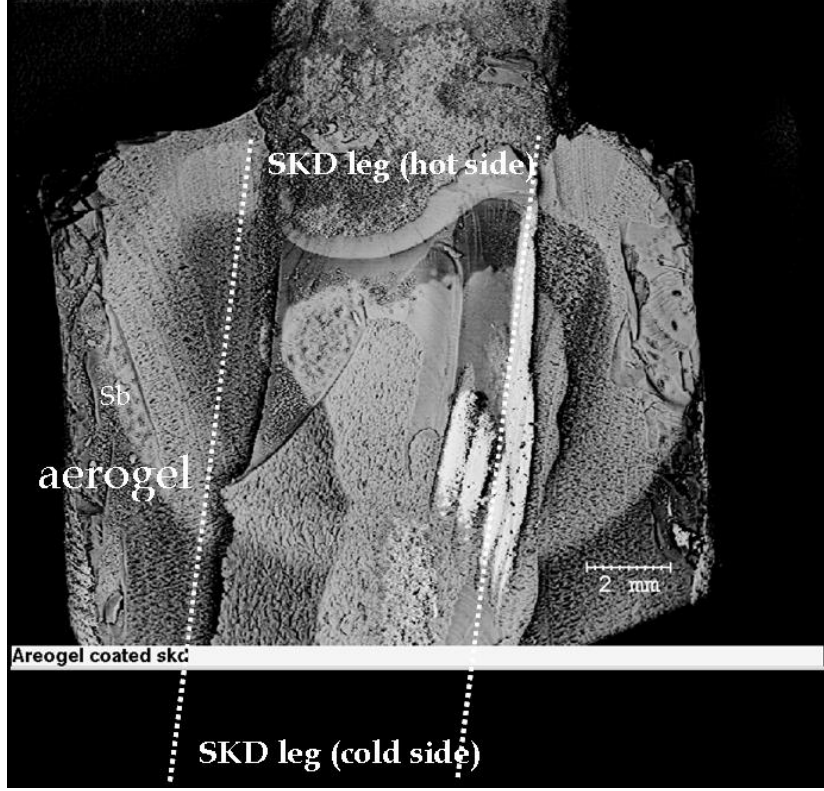
- **50mg/cc aerogel in TGA-2.98x 10^{-3} g/cm^{2}h it the in-gradient test should have resulted in ~0.2 mm depletion band in 14 days (easily observable at low mag)**

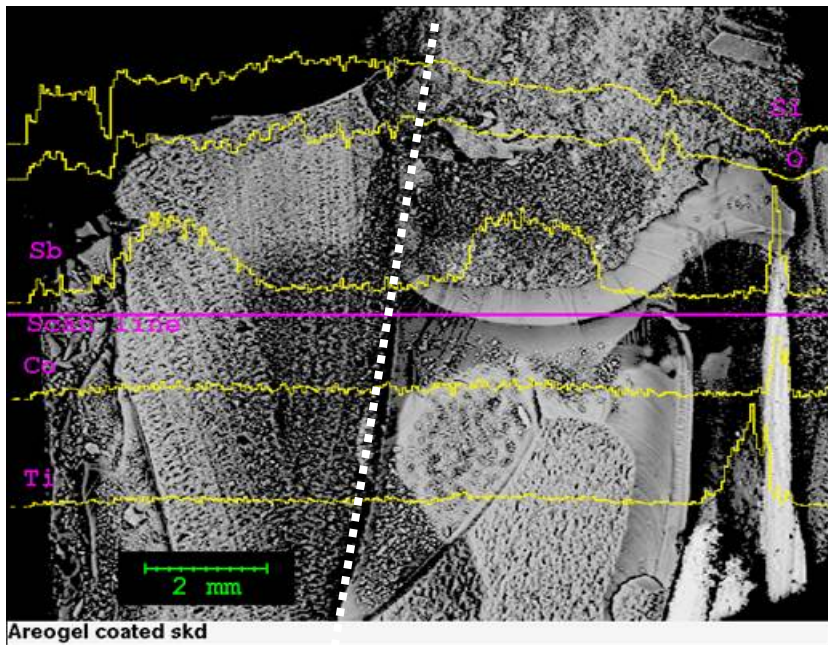
Non-refractory n-leg encapsulated in opacified aerogel (700C$_{hot}$:45C$_{cold}$ -16 days under 10^{-6} Torr)

