Developing Hydrophobic Silica Aerogels for Cherenkov Detectors

Makoto Tabata

Chiba University

Aerogel Factory Co., Ltd.

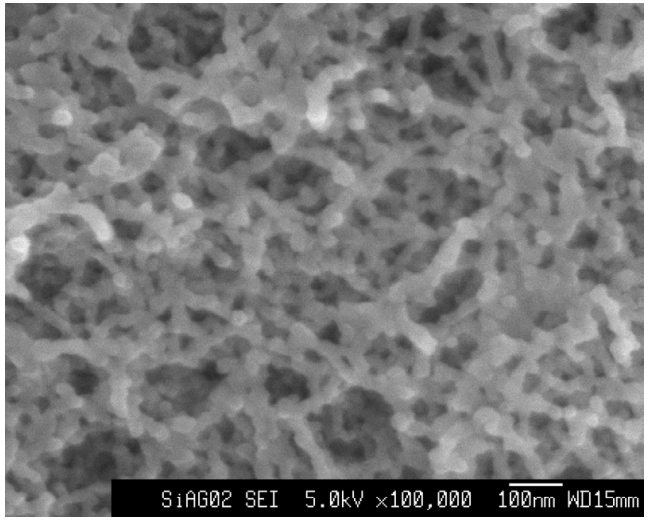
Aerogel Factory

XII International Workshop on Ring Imaging Cherenkov Detectors (RICH2025)

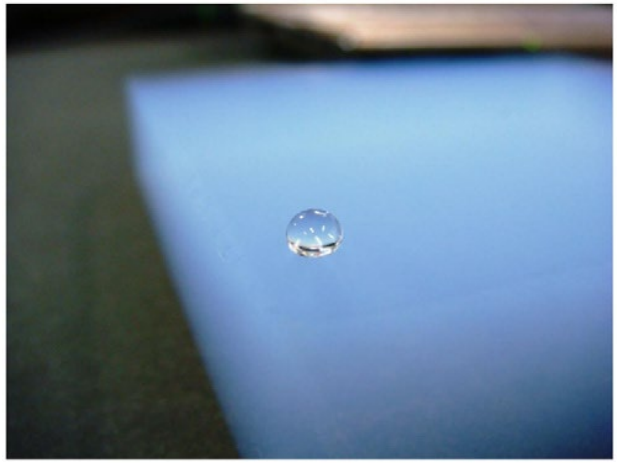
Outline

- Introduction to Silica Aerogel.
- Review of the achievement of the Belle II aerogels.
- Future direction:
  Lower index & Larger tile production.
  Key technology: Supercritical drying (while eliminating tile cracking).

Basics of Silica Aerogel



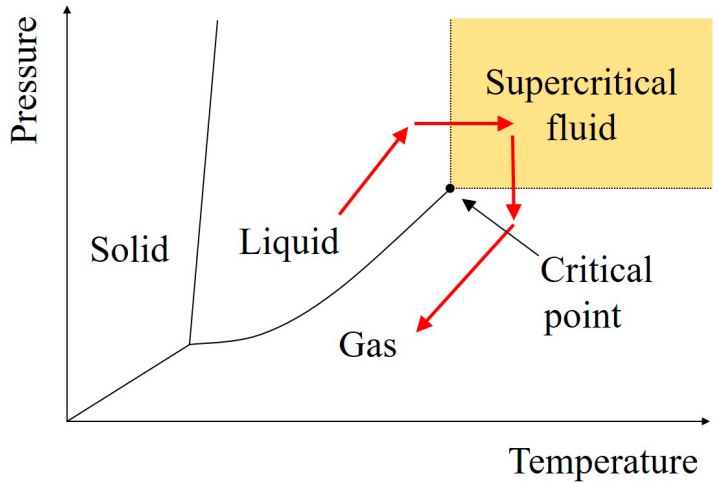
- Nano-structured material made of 3D networks of silica (SiO_2) particle clusters.
- Optical properties derived from the distribution of silica clusters and air-filled pores.
- Originally hydrophilic (absorbing environmental moisture).
- One can render aerogels hydrophobic during production by a silane-based reagent.
  Chemical surface modification (not aerogel tile surface but individual silica cluster surface.)
  Including carbon elements derived from methyl groups.
  Can be cut by a water-jet machine.



- Refractive index–density (ρ) relationship:
  $n(\lambda)-1=k(\lambda)\rho$
  $k \sim 0.27\ cm^3/g$ for hydrophobic aerogel,
  Slightly depends on the nanostructures.

Production Procedures

1. Sol–gel polymerization: synthesizing an alcogel block.
2. Aging under an optimized temperature.
3. Hydrophobic modification → Ammonia as a byproduct.
4. Ammonia removal.
   (Still wet alcogel here)
5. Liquid solvent extraction under the supercritical phase.
   (Supercritical “drying” with an autoclave)



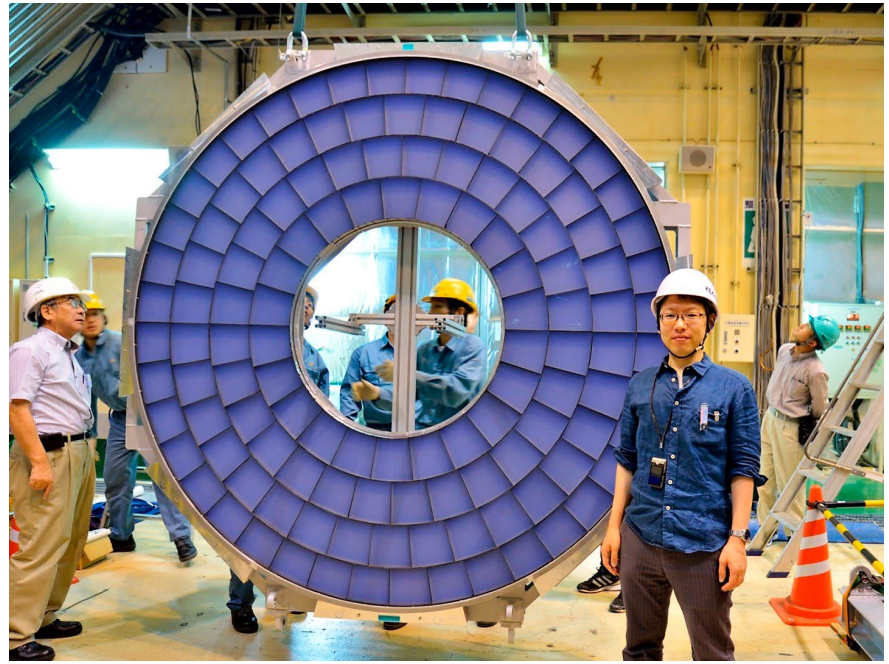
Review: Belle II ARICH Aerogel

- n=1.045+1.055 (separated two layers).

- 18x18x2 cm^3 tiles: ~450 tiles mass-produced, 124+124 tiles installed .
- Water-jet cutting to fan shapes.

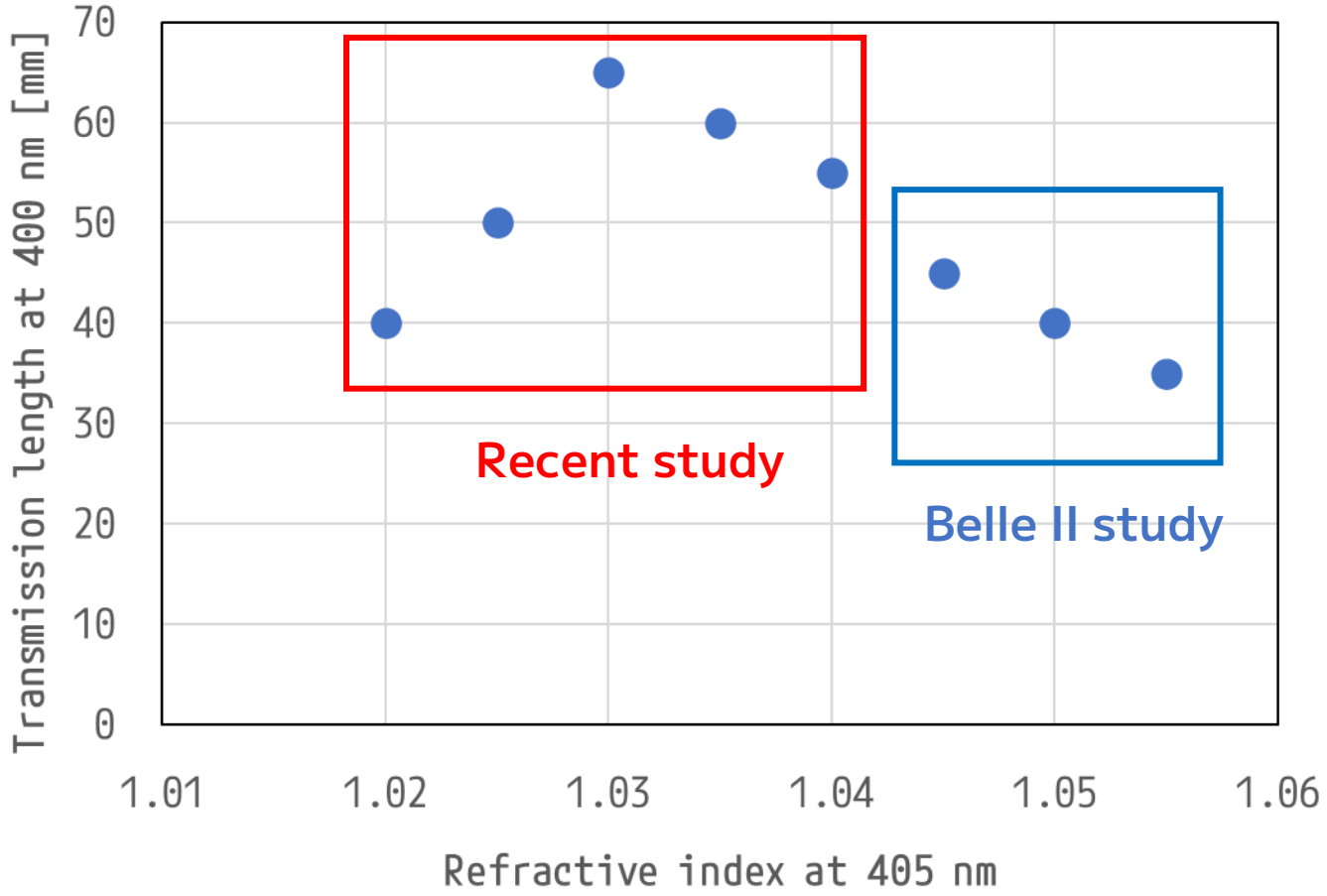
- Transmission length 45 and 35 mm as produced.
  Kept ~40 and ~30 mm after water-jetting.

  Degradation occurs not due to water contact itself, but rather from the machining procedures (handling by machining professionals and transportation).



- Special thanks to Belle II ARICH group!

Optical Property (Recent Progress)



Supercritical Drying

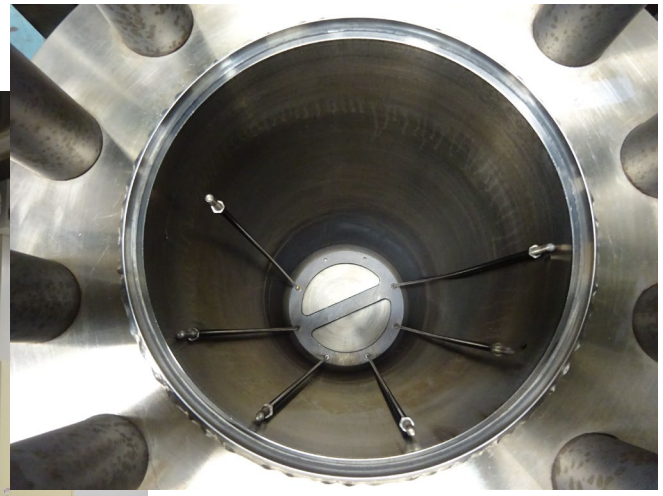
At Chiba Univ.

CO_2 autoclave (7.6 L)
Max. 80 °C., 10 MPa during operation.

Alcohol–CO_2 exchange in high pressure.
Can be applied in any index.

Alcohol autoclave (31 L)
Max. 260 degrees C., 7.3 MPa

Can be applied in n<1.08.

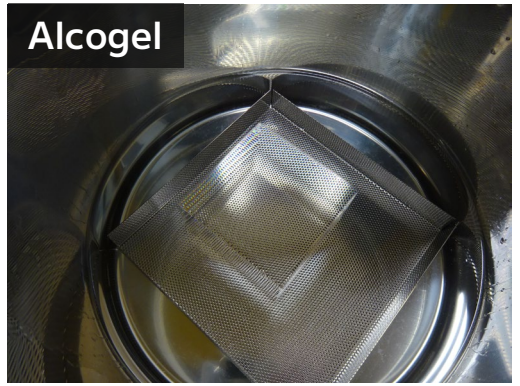


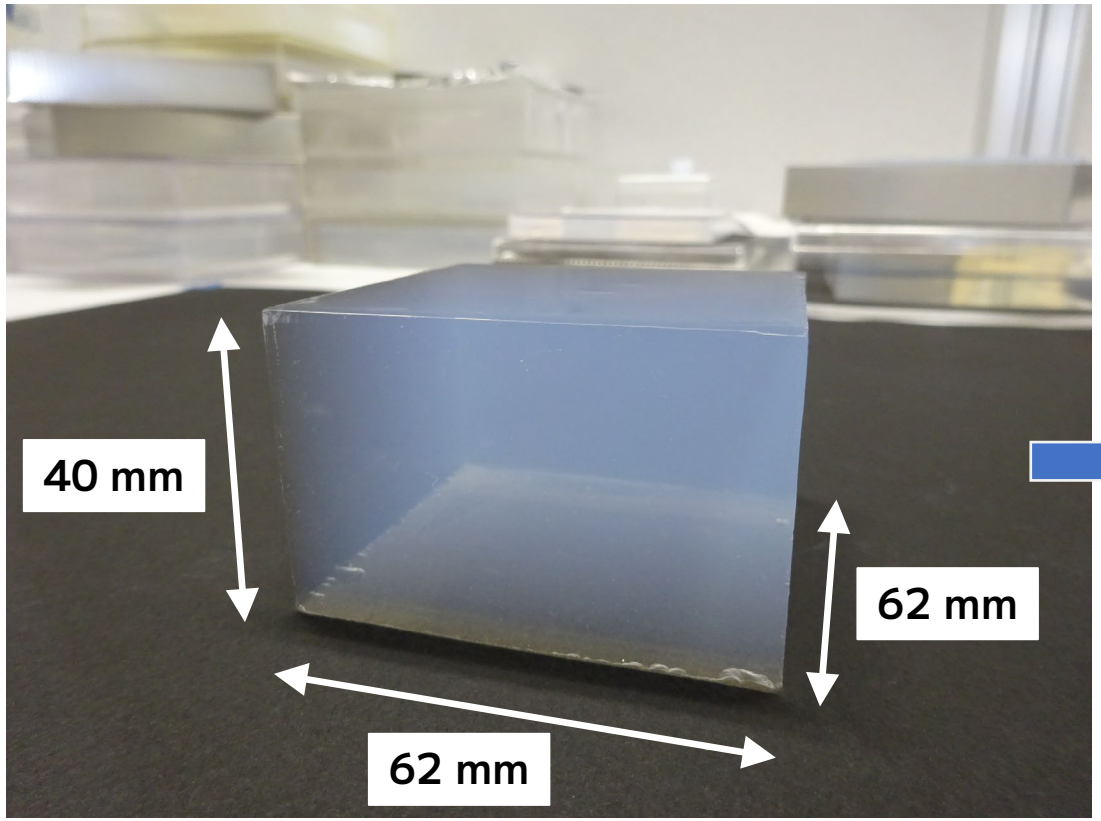
Increasing Tile Thickness

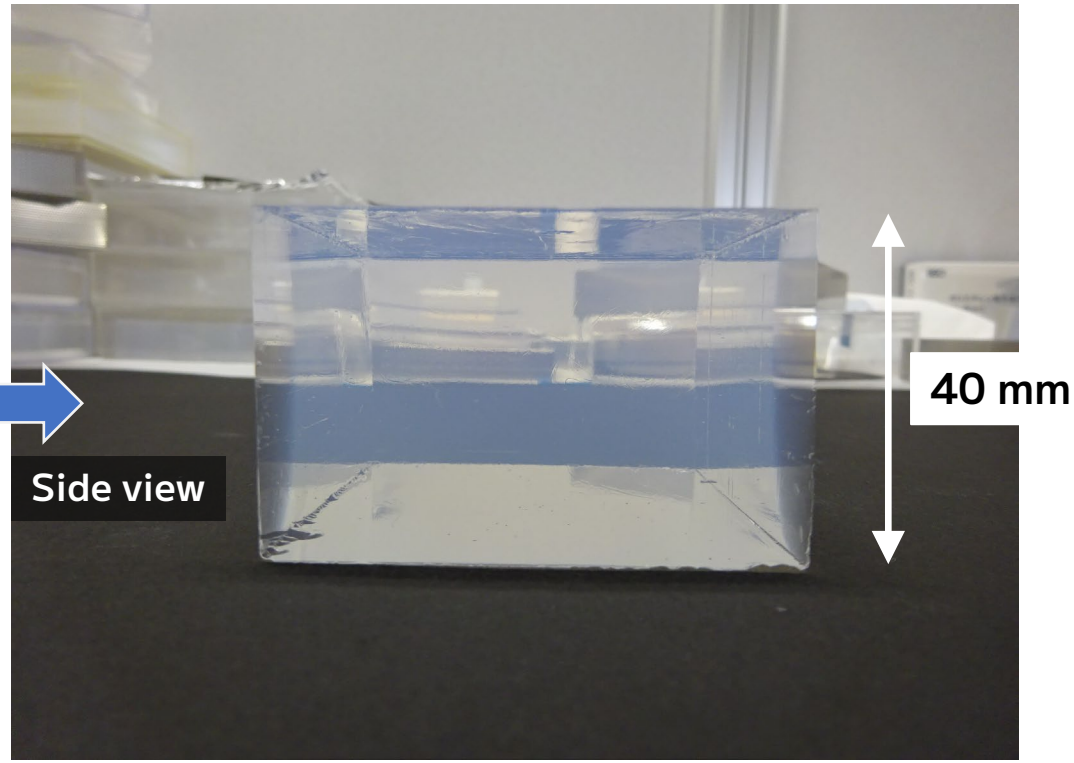
Beyond 3 cm

Thick Block with CO_2 Drying

- Using the small autoclave at Chiba.
- Applying the low-rate depressurization method.
- n=1.048, TL=43 mm, V=(62x62 mm^2, 40 mm thick).
- Crack-free yield is not so high (below 50%) as of Jan. 2024.