40 mg/cc silica/graphite aerogel coating

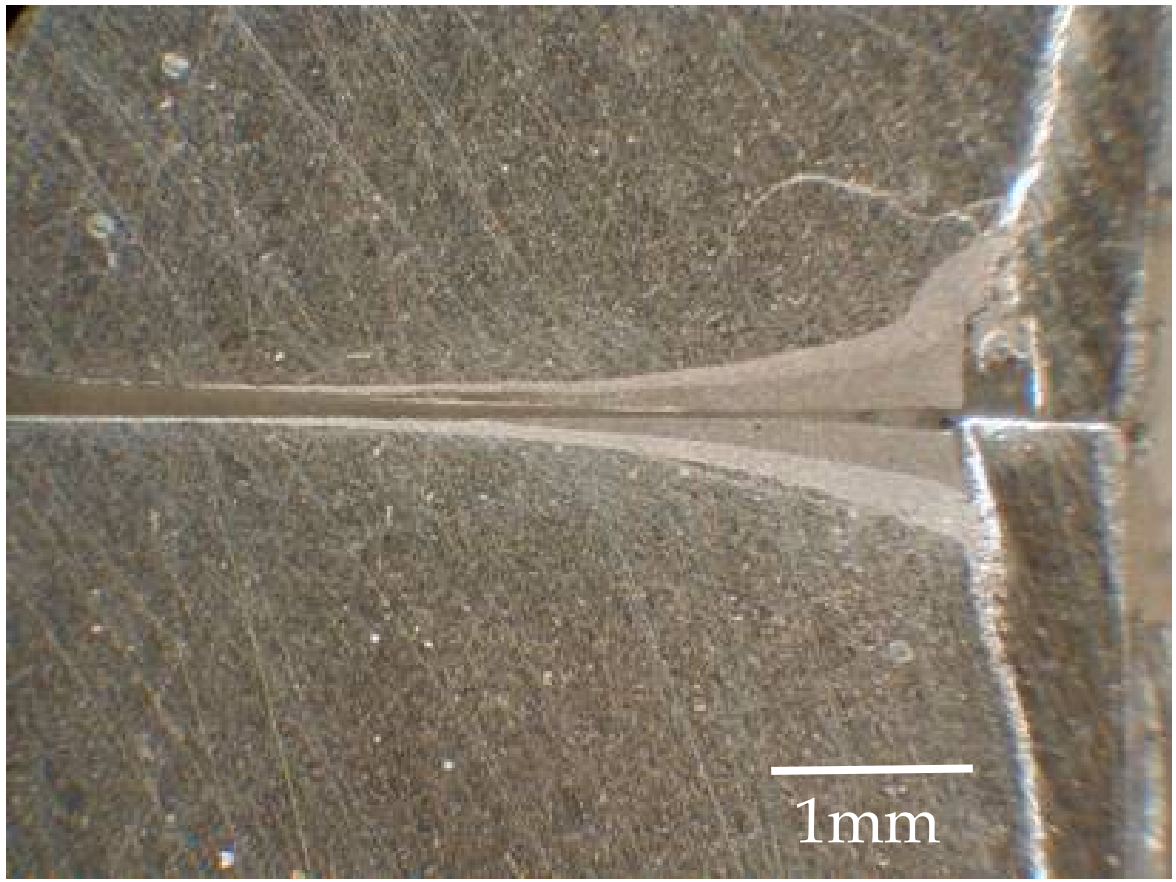
Cross-section

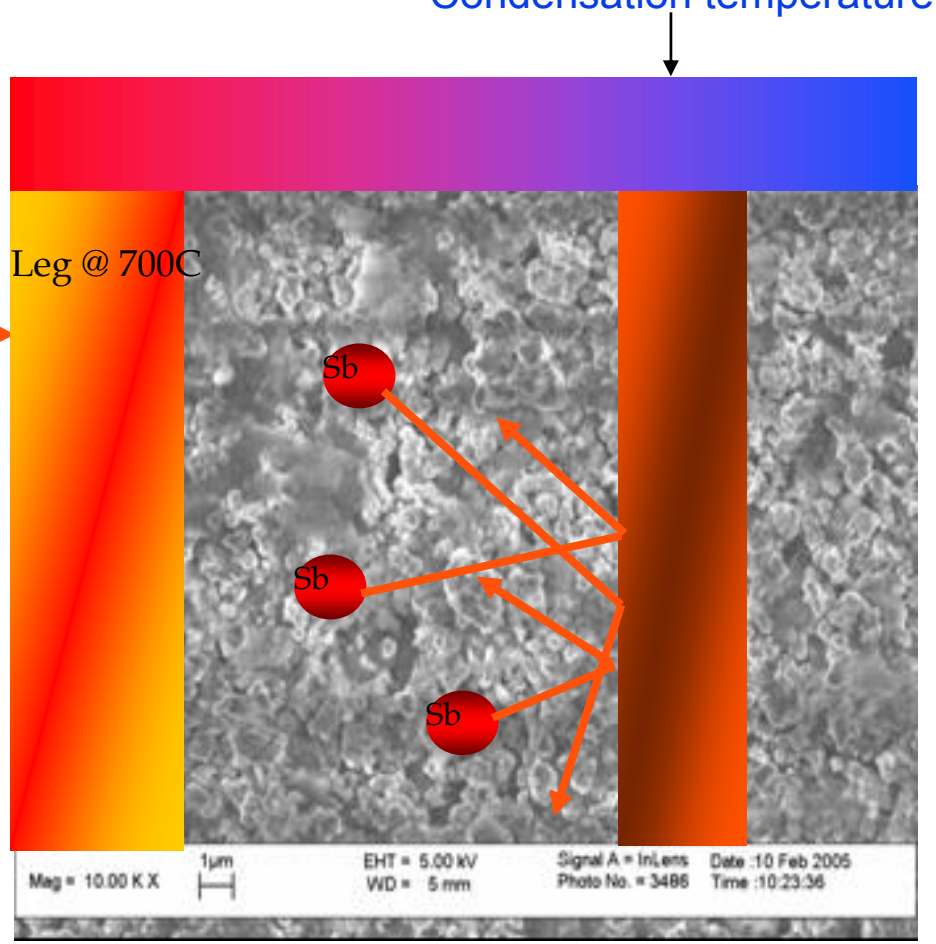






Uncoated leg-in gradient 700C hot side 45C cold side 10^{-6} Torr 14 days

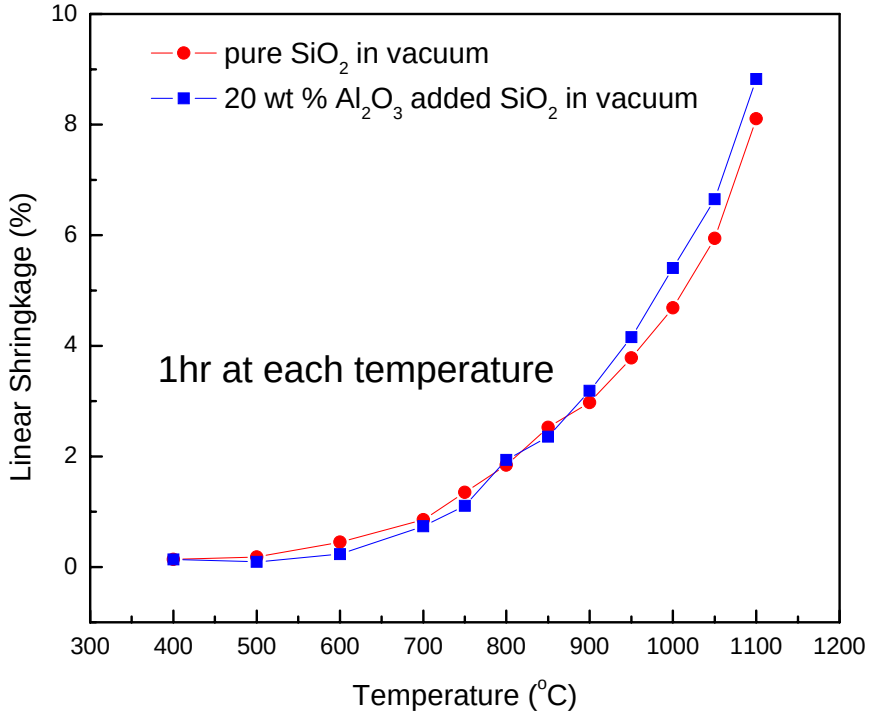


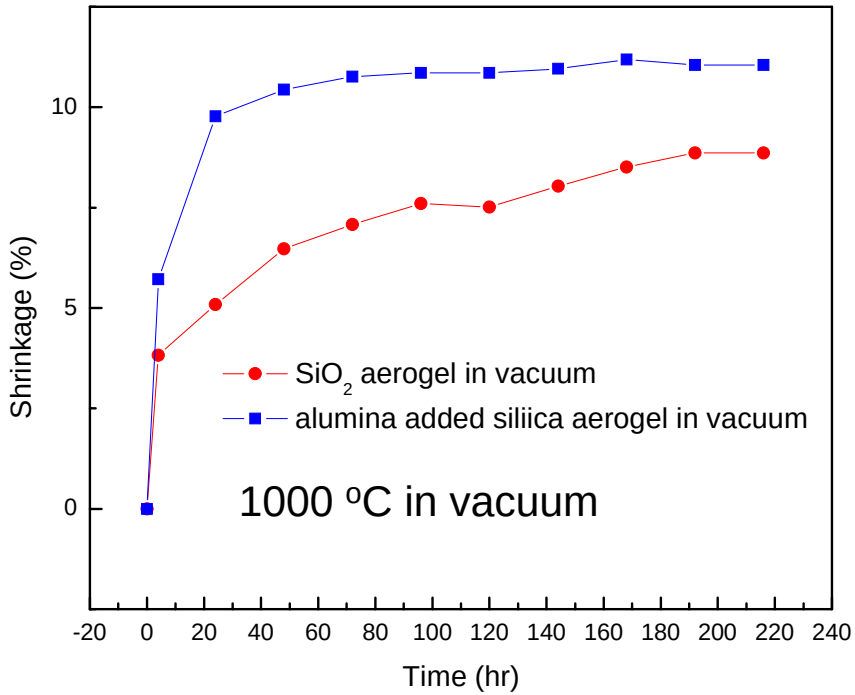


❖ ***As metal vapor condenses it plugs pores "self-sealing"***