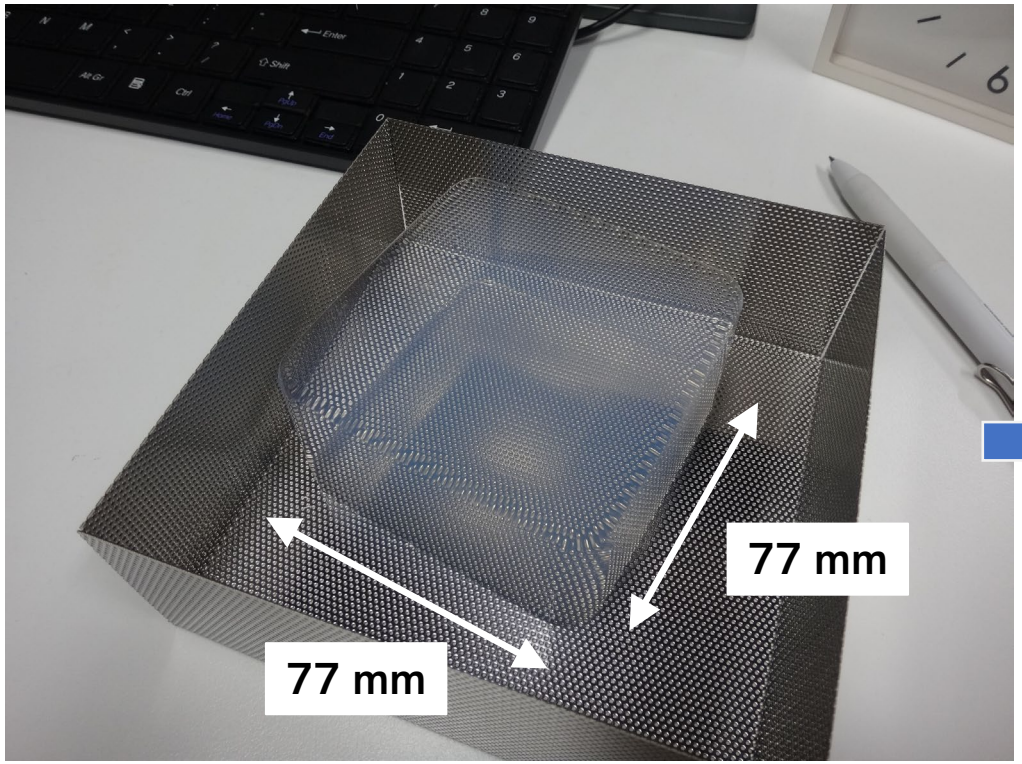


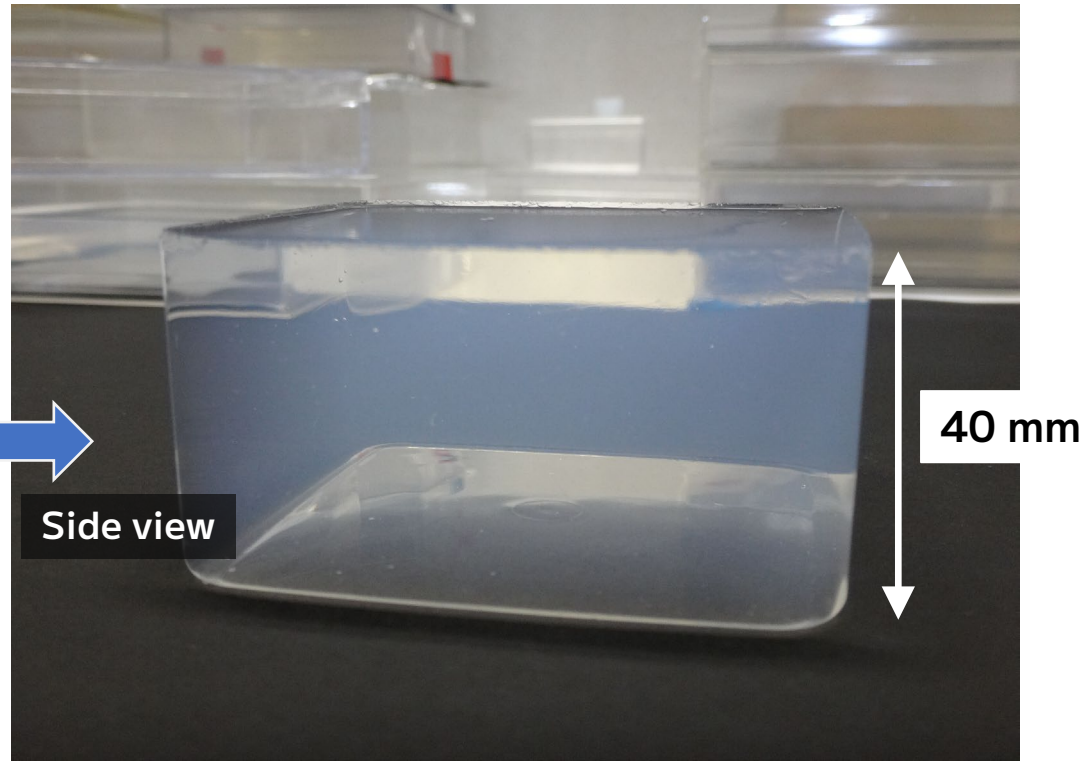




Thick Block with Alcohol Drying

- Using the medium-sized autoclave at Chiba.
- Applying the low-rate depressurization method.
- n=1.039, TL=49 mm, V=(77x77 mm^2, 40 mm thick).
- The first crack-free block in Aug. 2025. → Next steps: 50 mm thick and yield check.





Increasing Tile Area

Beyond 18x18 cm^2

Choice of Drying Method

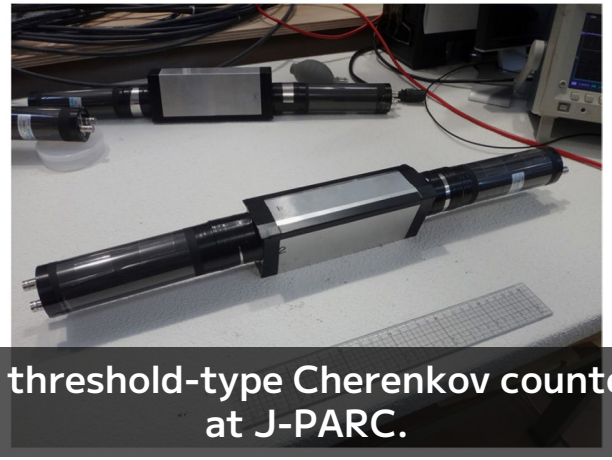
1. CO_2 drying has the disadvantage of tiles being likely cracked during solvent exchange (alcohol* to CO_2) under high pressure.
   (* Alcohol used as ammonia removal)

2. The CO_2 autoclave used in Belle II aerogel production was commercially operated by a company in Japan.
   → Continuous availability is not ensured.

3. If we build a new autoclave in the future, an alcohol autoclave has advantages in building costs and compliance with laws and regulations in Japan.

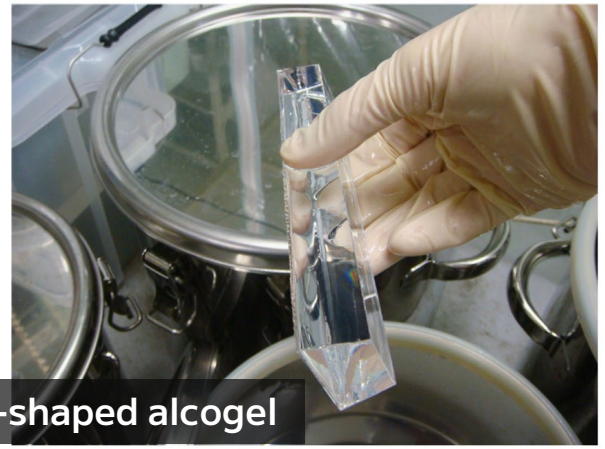
We chose alcohol drying for later study, aiming at larger tiles.

A Proved Method: Vertical Storing in CO_2 Autoclave NIMA 795 (2015) 206.



A threshold-type Cherenkov counter at J-PARC.

Fig. 2. Assembled AC counter module. Two PMTs are oriented to the kaon beam axis. The length of the counter housing (aerogel box) is 18 cm.

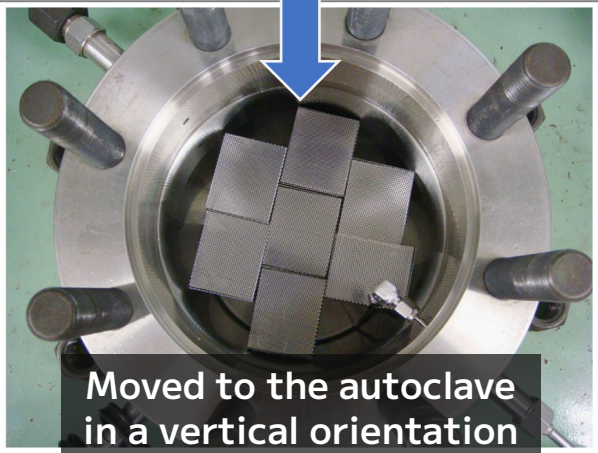


Bar-shaped alcogel

Fig. 5. A wet gel bar detached from the mold. When the aerogel density was more than ~ 0.1 g/cm^3 ($n=1.08$ corresponding to $\rho=0.27$ g/cm^3), direct handling of the wet gel was possible. The wet gel needed to be returned to the ethanol bath within several tens of seconds to avoid cracking because of drying.

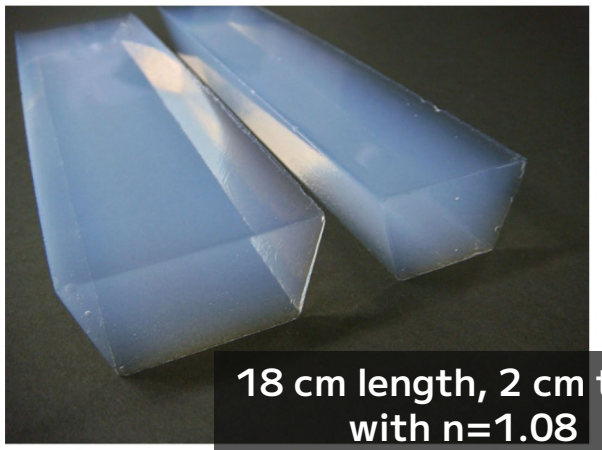
Stored in punched SUS containers

Fig. 6. Wet gel in the hydrophobic treatment process. The wet gel bars were placed in the punched trays and soaked in a solution for the hydrophobic treatment.



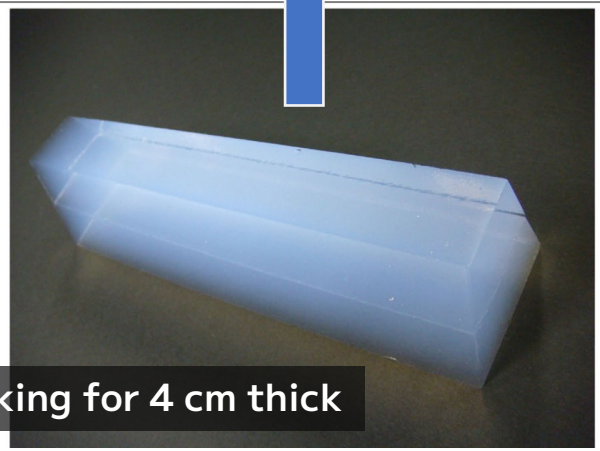
Moved to the autoclave in a vertical orientation

Fig. 7. Punched trays placed in the autoclave of supercritical carbon dioxide drying apparatus. Each tray contained two wet gel bars. The autoclave was filled with ethanol at the beginning of the drying operation.



18 cm length, 2 cm thick with n=1.08

Fig. 8. Crack-free aerogel bars for (left) downstream and (right) upstream layers obtained for the final production. Both the aerogel bars had a longitudinal length of approximately 18 cm and a thickness of 2 cm.

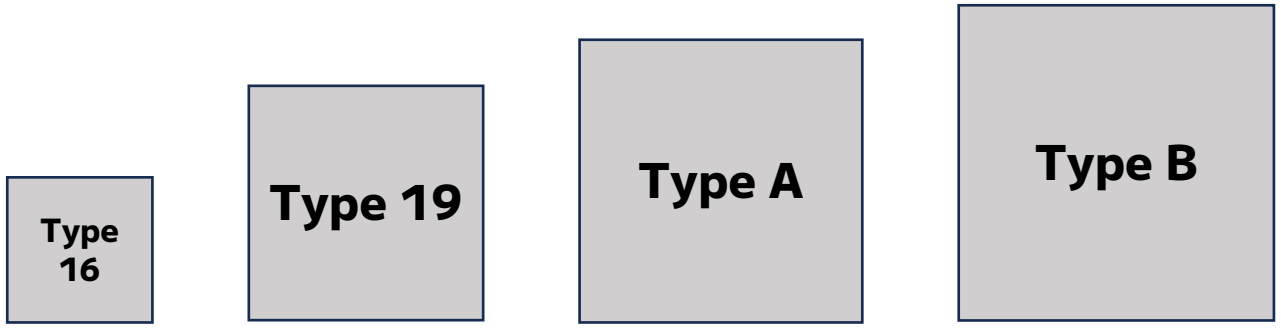


Stacking for 4 cm thick

Fig. 13. Upstream aerogel bar stacked on top of a downstream one. The longitudinal length and total thickness are approximately 18 cm and 4 cm, respectively.

Polystyrene Molds for Alcogel Production

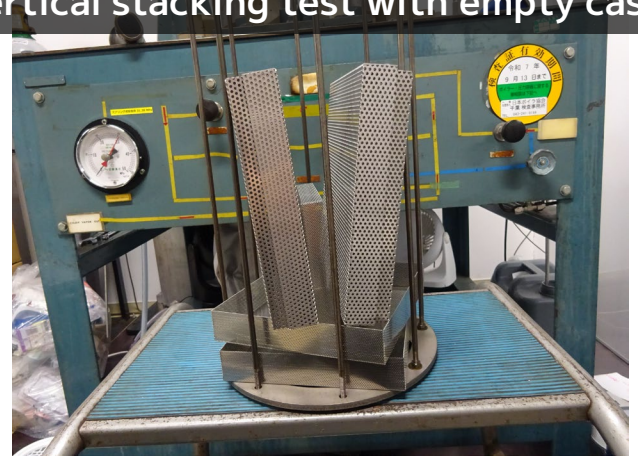
Type	Inner size	Utilization	Final aerogel size (Approximate)
Type 16	96 mm	Basic R&D size	9 cm
Type 19	155 mm	Fit alcohol autoclave	15 cm
Type A	187 mm	Belle II actual use	18 cm
Type B	207 mm	Belle II extra R&D	19 cm

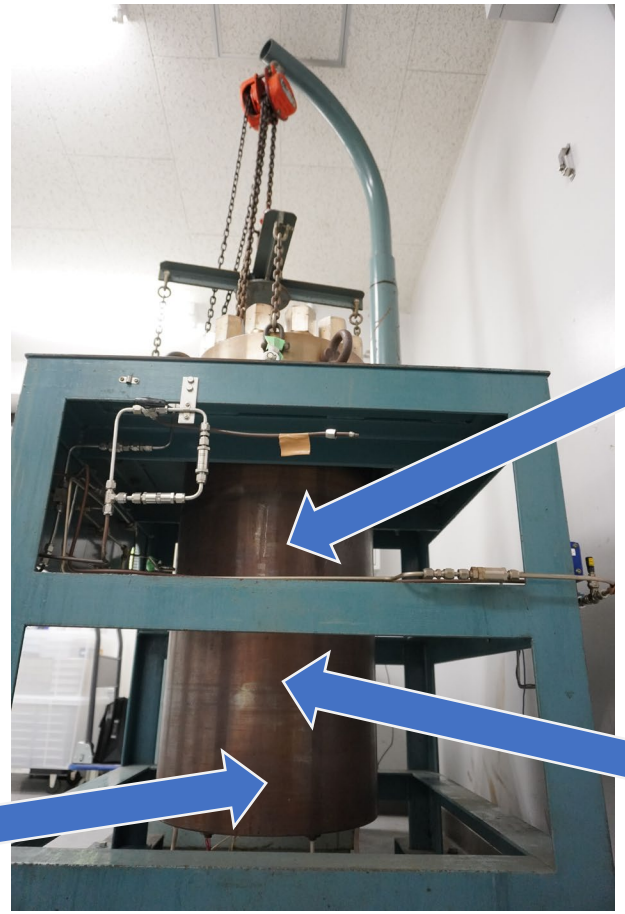


- Try to use types A and B with alcohol drying

Alcohol Autoclave Setup

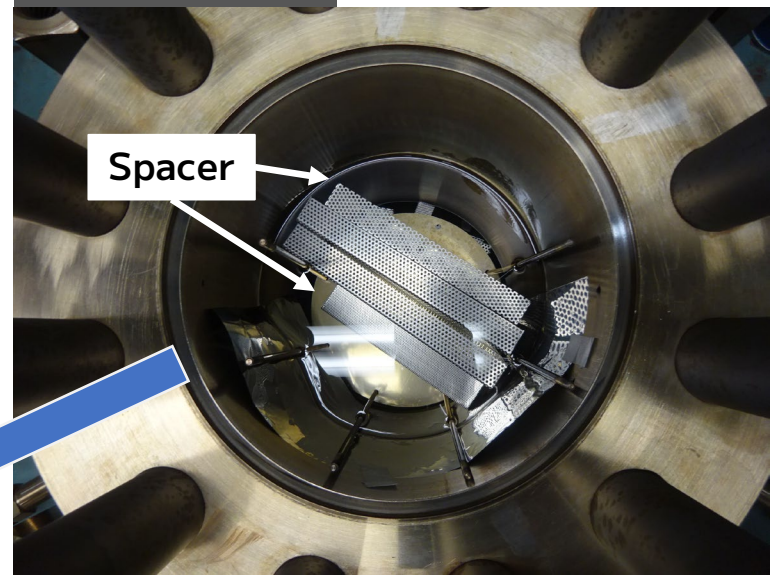
Vertical stacking test with empty cases



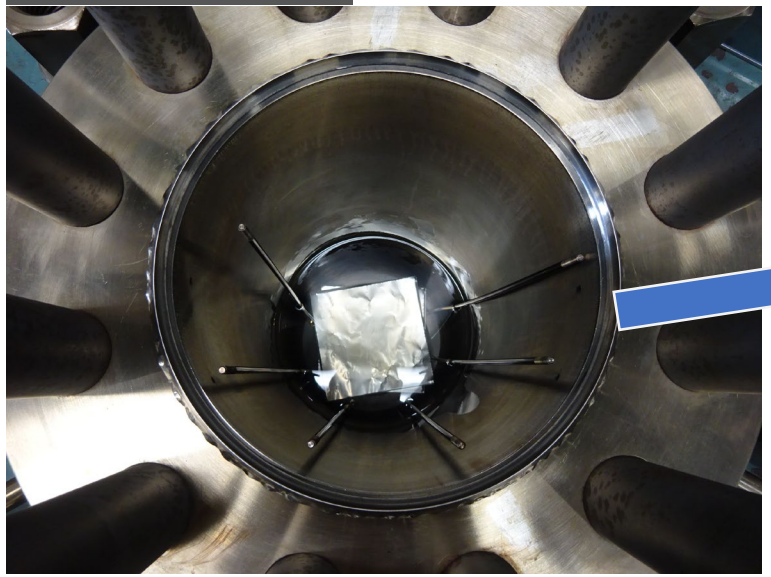


While filled with alcohol

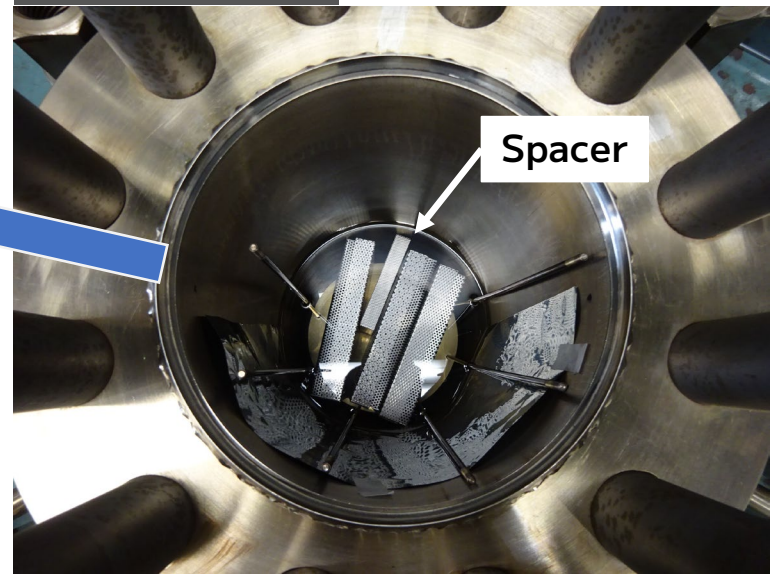
Type B (2 tiles)



Type 19 (2 tiles)

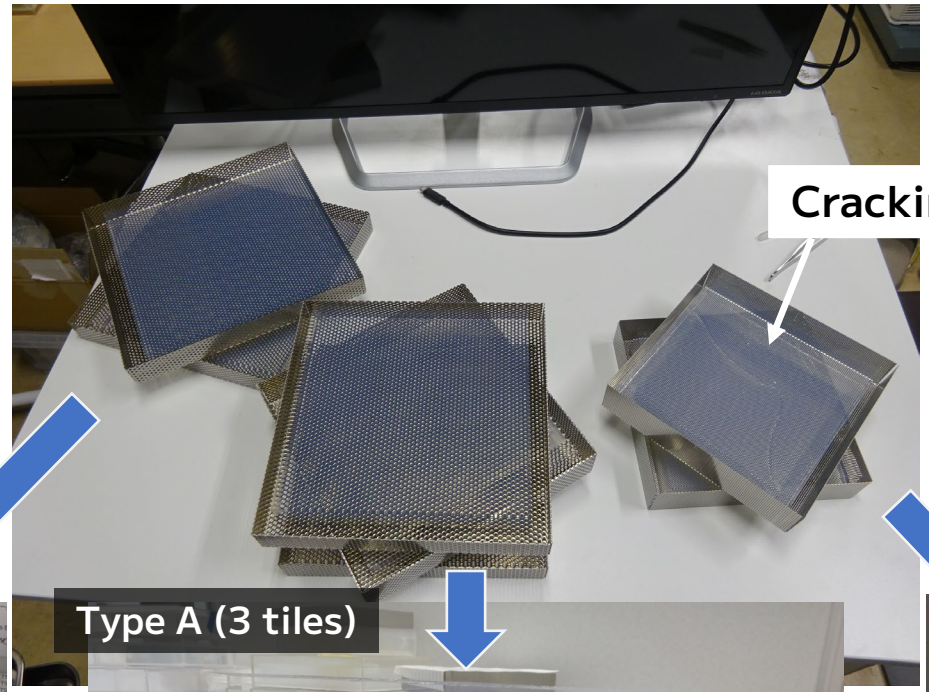


Type A (3 tiles)

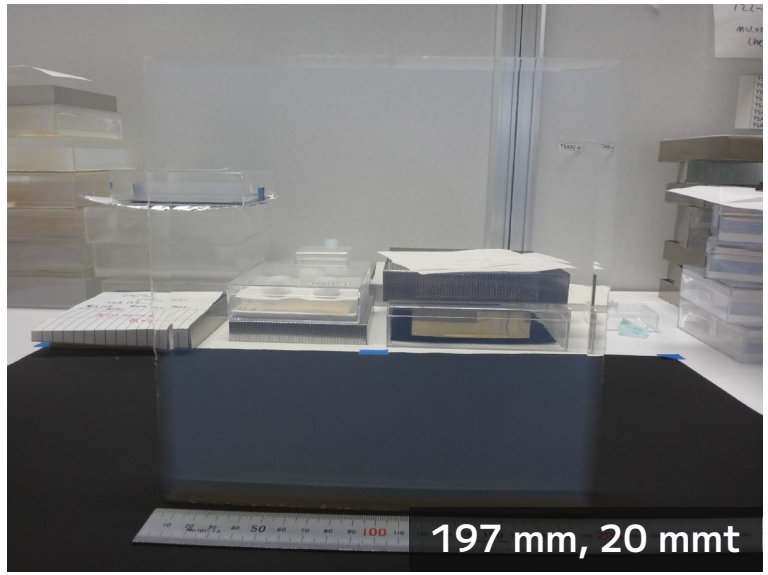


Results from a Single Batch (n=1.026)

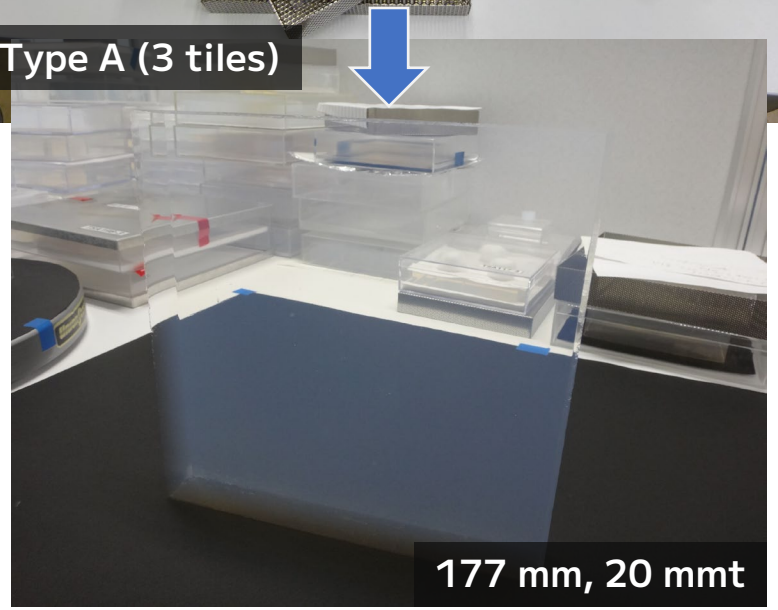
As of Dec. 2024



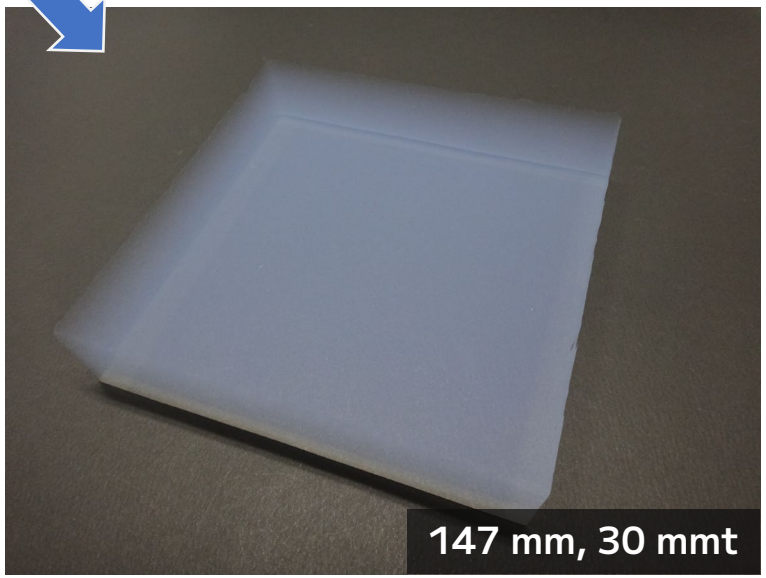
Type B (2 tiles)



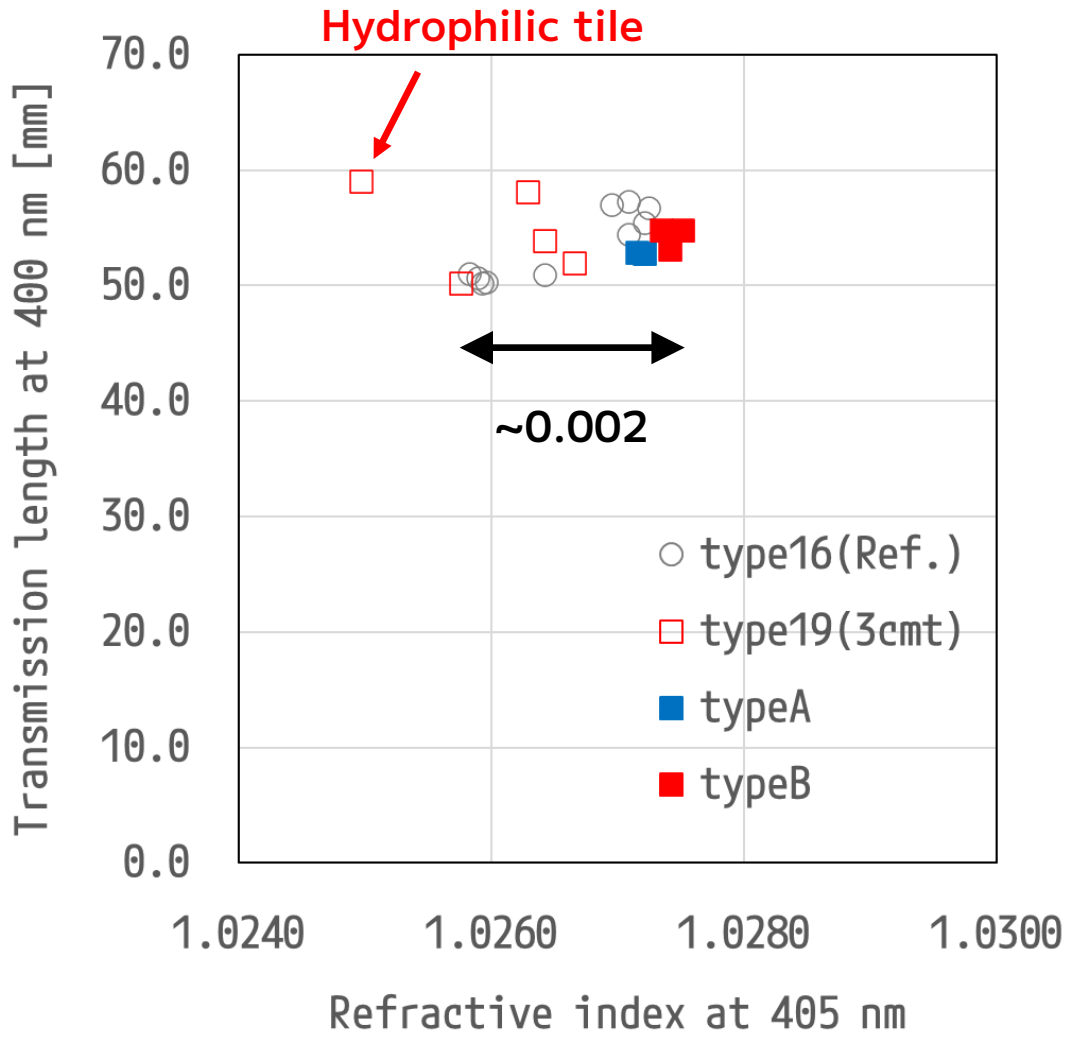
Type A (3 tiles)



Type 19 (2 tiles)



Optical Properties of Lager Tiles



- No significant differences compared with small tiles.
- Refractive index distribution within the production tolerance (reproducibility ±0.001).
- Comparison with hydrophilic tile.
  Low refractive index and high transmission length.

Summary

- Results from large-volume aerogel tile R&D were reported.
- As of today, ~20x20x2 cm^3 hydrophobic tiles were obtained with no cracking using the alcohol drying method.

Next step.

- An alcohol-type large autoclave is under design.
- Inner diameter = 47 cm, depth = 66 cm (~115 L)
- Maximum size of ~30x30 cm^2 can be stored.
- The first engineering operation is expected in May 2026.

- Hopefully, results from the large autoclave will be shared at the next RICH conference!

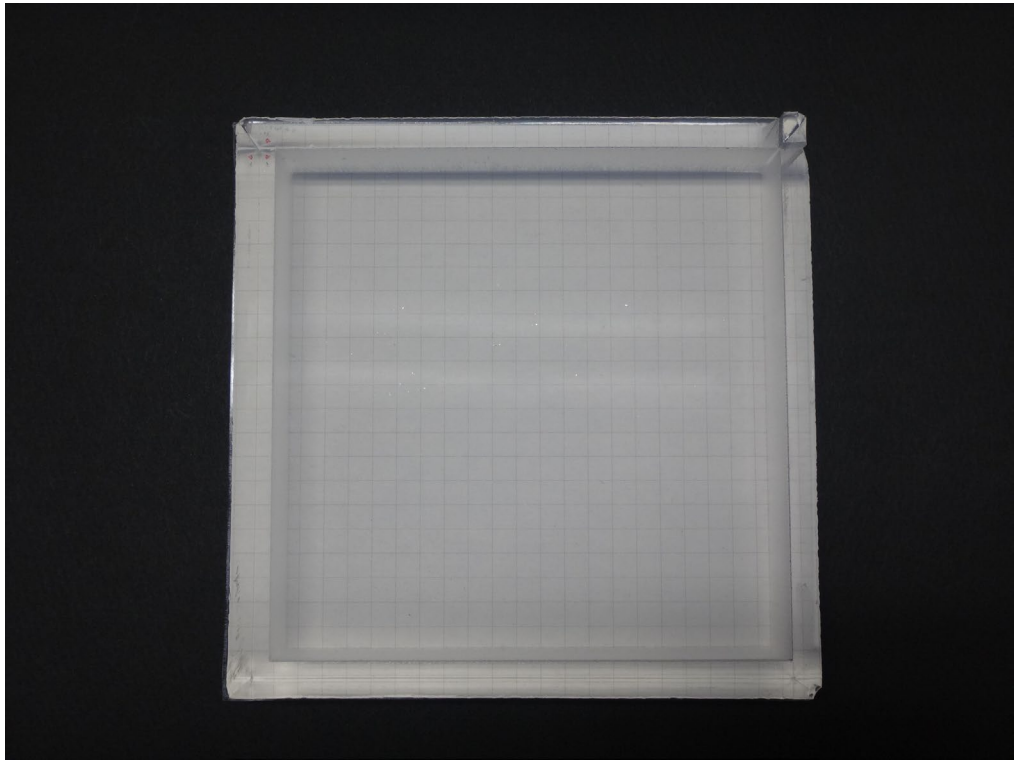
Backup Info

- Excellent review by I. Adachi (KEK)!
  Selected slides are attached to the following pages.

- In the workshop, fruitful focused characterizations in the individual experimental collaborations!
  ePIC dRICH & pfRICH, ALICE3, HELIX, etc.
  Each feedback is vital for improving aerogel production!

Water-jetting

- Continuous line cutting (Recommended).
- Need extra volume outside the designed shape (~7mm or more).
- Ex. preparing a 114mm tile for getting a 100mm square.
- The success of cutting proves the hydrophobic property.



- Basically, no degradation of optical properties by cutting itself.
- However, potential surface damage from the handling of tiles by cutting experts in a company. Also, during transportation.