Thermal stability of Aerogel

Thermal stability of aerogels





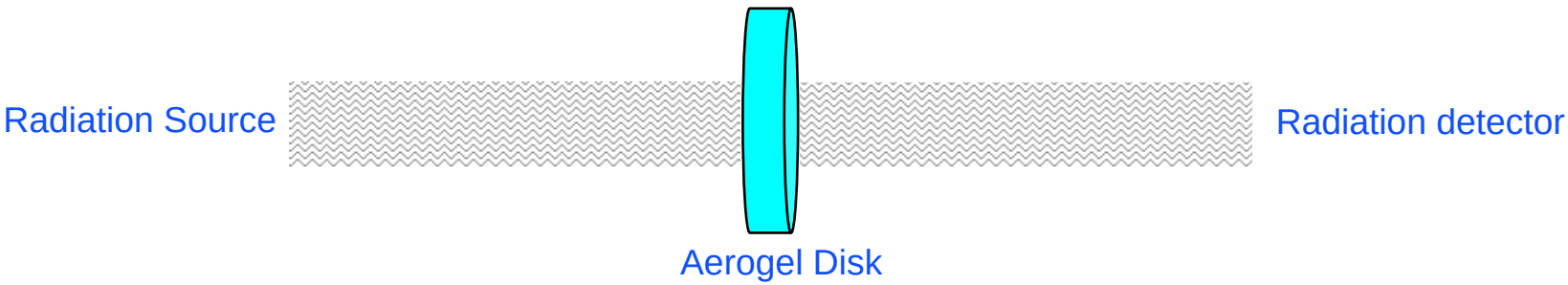
- Linear Shrinkage at 700 ^{o} C in vacuum is ~ 1 %.