KEK

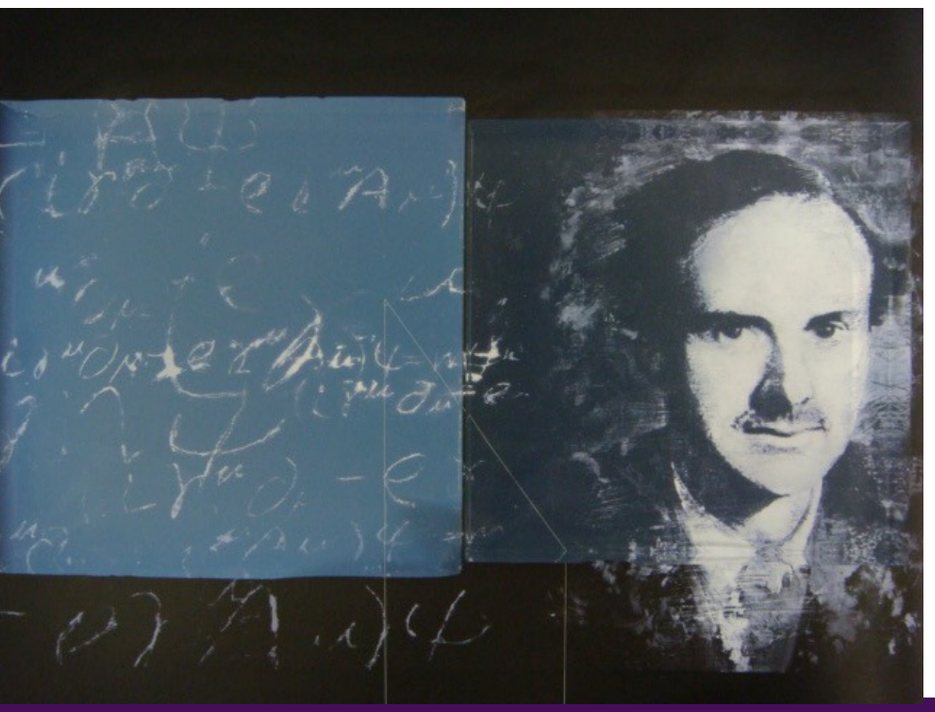
HIGH ENERGY ACCELERATOR RESEARCH ORGANIZATION

Status and Perspectives of High Quality Silica Aerogel

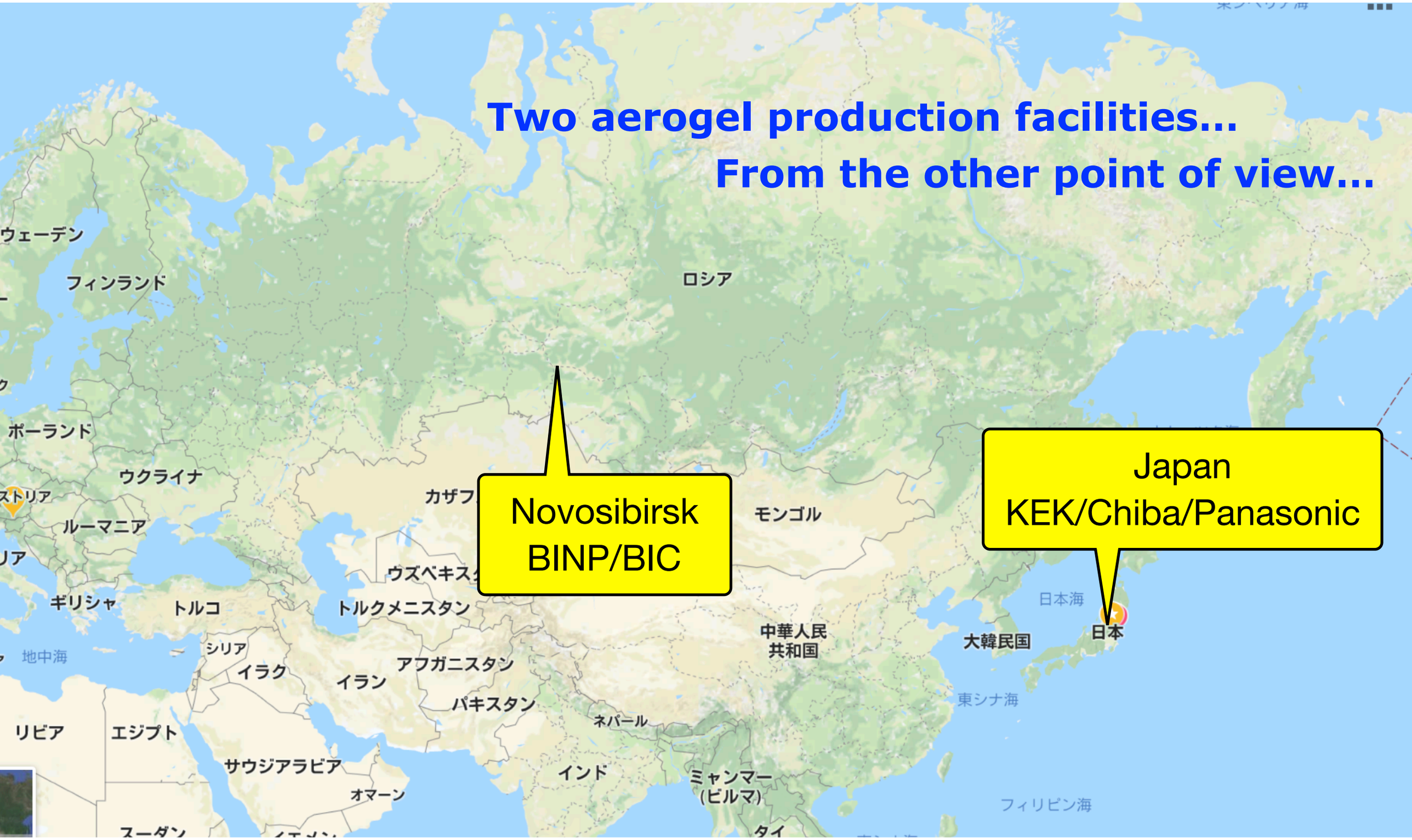
Ichiro Adachi

KEK

2018.08.03

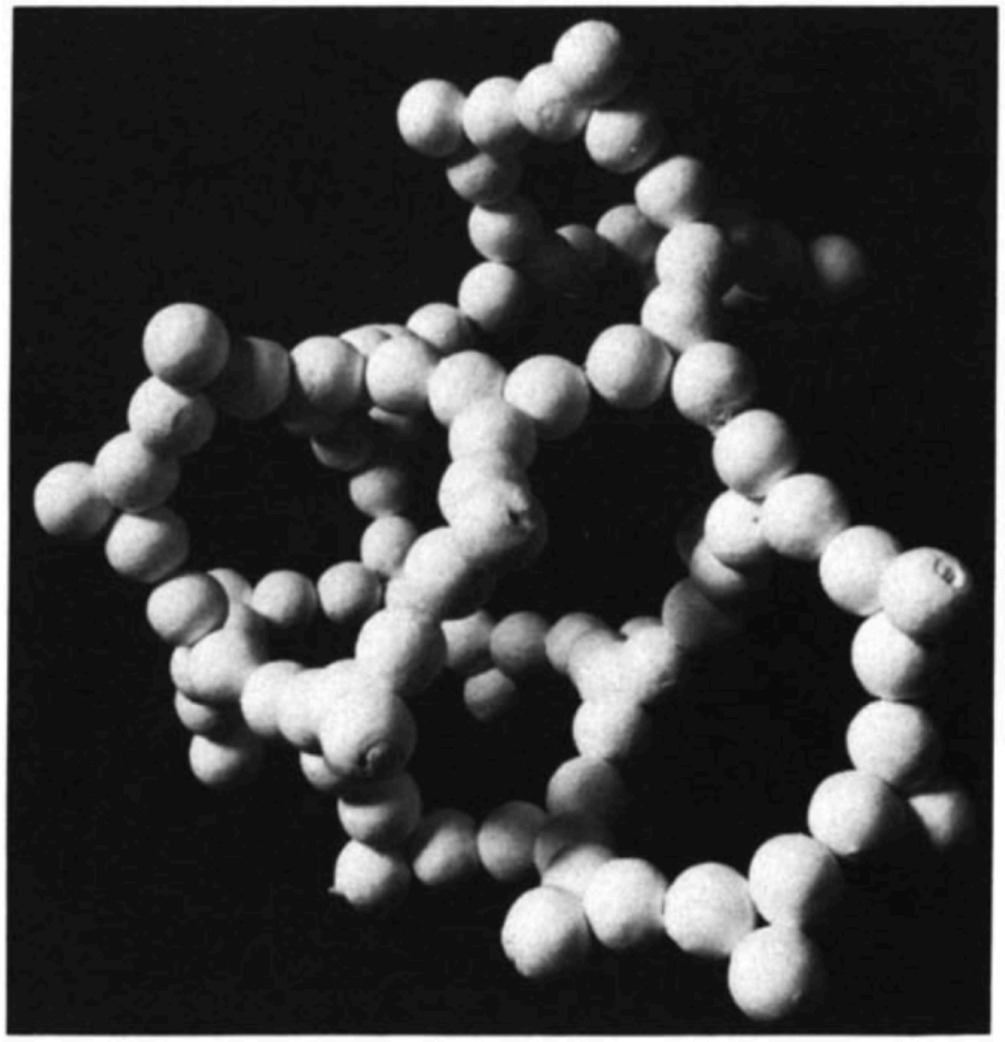


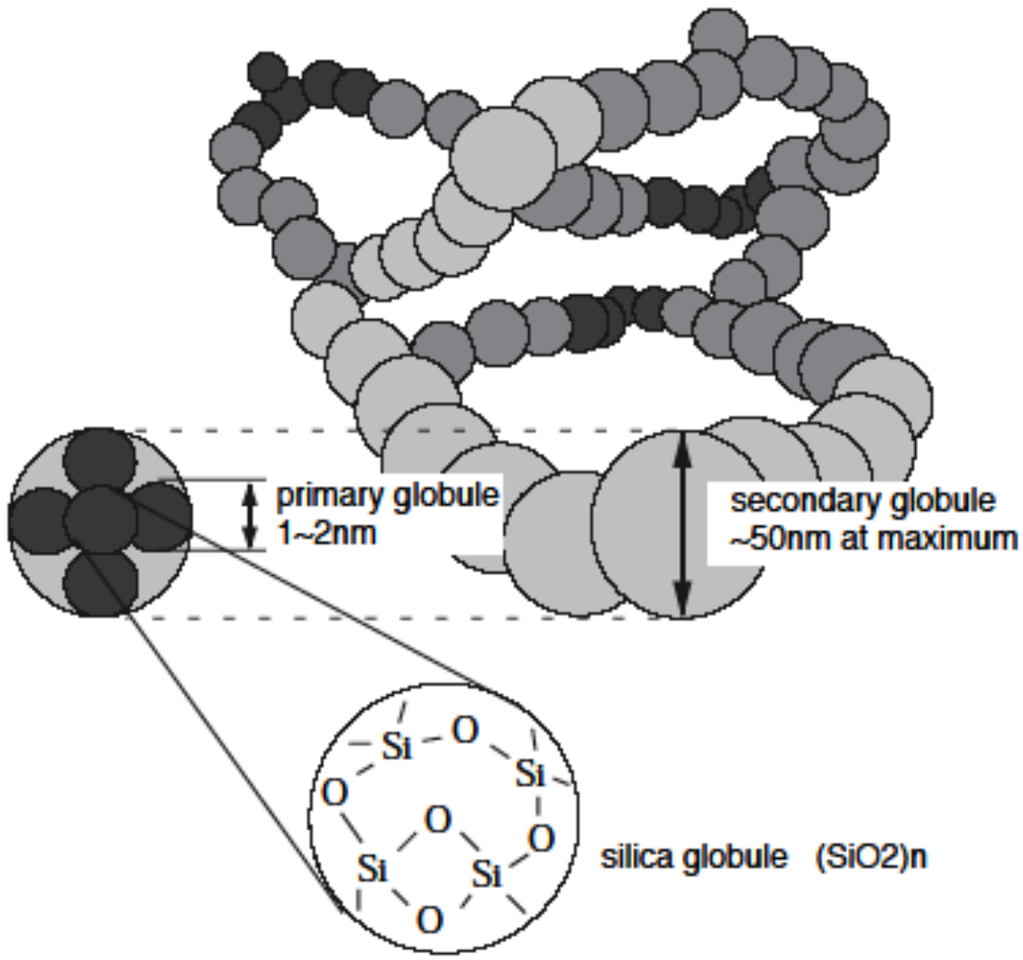
Two aerogel production facilities...
From the other point of view...



Silica Aerogel

- Highly porous material of silica clusters
  - 3 dimensional network of $(SiO_2)n$
  - Micro-structure smaller than the wavelength of visible light.
  - More than 90 % air inside volume





Production Process

- Two subsequent reactions for sol-gel polymerization

$$n\mathrm{Si(OR)_4} + 4n\mathrm{H_2O} \longrightarrow n\mathrm{Si(OH)_4} + 4n\mathrm{ROH} \qquad \textbf{Hydrolysis}$$

$$n\mathrm{Si(OH)_4} \longrightarrow \underline{(\mathrm{SiO_2})_n} + 2n\mathrm{H_2O} \qquad \textbf{Condensation}$$

Alco-gel

- **Hydrophobic treatment**
  - **Introduced in 1990's at KEK**

- Aging
  - Stabilize 3D network of SiO_2 clusters

- Supercritical drying (SCD) to convert from alco-gel to aerogel.
  - Critical point
    - CO_2 : T=31℃ & P=7.4MPa
    - Methanol : T=240℃ & P=8.1MPa

Optical Quality

- Refractive Index
  - Density (in other words)
  - **Fraction of silica clusters defines material density.**
- Transparency
  - Transmission length
  - Clarity parameters
  - **Uniformity and dimensions of silica clusters are related to transparency.**
    - For high transparency, synthesis parameters (gelling time etc) should be optimized.

Refractive Index

- Unique refractive index
  - It is related to quantity of SiO_2 clusters.

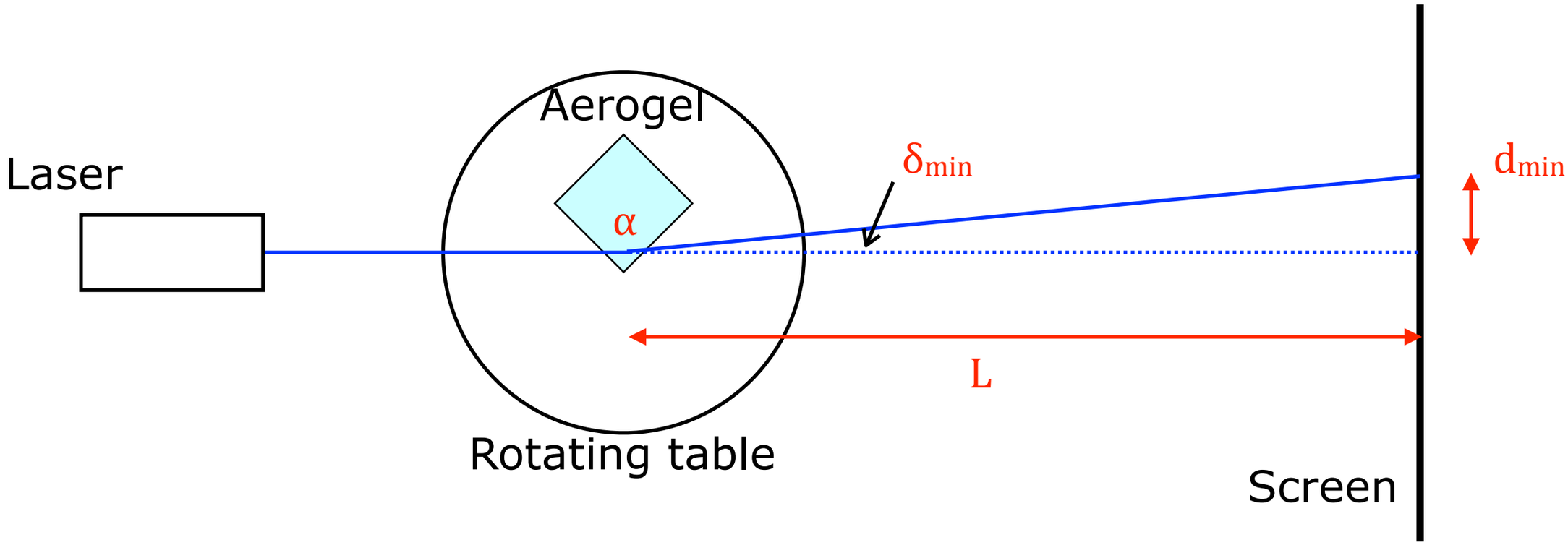
Cherenkov radiation

Threshold momentum P_{th} is related to refractive index (n) of radiator medium and incident particle mass (m) .

$$P_{th} = m / \sqrt{(n^2 - 1)}$$

Refractive Index Measurement

- Refractive index is calculated from a deflection angle in Fraunhofer method.



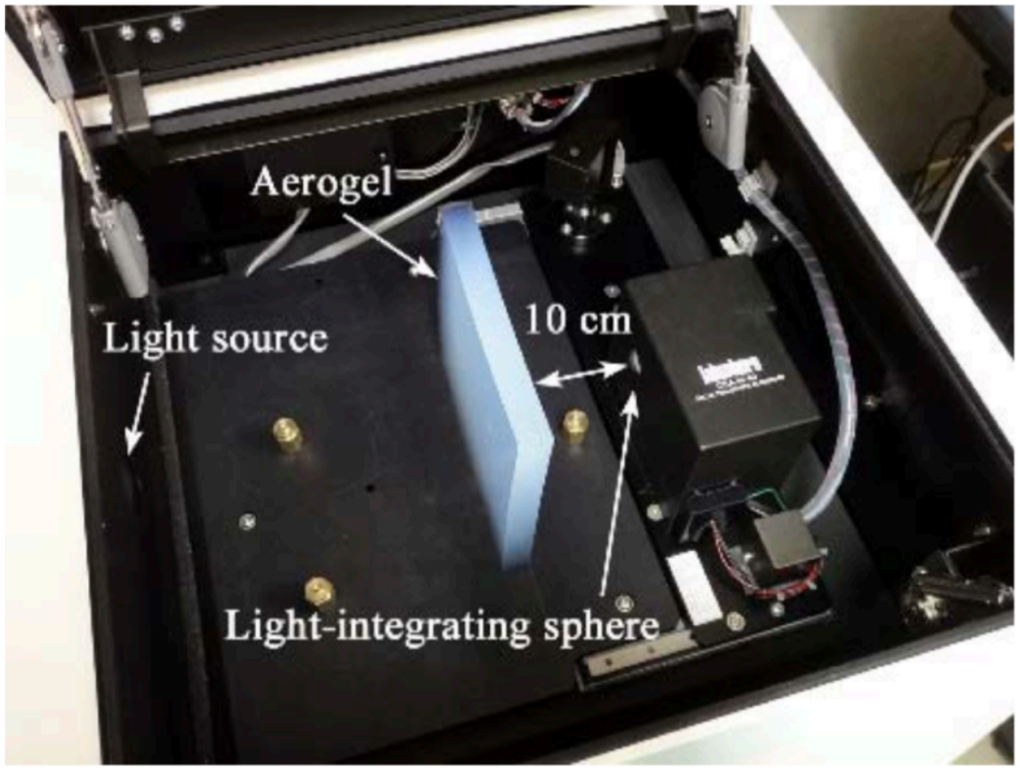
Prism formula

$$n = n_{air} \cdot \sin((\alpha+\delta_{min})/2)[1/\sin(\alpha/2)]$$

$$\delta_{min} = \tan^{-1}(d_{min}/L)$$

Transmittance

- Transmittance is measured using a spectrophotometer.
  - At KEK, aerogel tile is placed by 10 cm from a light-integrating sphere.



$T = T_0 \exp(-d/\Lambda)$

T_0: initial intensity
d : thickness
Λ : transmittance length

$\Lambda(\lambda) = -d/\ln(T/T_0)$

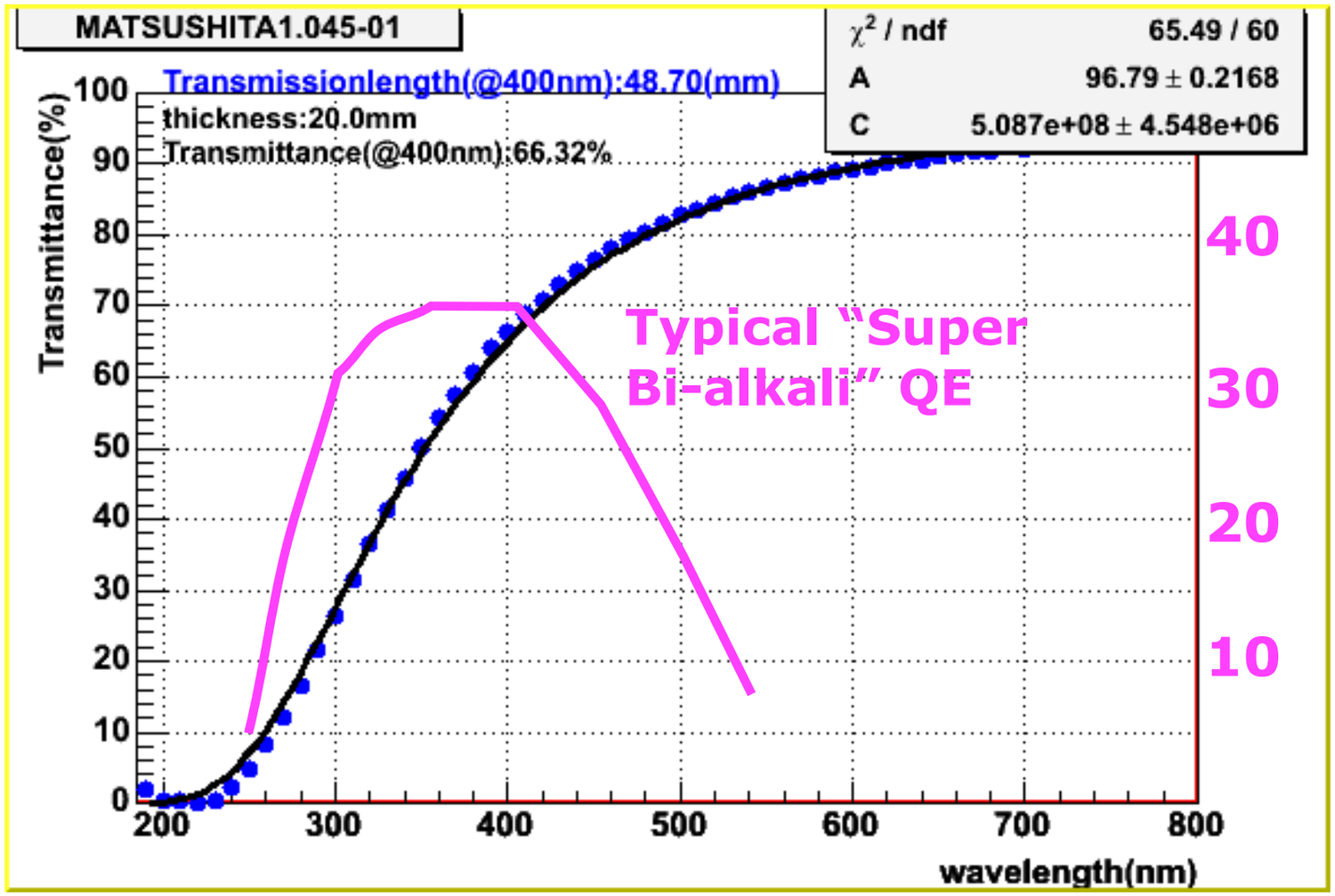
$\Lambda(\lambda=400nm)$ often used to characterize aerogel transparency

Λ depends on the position, where aerogel tile is placed in the spectrophotometer.

Clarity parameters also used.
$T = A \exp(-C \cdot t/\lambda^4)$

Transmittance

- Transparent for visible light region
- **This makes photon detection more straightforward.**



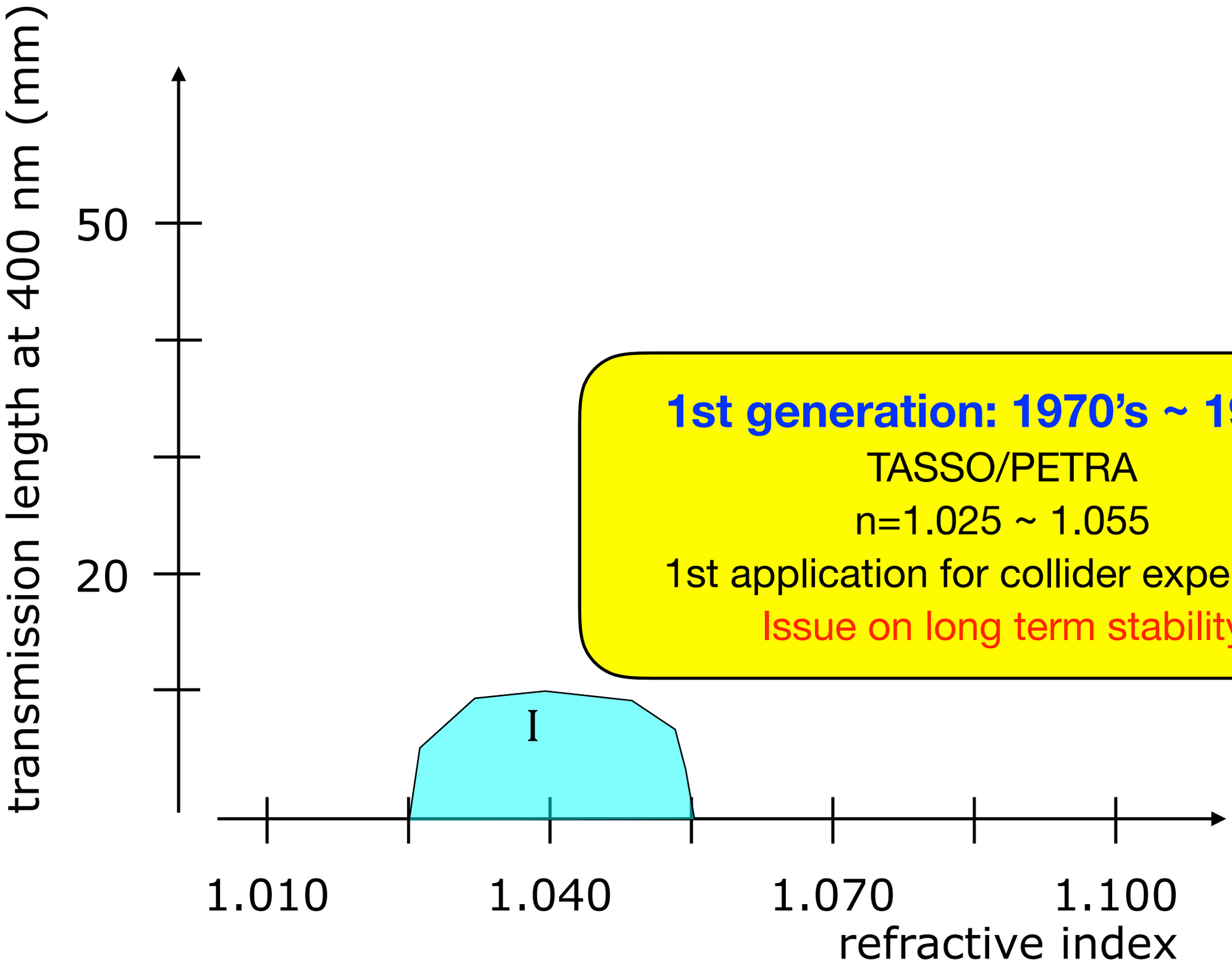
Aerogel Production Centers

- **Japan**
  - KEK/Chiba/Panasonic groups
    - Panasonic no longer deal with aerogel production.
    - Technological transfer to Japan Fine Ceramics Center (JFCC).
    - SCD is outsourced to Mohri oil company.
      - Facility with 70-liter dry volume
    - Chiba university has their own SCD facility.
      - Only academic center to handle aerogel production from synthesis steps to SCD.

- **Russia**
  - Budker INP and Boreskov institute of Catalysis.
  - Their own SCD facilities.
    - Please see a nice poster

History of Aerogel Radiator & Development of Cherenkov Counters

History of Aerogel Radiators



1st generation: 1970's ~ 1980's

TASSO/PETRA

n=1.025 ~ 1.055

1st application for collider experiment

Issue on long term stability

History of Aerogel Radiators

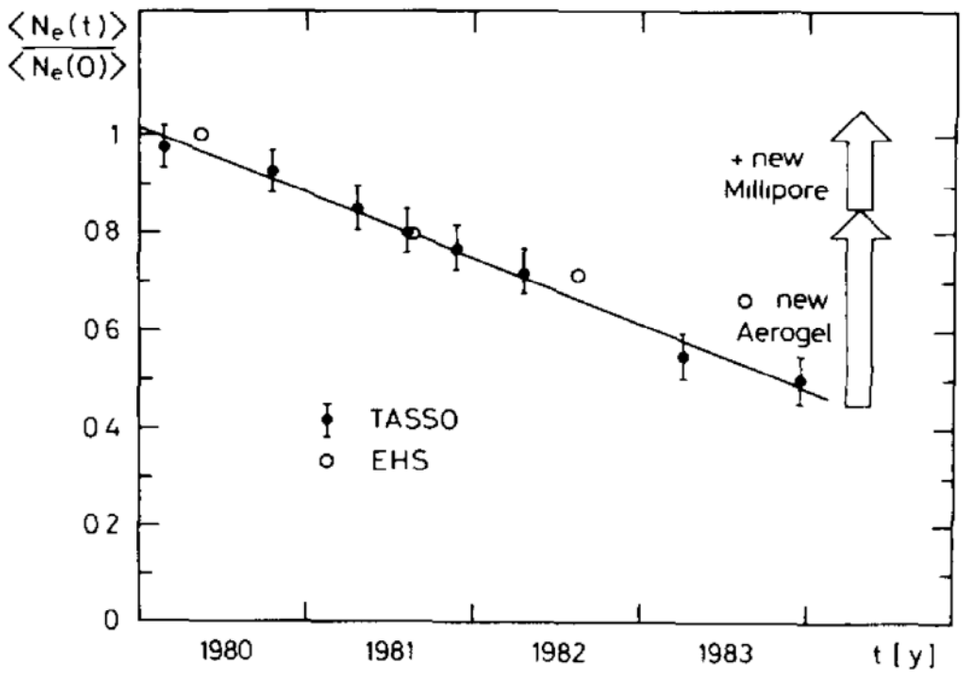


Fig. 24. Photoelectron yield of the TASSO aerogel counters for relativistic particles along the time of operation. The yield decreases with a slope of 0.5 yr^{-1}. The arrows show the improvement obtained when new aerogel and new millipore was recently installed in one cell. The data from the EHS detector [16] indicate a similar decrease but suggest an exponential decay with a time constant of 7.5 yr.