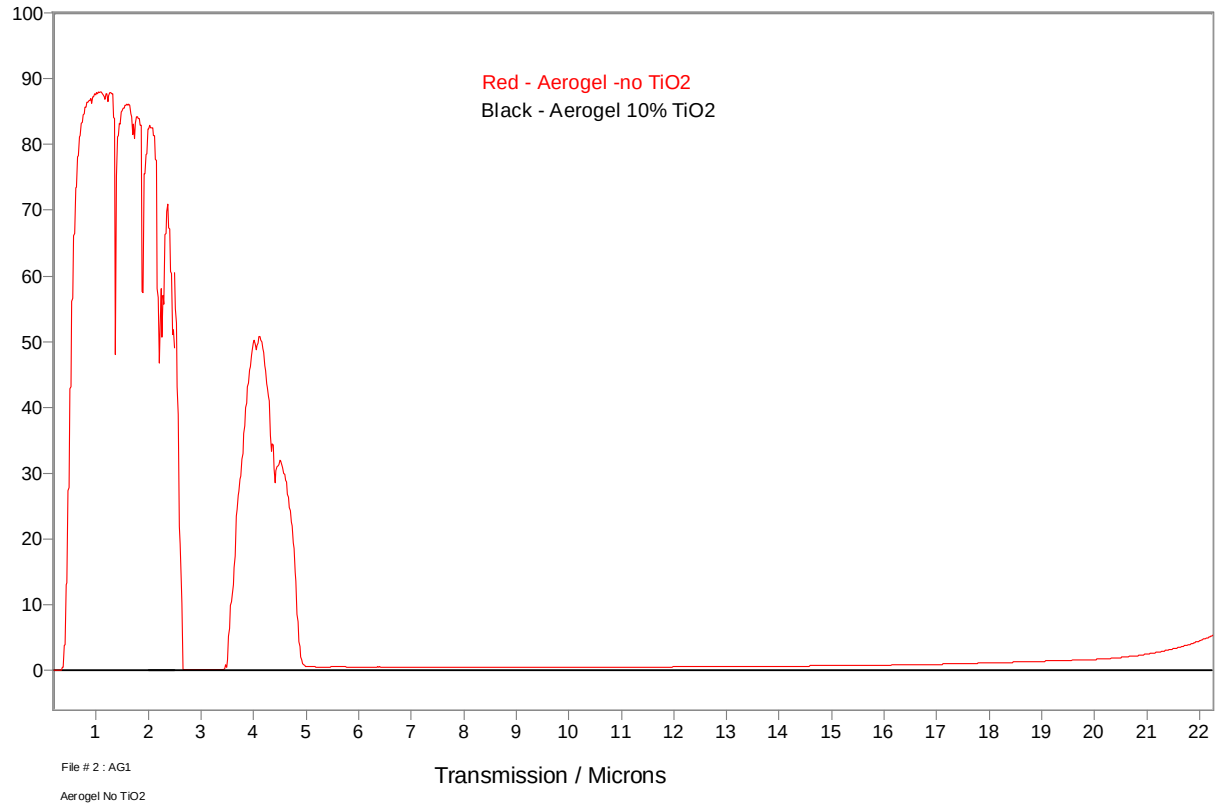
Characterizing Aerogel Opacification

Non-opacified aerogel : 150 mg/cc (SiO_2)