NIMA248(1986)118

N_{pe} decreased by 0.5/yr

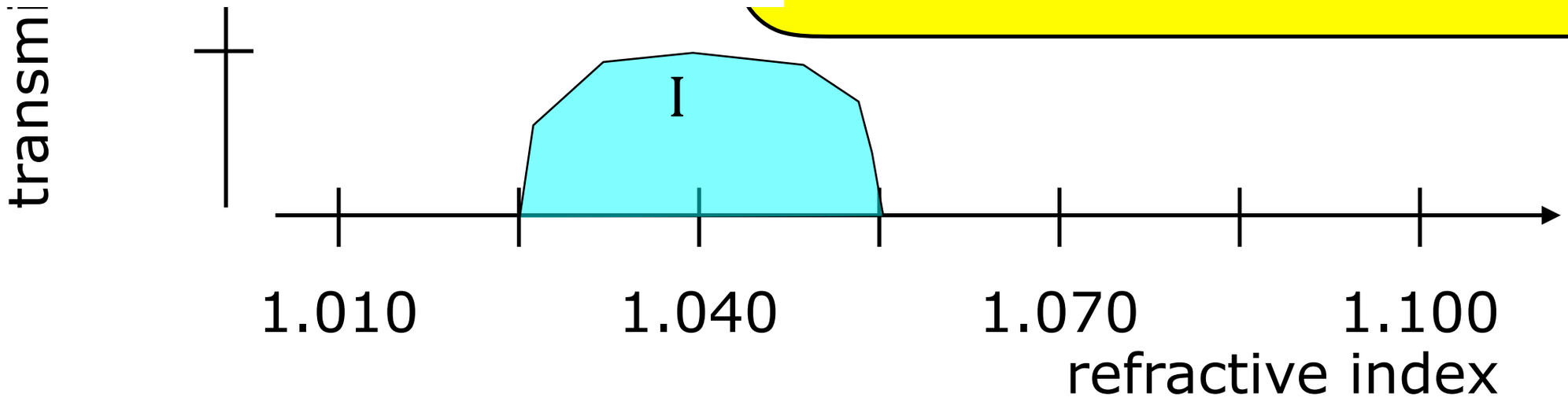
1st generation: 1970's ~ 1980's

TASSO/PETRA

n=1.025 ~ 1.055

1st application for collider experiment

Issue on long term stability



History of Aerogel Radiators

2nd generation: 1992 ~ 2002

Belle Aerogel threshold counter/KEKB

HERMES RICH/HERA

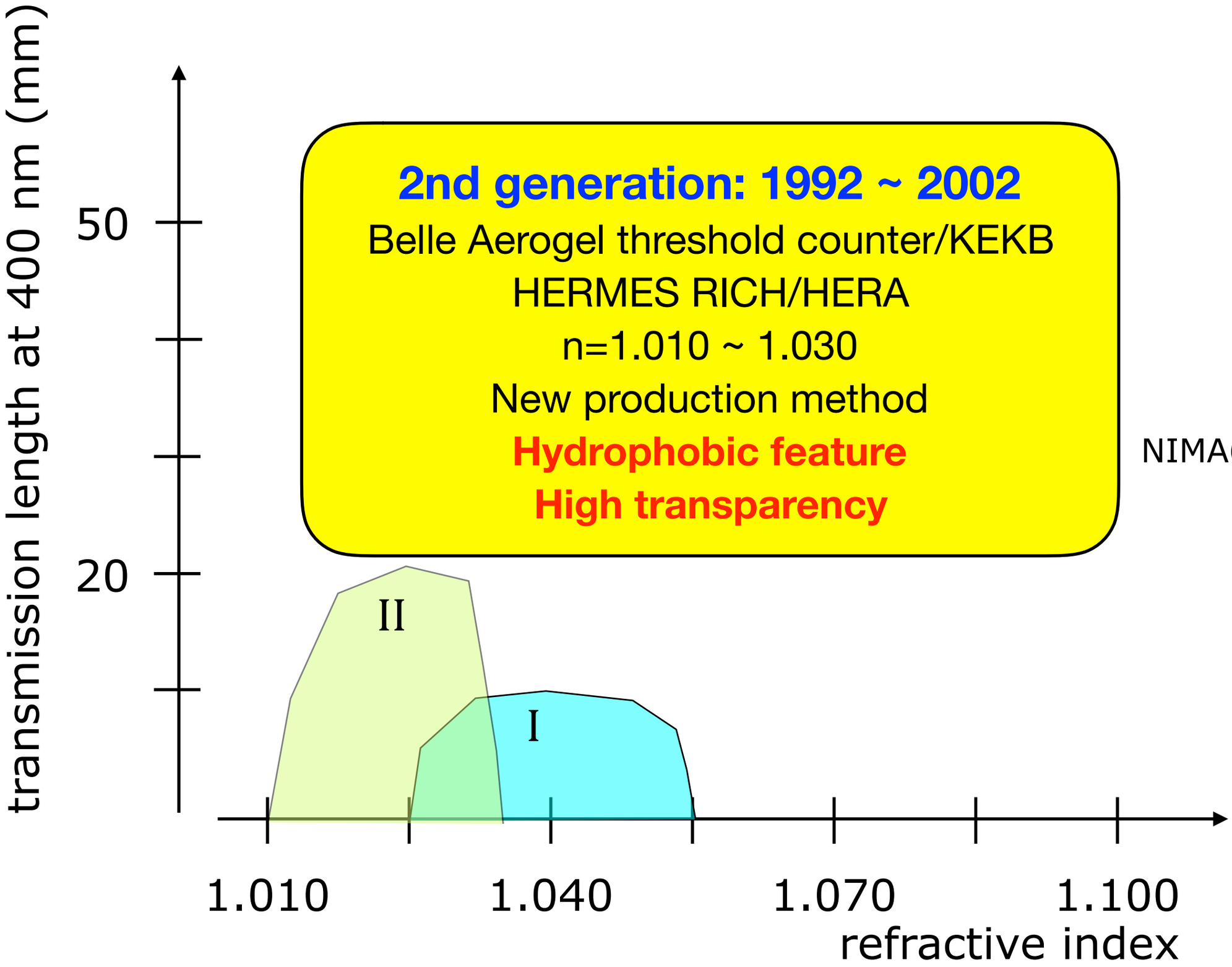
n=1.010 ~ 1.030

New production method

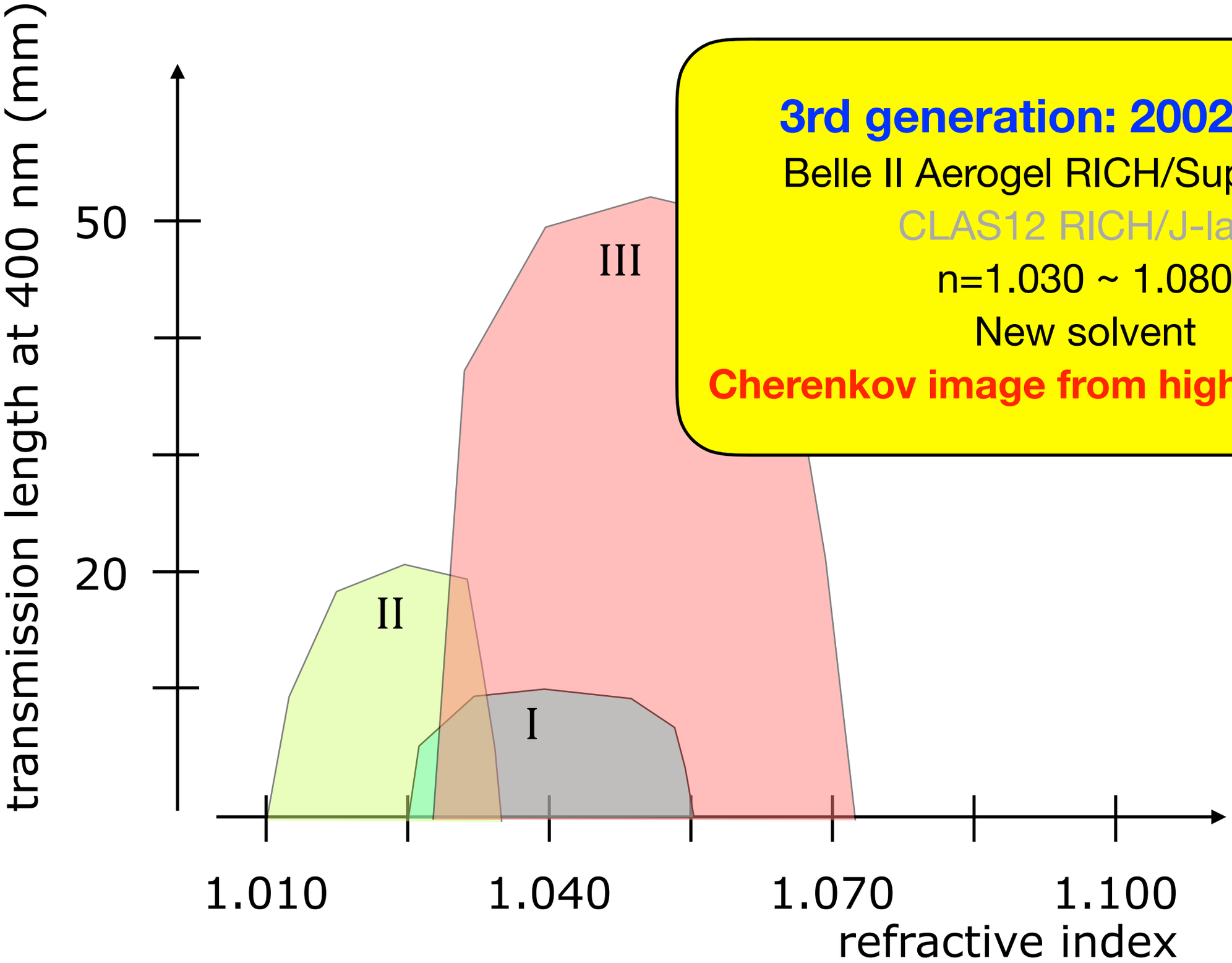
Hydrophobic feature

High transparency

NIMA668(2012)64



History of Aerogel Radiators



3rd generation: 2002 ~ 2014

Belle II Aerogel RICH/SuperKEKB

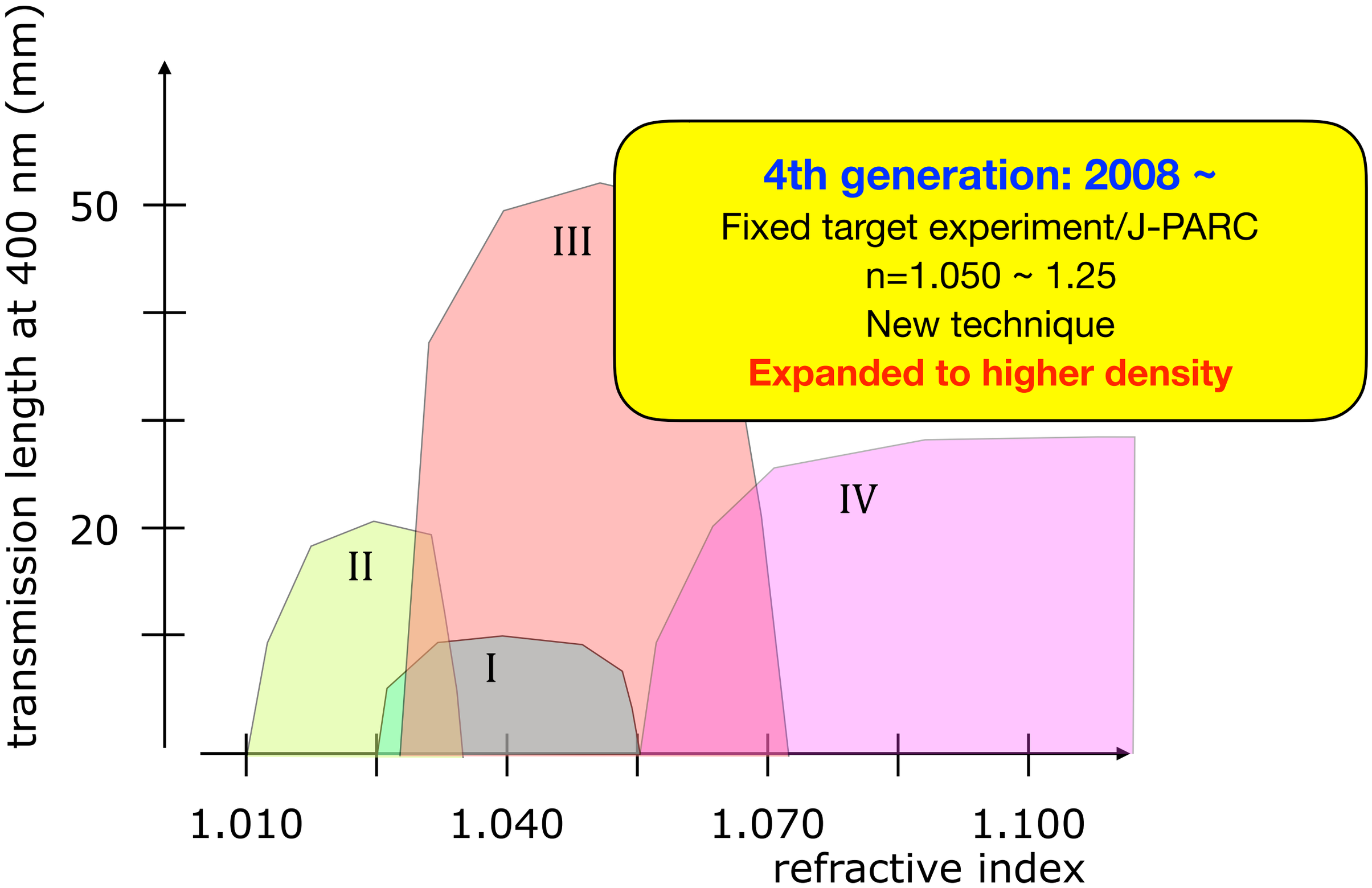
CLAS12 RICH/J-lab.

n=1.030 ~ 1.080

New solvent

Cherenkov image from high density gel

History of Aerogel Radiators



4th generation: 2008 ~

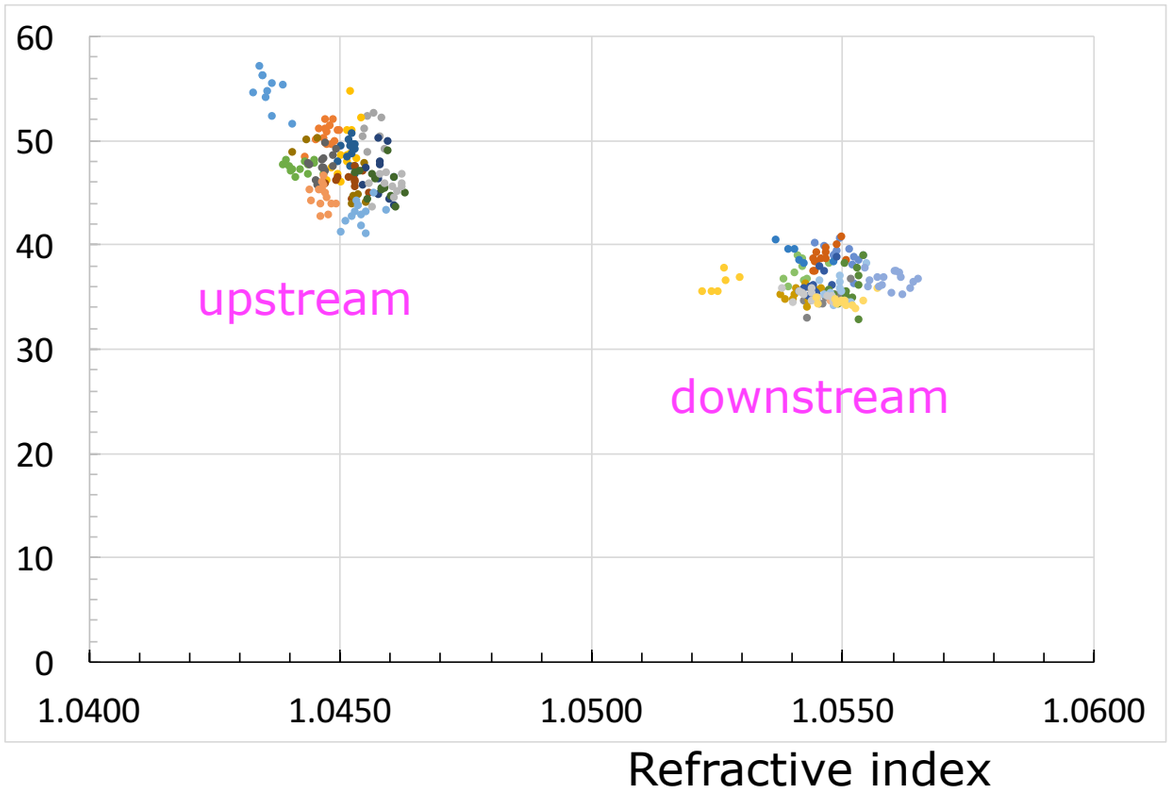
Fixed target experiment/J-PARC

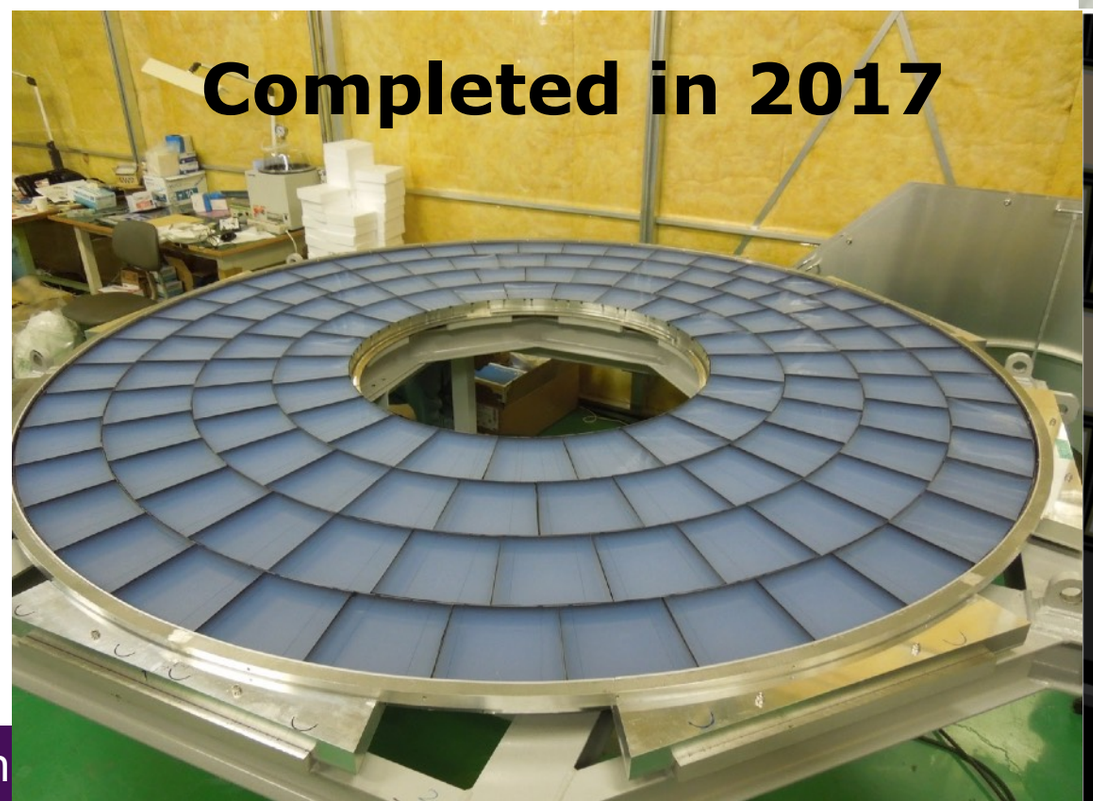
n=1.050 ~ 1.25

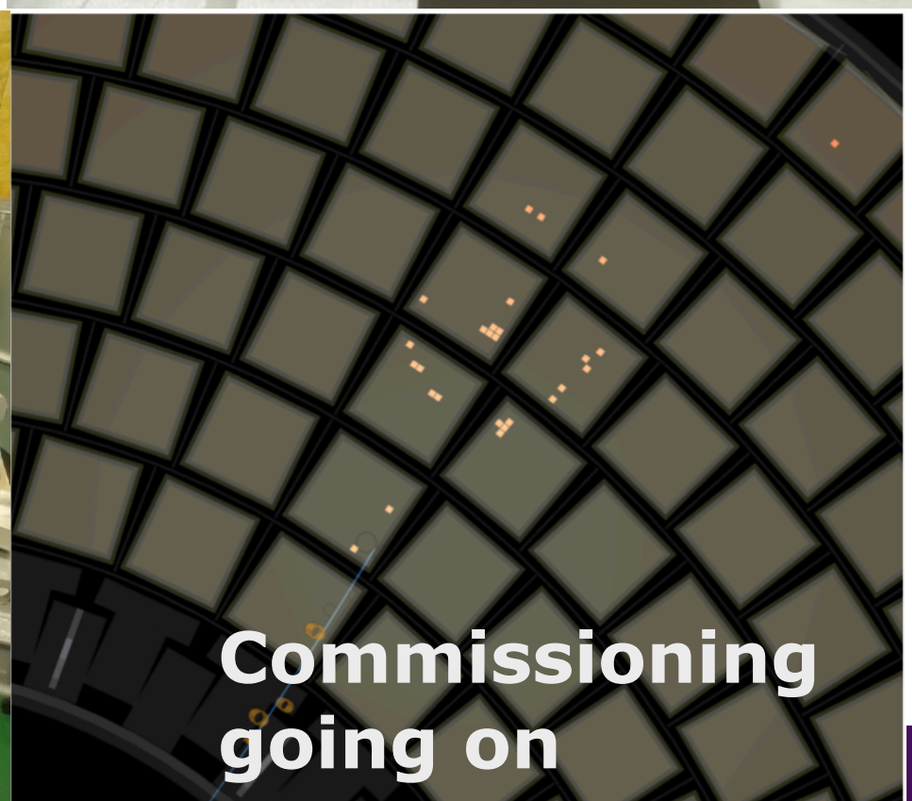
New technique

Expanded to higher density

Belle II RICH

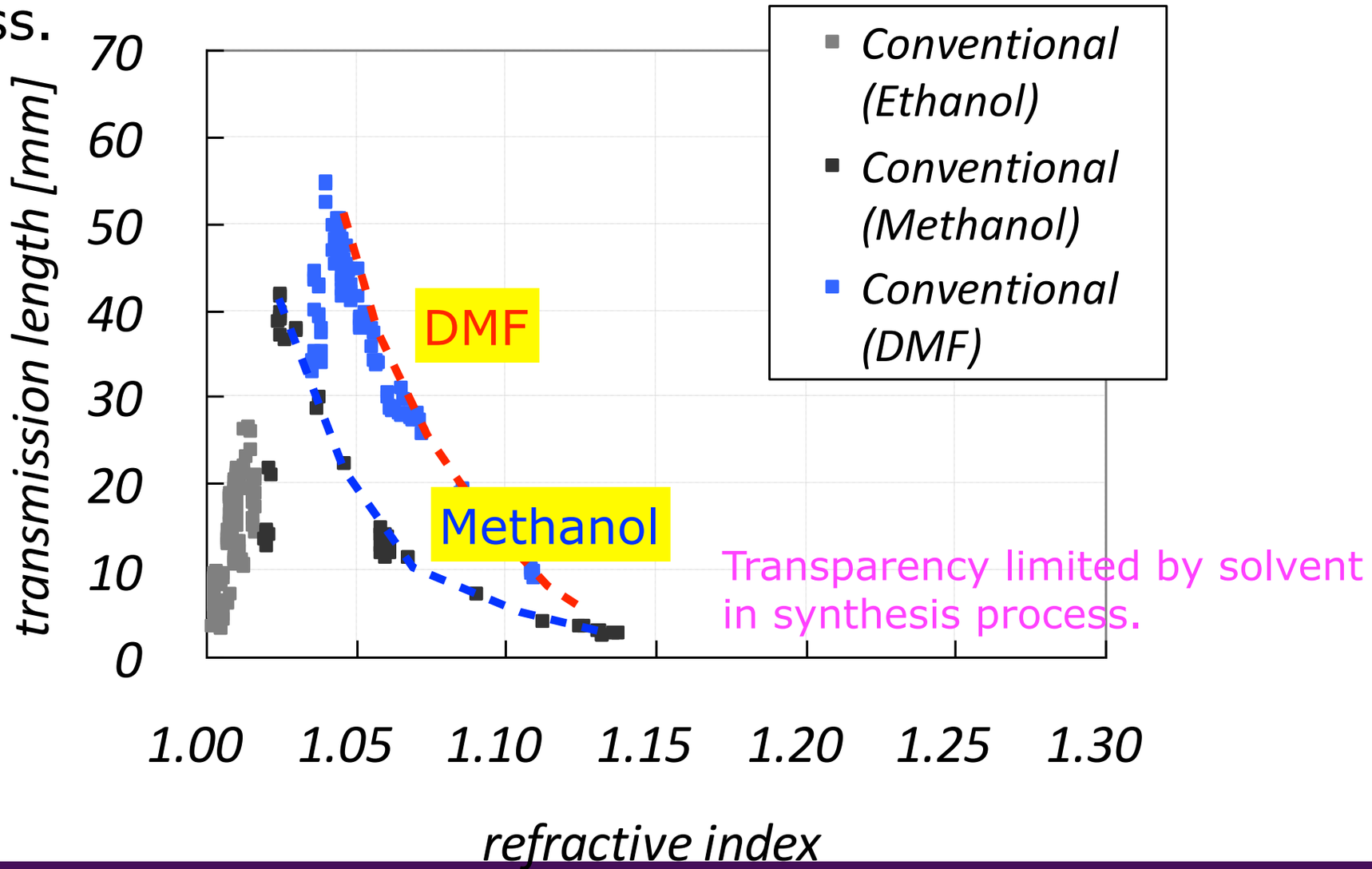






4th Generation

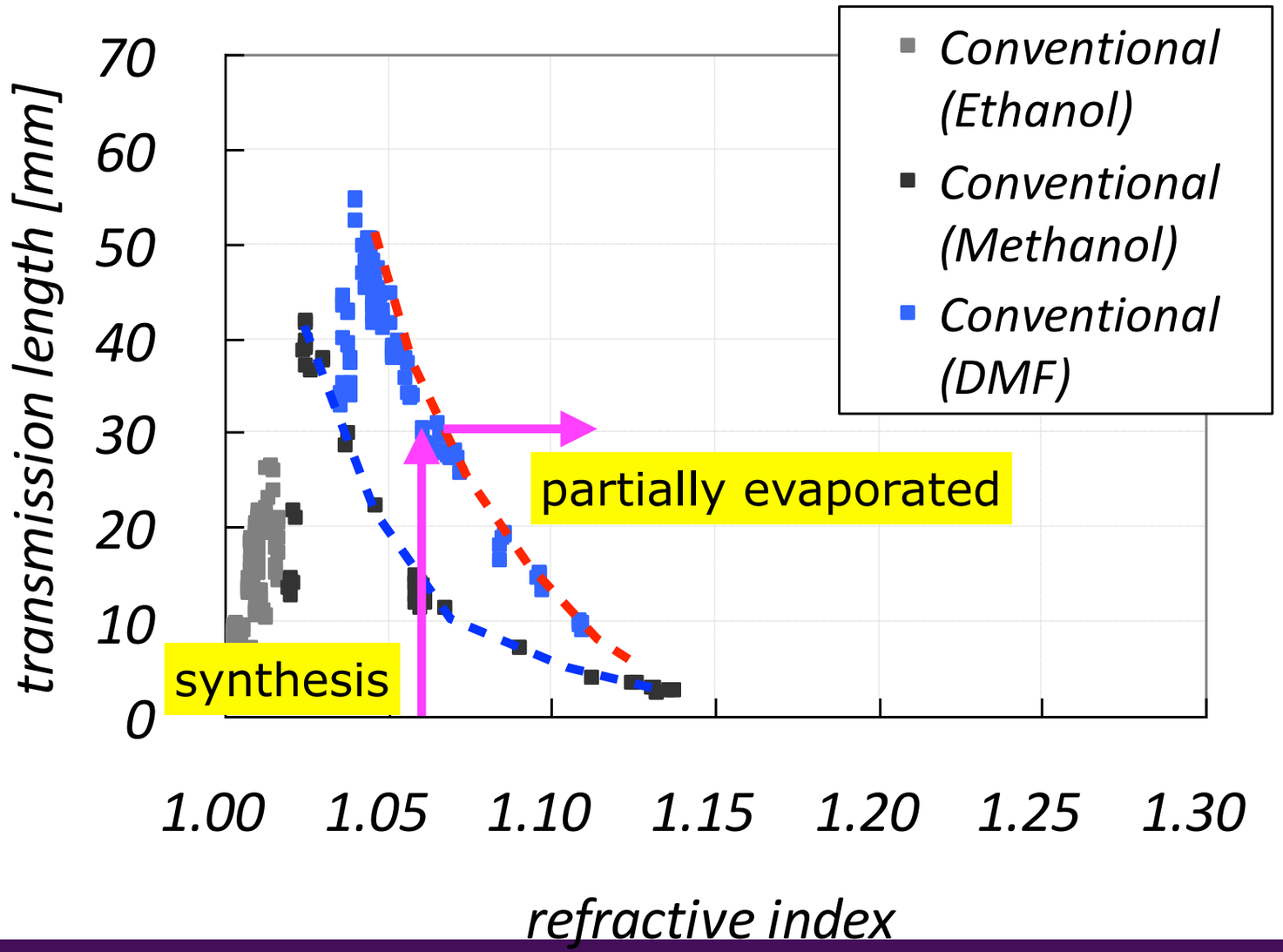
- High refractive index (>~1.14)
  - Transparency limited by solvent in synthesis step.
  - Difficult to produce alco-gels since too much silica particles can not undergo smooth gelation.
  - This results in non-transparent aerogel after supercritical drying process.



4th Generation

Synthesis process targeting n~1.06, then alco-gel obtained is partially evaporated in controlled environment to get target index(=density).

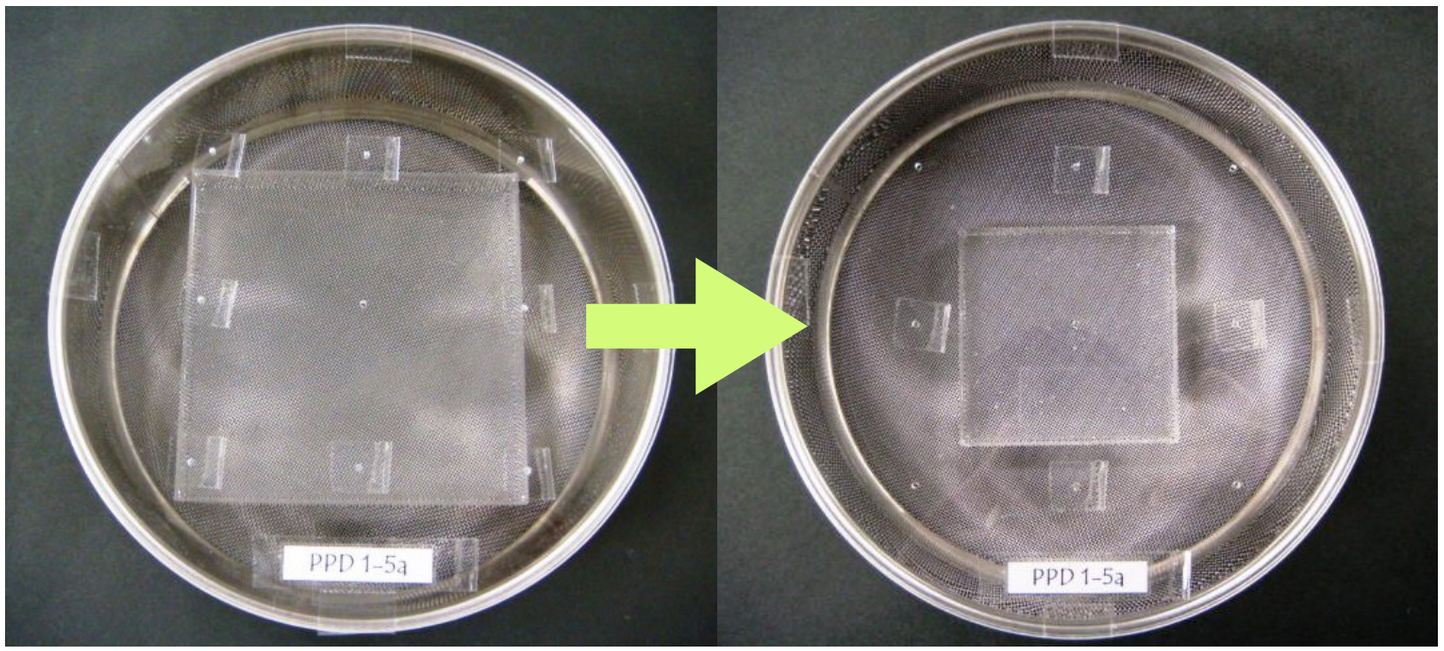
Pin-drying(PD) method by Chiba university group



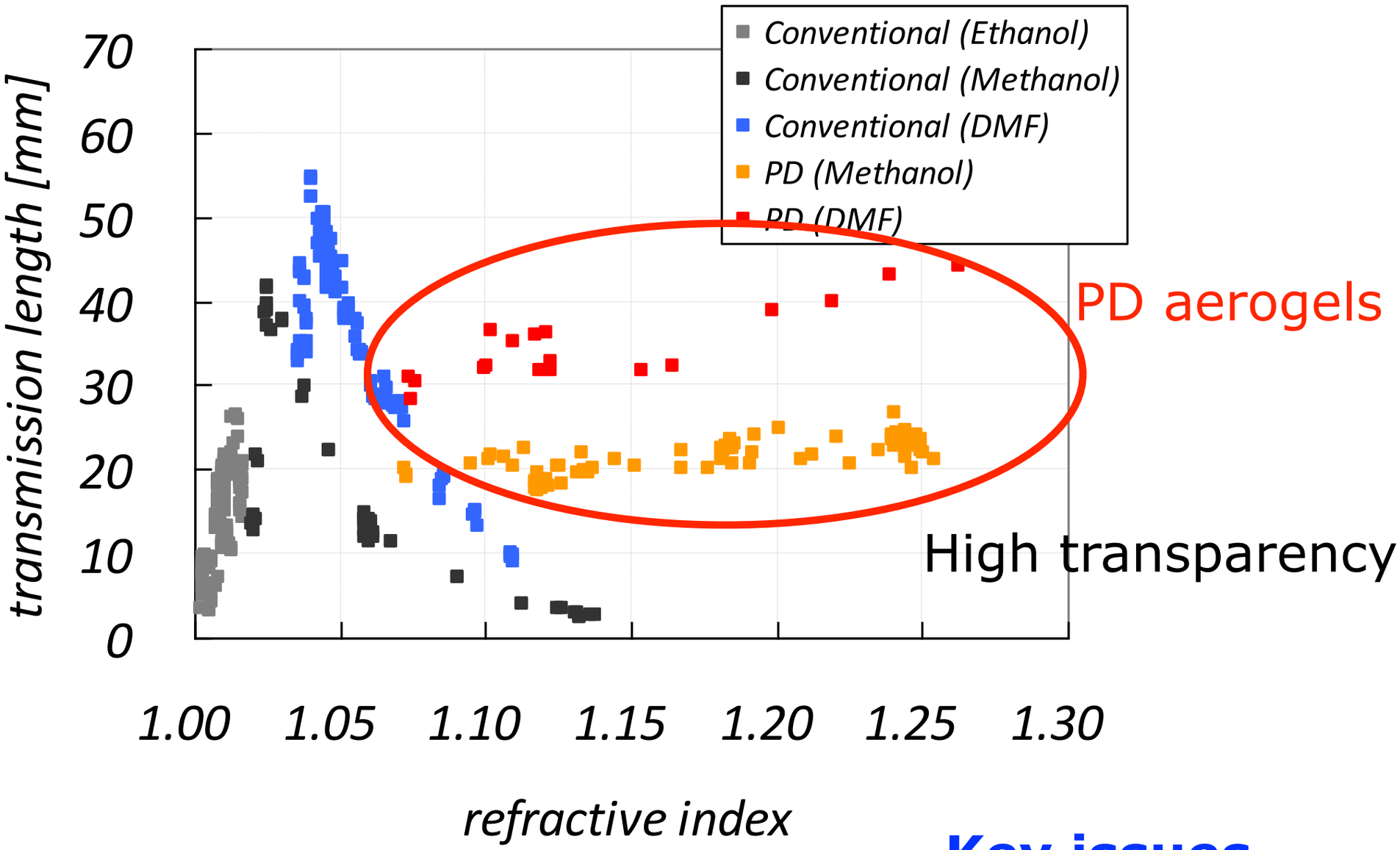
4th Generation

Synthesis process targeting n~1.06, then alco-gel obtained is partially evaporated in controlled environment to get target index(=density).

Pin-drying(PD) method by Chiba university group



4th Generation



High transparency obtained !

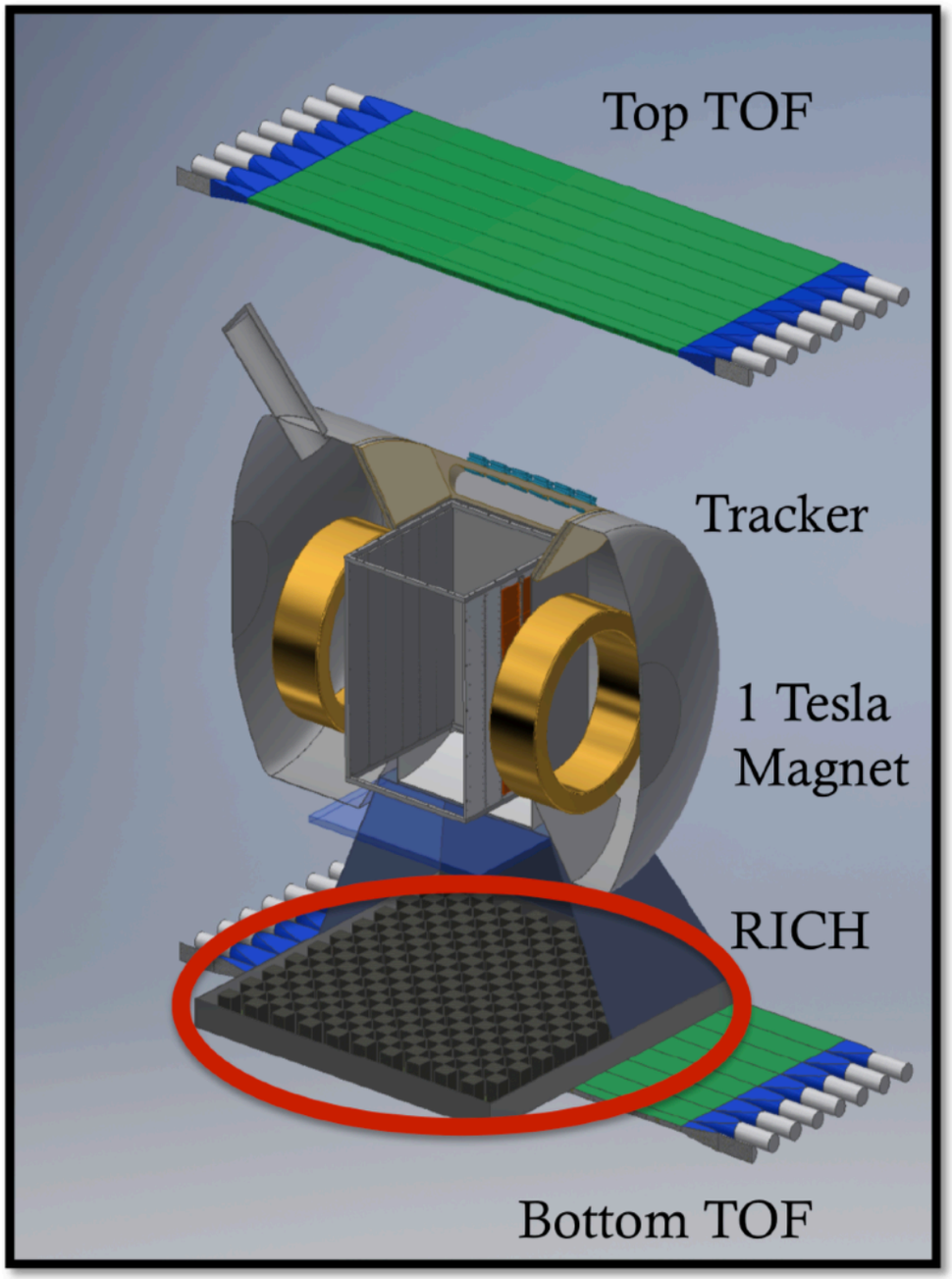
Key issues

Tile size and uniformity
Duration of production

Talk by M.Tabata

HELIX RICH

- HELIX is a magnet spectrometer for a balloon experiment around the south pole. Launch ~ 2019-2020.