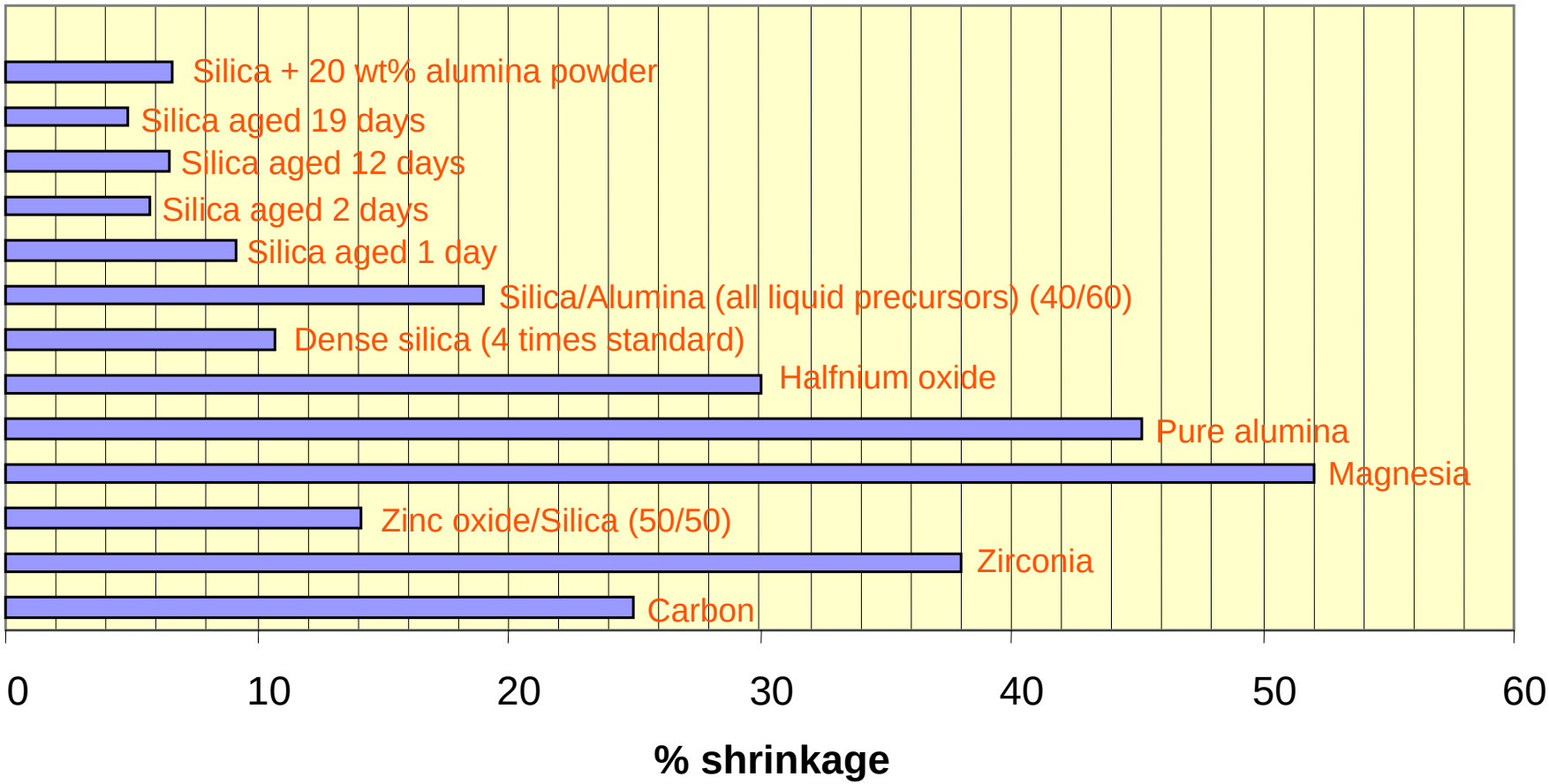
Opacified aerogel : 150 mg/cc (SiO_2) with ~ 10 wt% TiO_2 (16mg/cc)

Sample : disc shape (diameter : ~ 1.3 cm, thickness : ~ 0.4 cm)