Univ. Chicago …

The Ring-imaging Cherenkov Detector

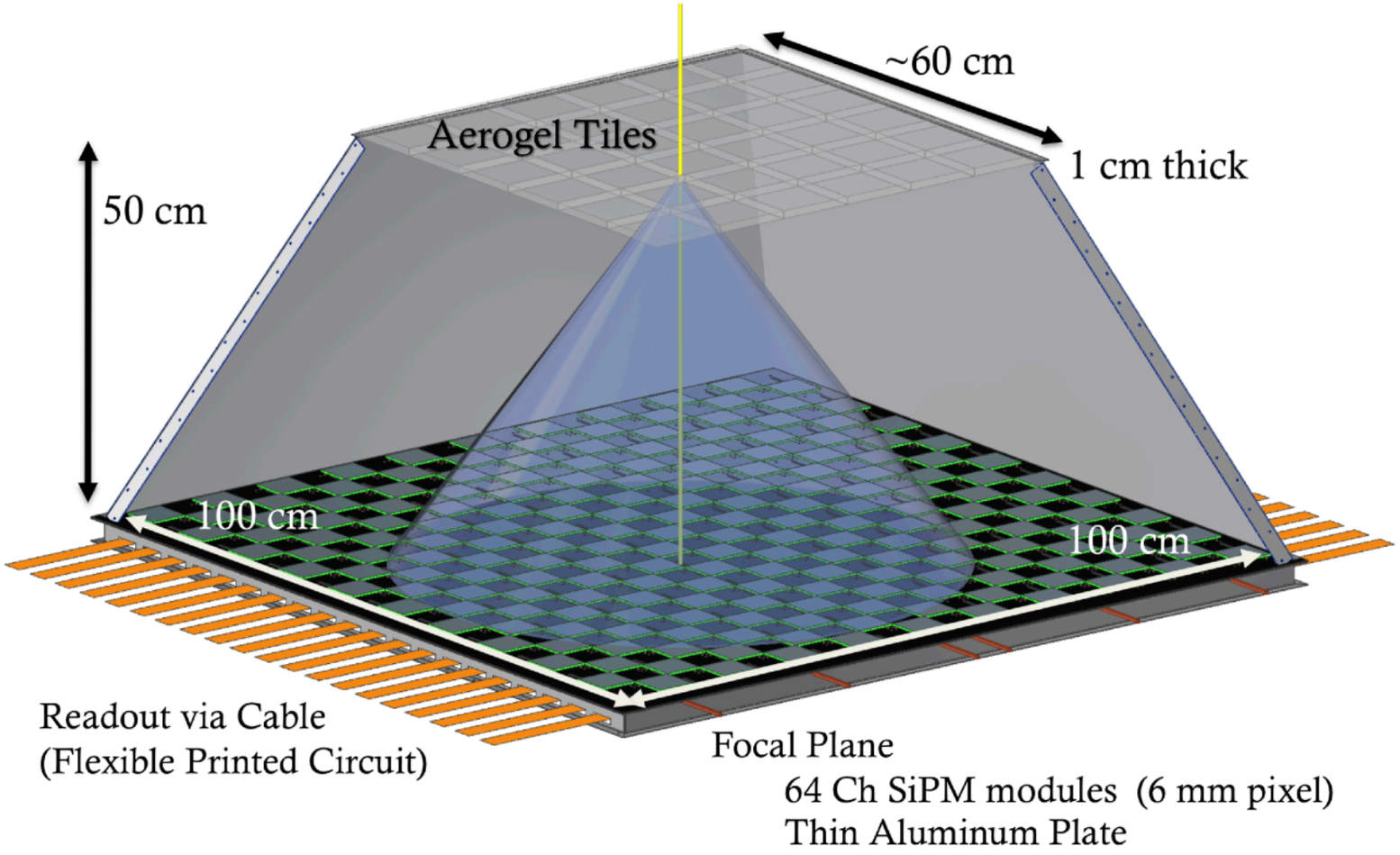
- Proximity-focused RICH w/ **SiPM** readout
- Design goal : **$\Delta\beta/\beta \sim 4\times10^{-4}$ for Z>3**
- Requires detector developments to reach goals

Presented at ICRC 2017

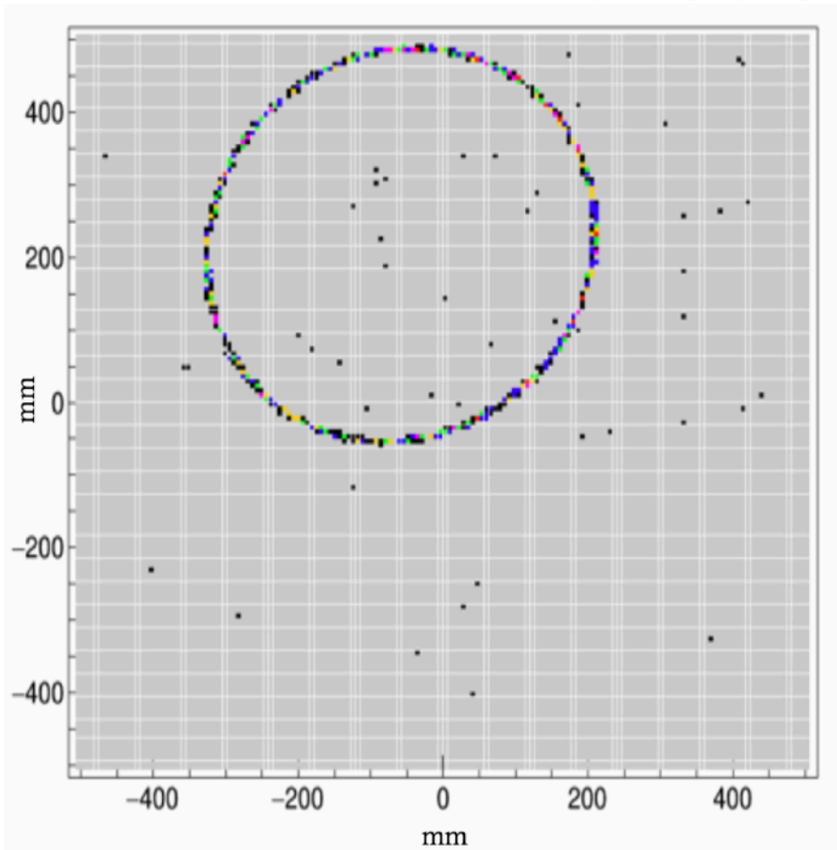
HELIX RICH

Cherenkov radiator system using 4th generation aerogel

- n=1.15 Aerogel from Chiba university group
- 36 tiles with 100×100×10mm^3
- Target transmission length at 400 nm > 30 mm

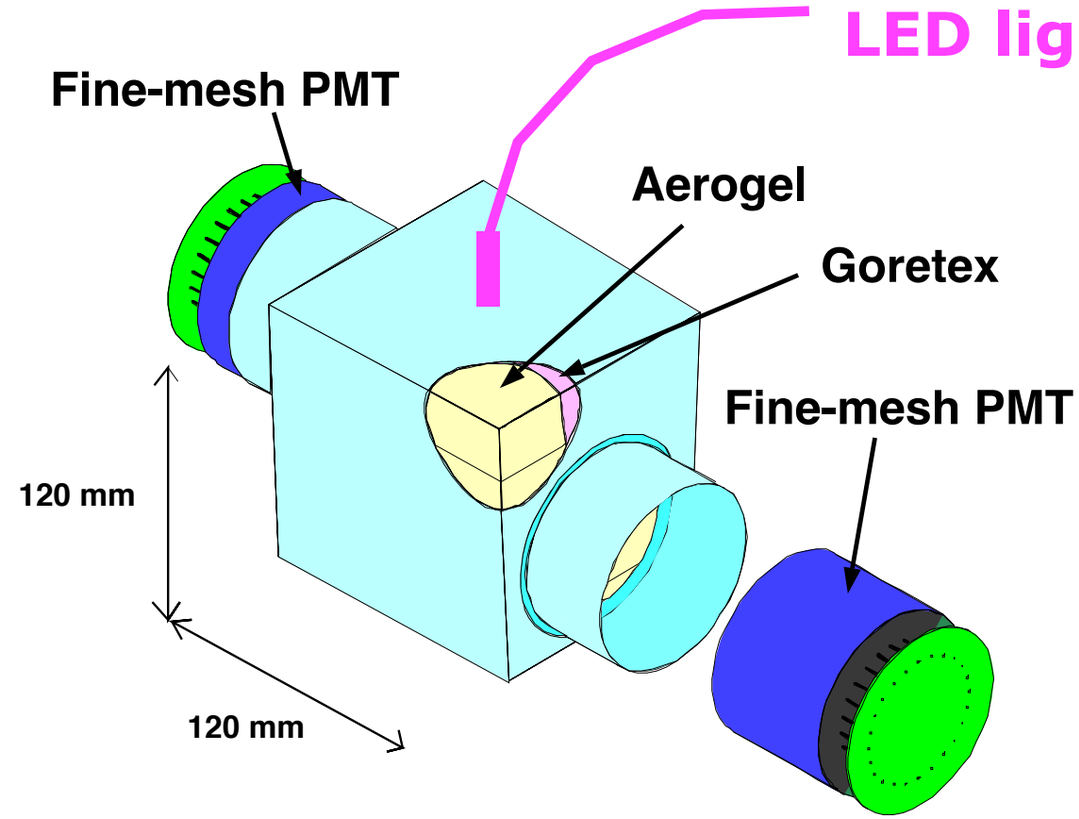


Simulation



Long-Term Stability

- In Belle aerogel Cherenkov counter we measured light output from PMTs for each counter by eliminating LED light.



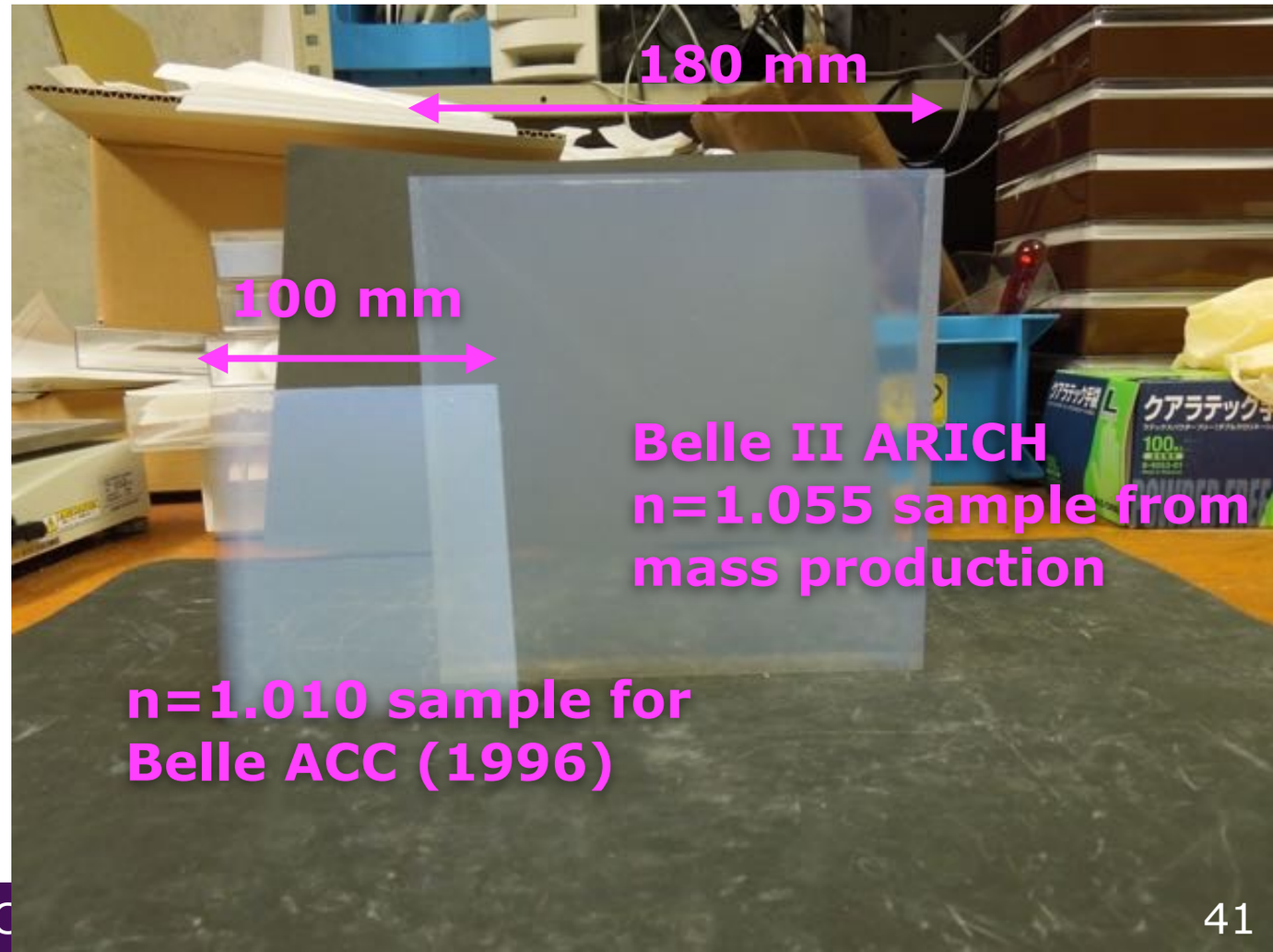
Aerogel tiles of n=1.01-1.03
They are hydrophobic

- Check long-term stability.

Tile Dimensions

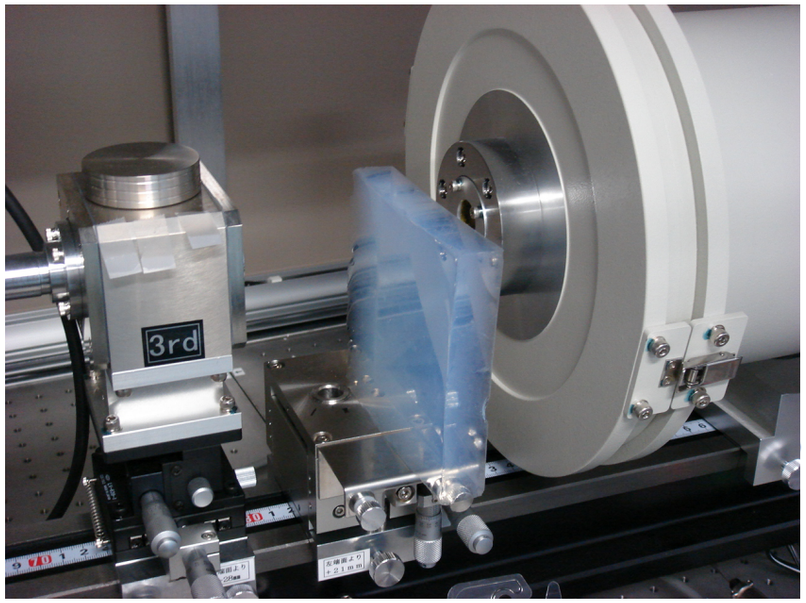
- If radiator medium needs to cover large area, basically big size tile reduces boundary region, where less Cherenkov photon yield is expected.
- Handling point of view, large tile needs more attention not only in production process but also in construction stage.
  - Crack-free yield/Tip-lost-at-corner yield/Related to thickness
  - Depends on tile index.
  - Optimizations in SCD step.
    - Pressure control

M.Tabata et al., The Journal of Supercritical Fluids, Vol.110, April 2016, Pages 183-192



Density Uniformity

- Uniformity scan was done using X-ray tomography device.



X-ray λ=0.156nm

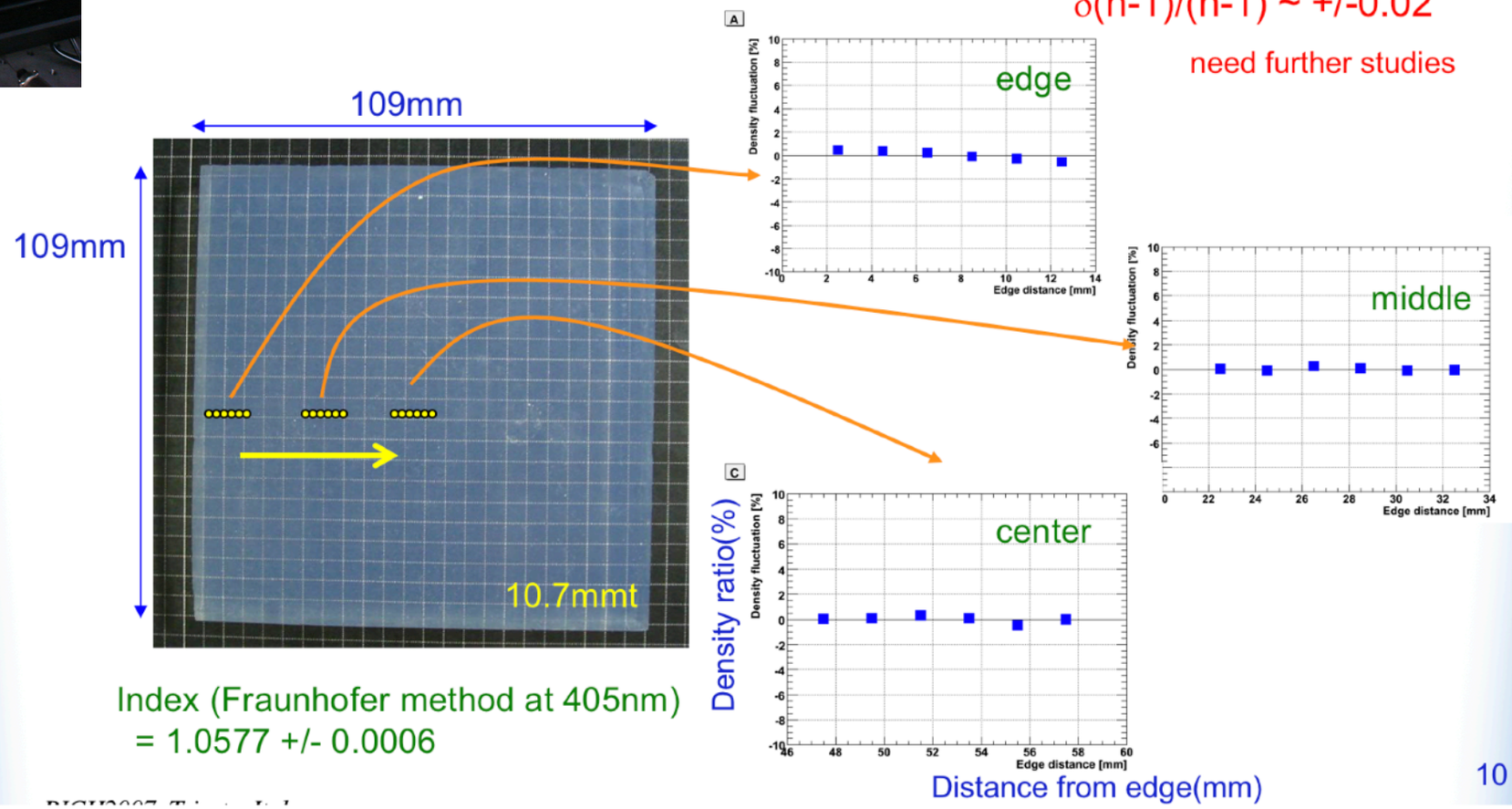
$\phi_{\text{beam spot}}$ < 1mm

density relative uniformity

preliminary value:

$\delta(n-1)/(n-1) \sim +/-0.02$

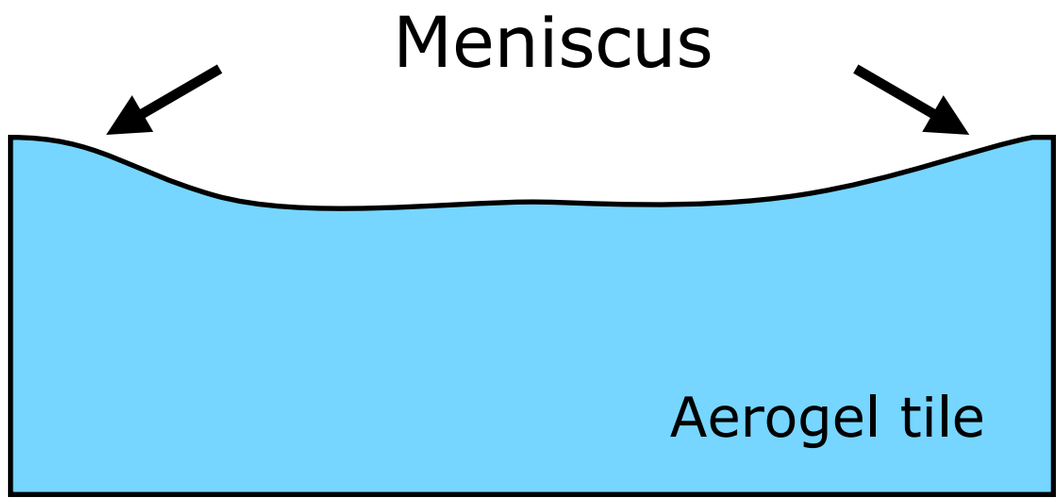
need further studies



Index (Fraunhofer method at 405nm)
= 1.0577 +/- 0.0006

Meniscus (1)

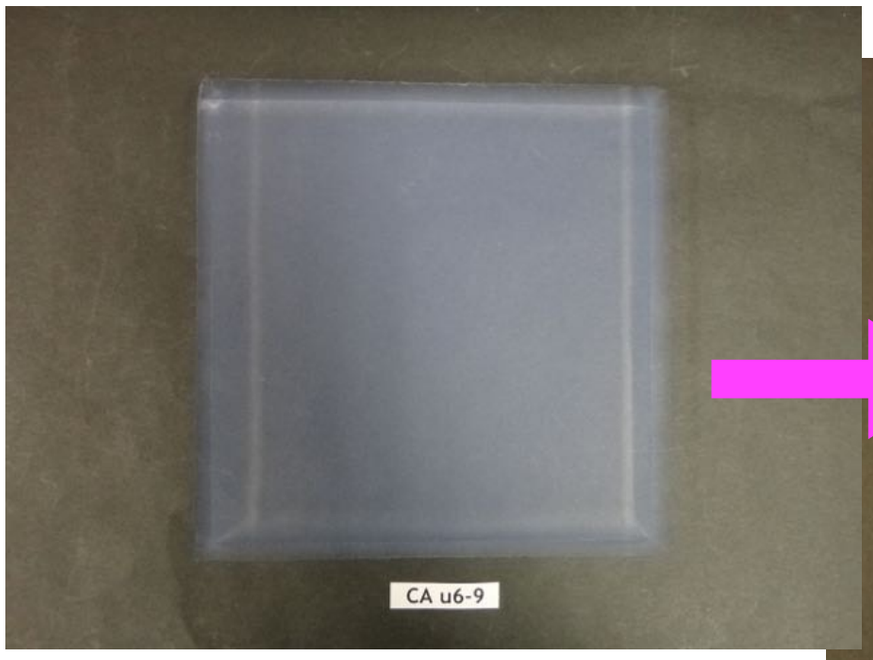
Aerogel tile has meniscus structure.
Meniscus structure partially related to production process.