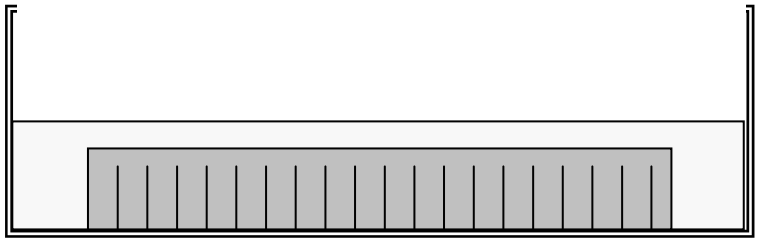


Brief summary of aerogel screening

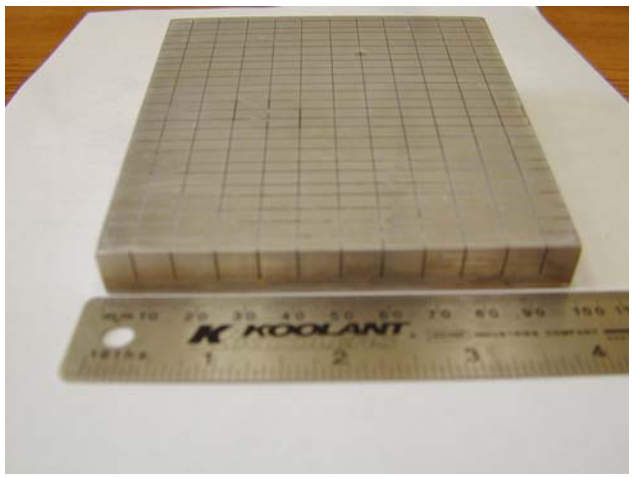


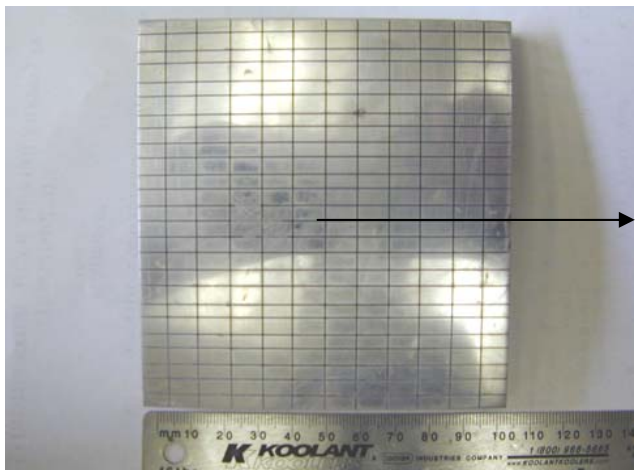
Thermoelectric module mock-up to test aerogel permeation

How it was made



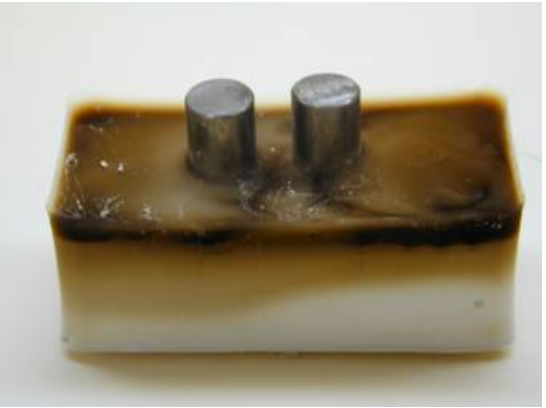
- Block placed upside down in mold so that notches were facing down.
- Liquid precursor (Sol) poured into mold. After several hours the liquid transformed into a free-standing gel
- The entire assembly including the mold was placed in the autoclave and supercritically dried.





- Overall, the aerogel permeated the mock-up network. There were a few slots that were not filled, which may be attributed to residual oil from machining.

Encapsulating Skutterudite Unicouples in Aerogel



Summary

- Developed new approach to suppressing sublimation
- Clearly demonstrated that aerogel does slow sublimation
- Quantified sublimation suppression objectives
- Adding refractory elements to Skutterudites significantly increases thermal stablility

Future Work:

- Combine and integrate latest accomplishments into extended period test > months