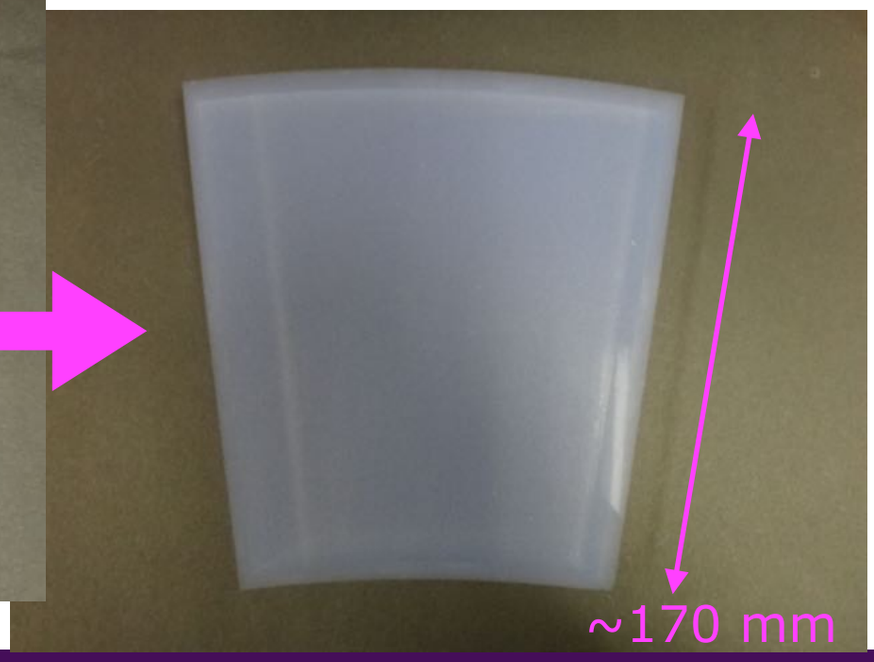
This could be a (*potential*) problem when Cherenkov radiator is organized by stacking # of aerogel tiles.

Meniscus (2)

- The best way is to remove tile edge regions, where there is meniscus.
- Hydrophobic feature allows us to use a water-jet machine without deteriorating optical transparency.
- In case of hydrophilic tiles, diamond cutter can be used for machining (like CLAS12 aerogels from BINP).



Belle II case

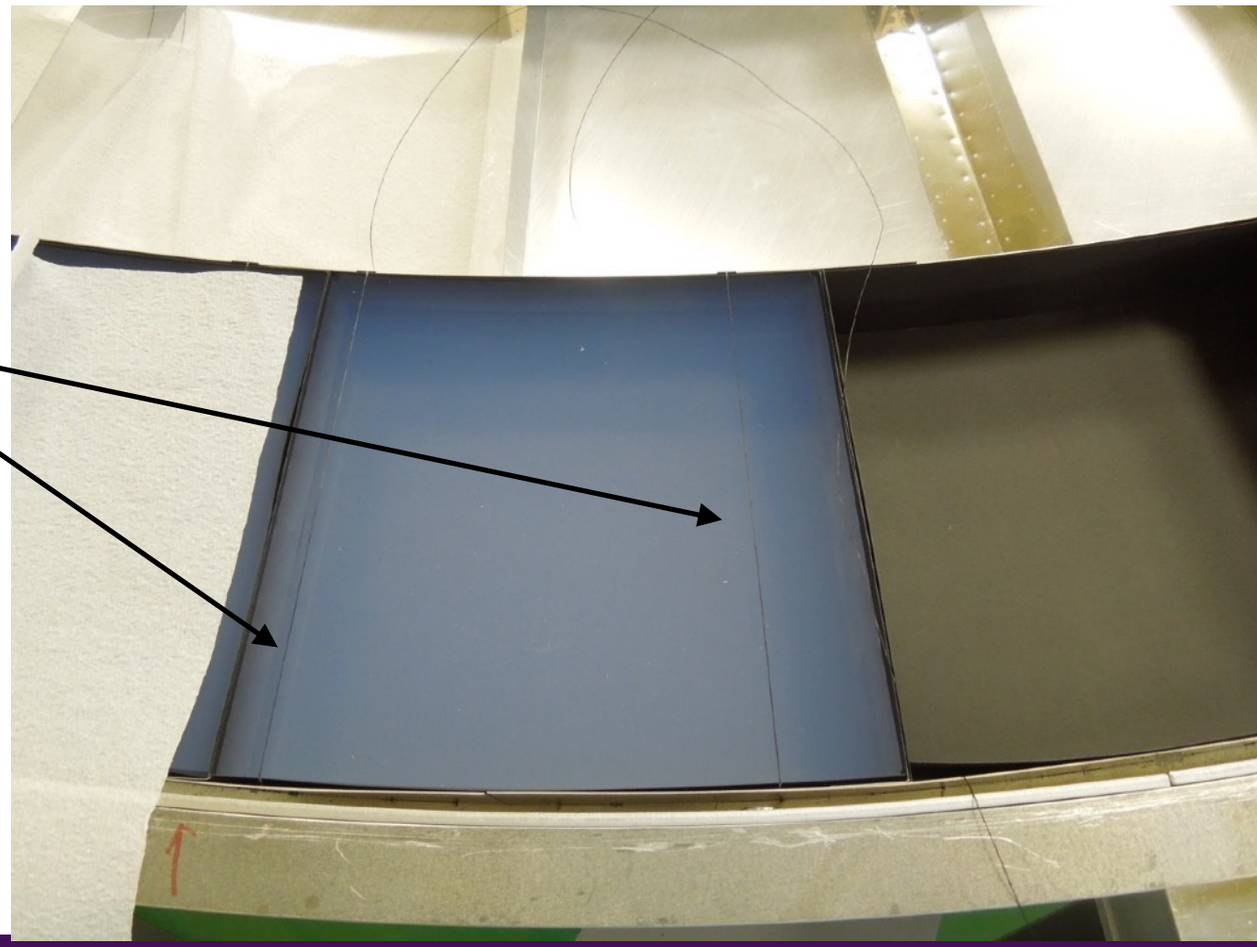


Housing

- To construct aerogel radiator system, each tile has to be fixed into the detector container.

- Aerogel is fragile and the way to fix tiles is rather limited.
  - Metal screws can not be used.
  - Wrapping transparent film and glue
  - Directly glue
    - One can not replace tiles.
  - Strings

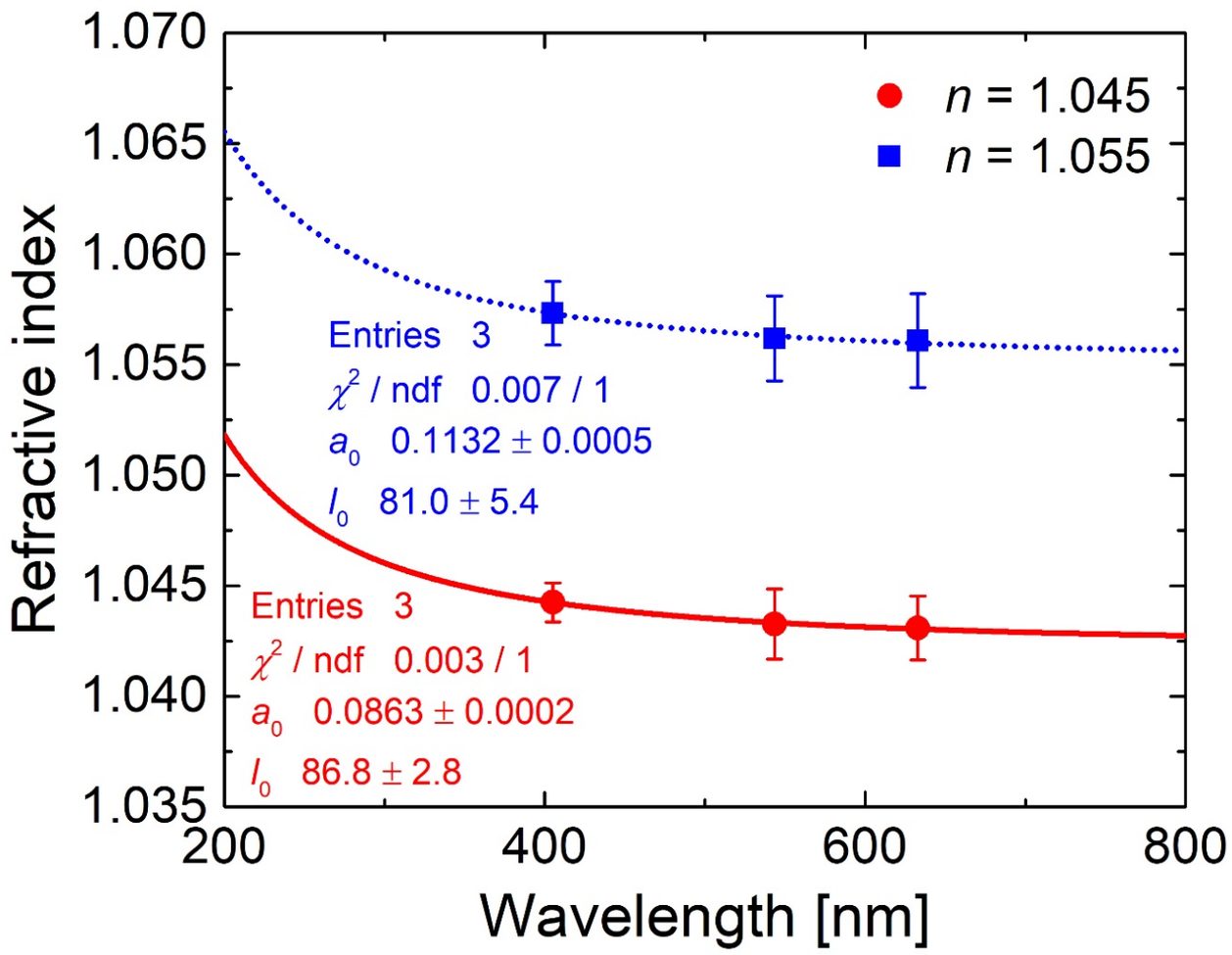
Belle II case
Glass fiber



It is not a problem, but (potential) worry…

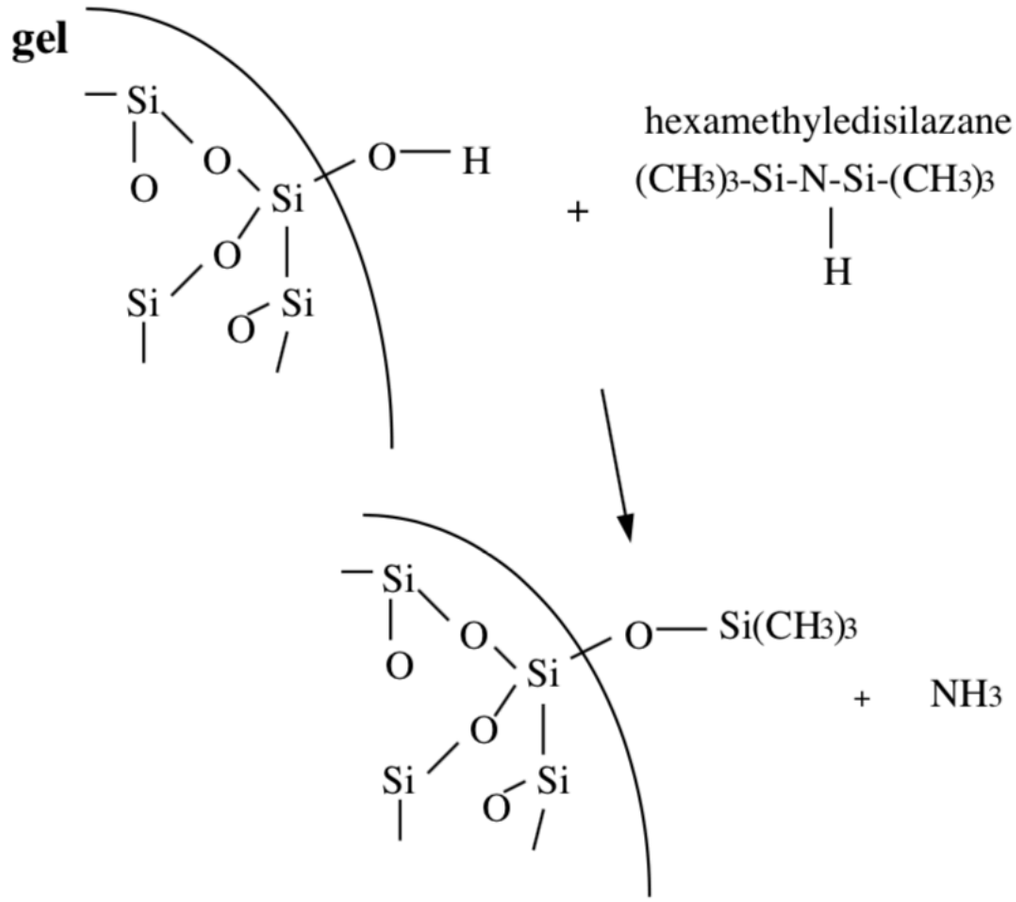
Chromaticity Dispersion

- Refractive index measured with lasers having different wave-length.
- Fitted with Sellmeier equation : $n^2 - 1 = a_0\lambda^2/(\lambda^2 - \lambda_0^2)$



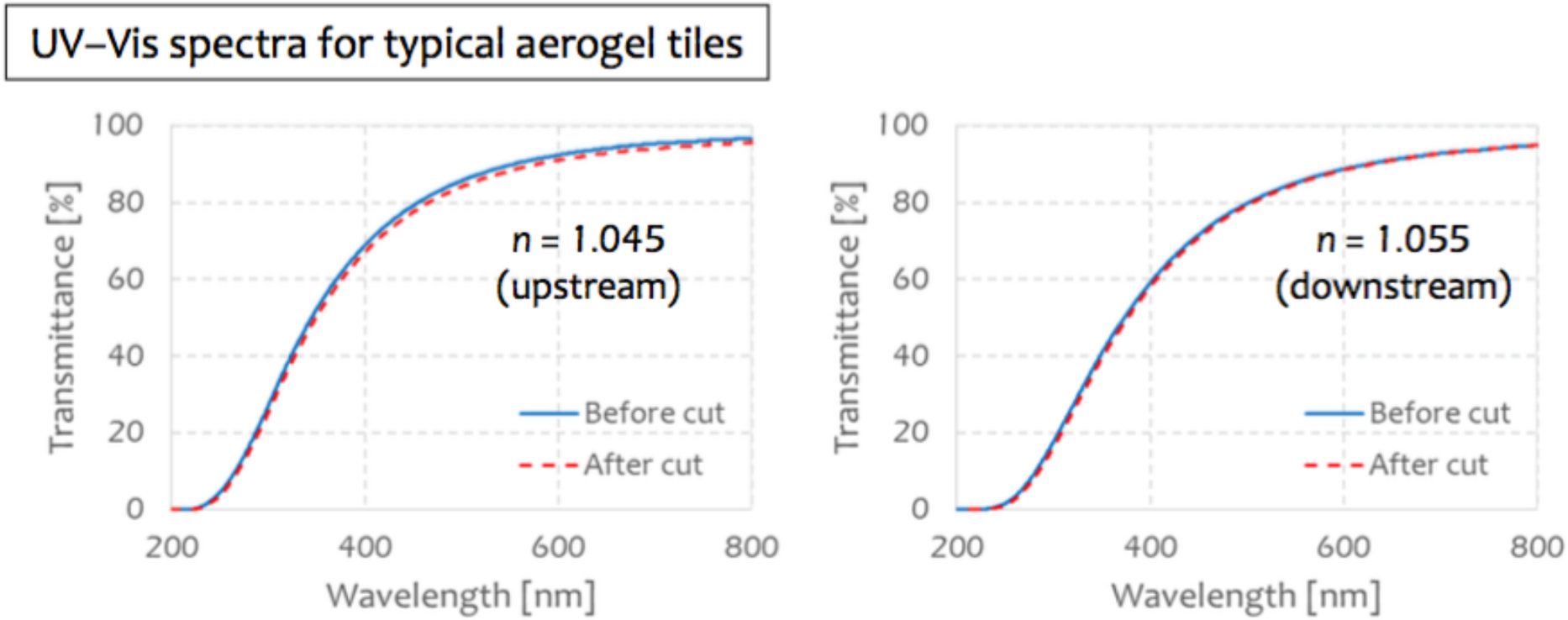
Hydrophobic Treatment

- -OH group in alco-gel is replaced into -O-Si$(CH_3)_3$
  - -OH group is likely to be charged and reacts with water.

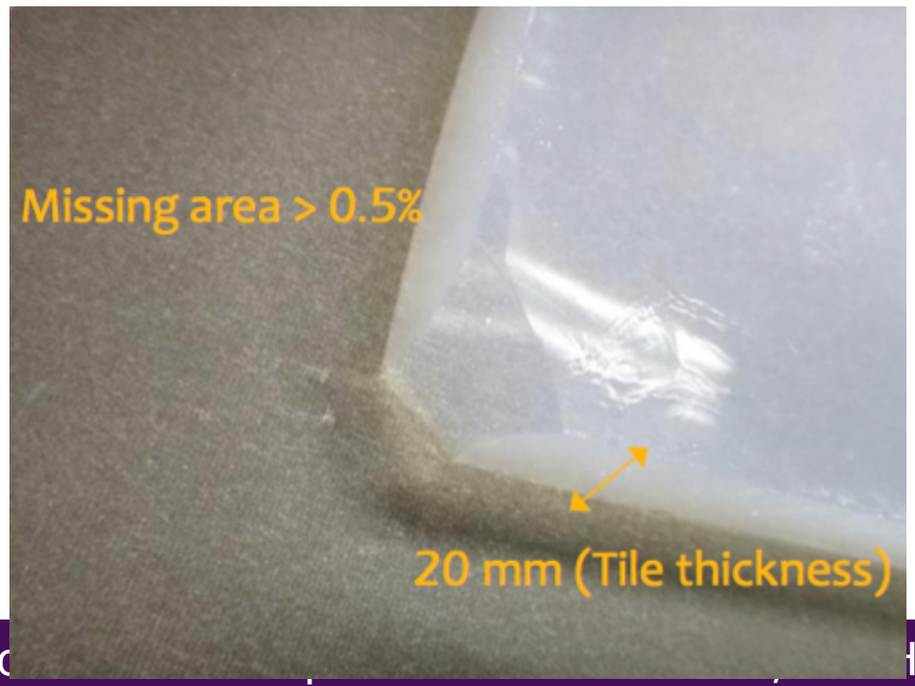


Tile Machining

No degradations in transparency due to this machining



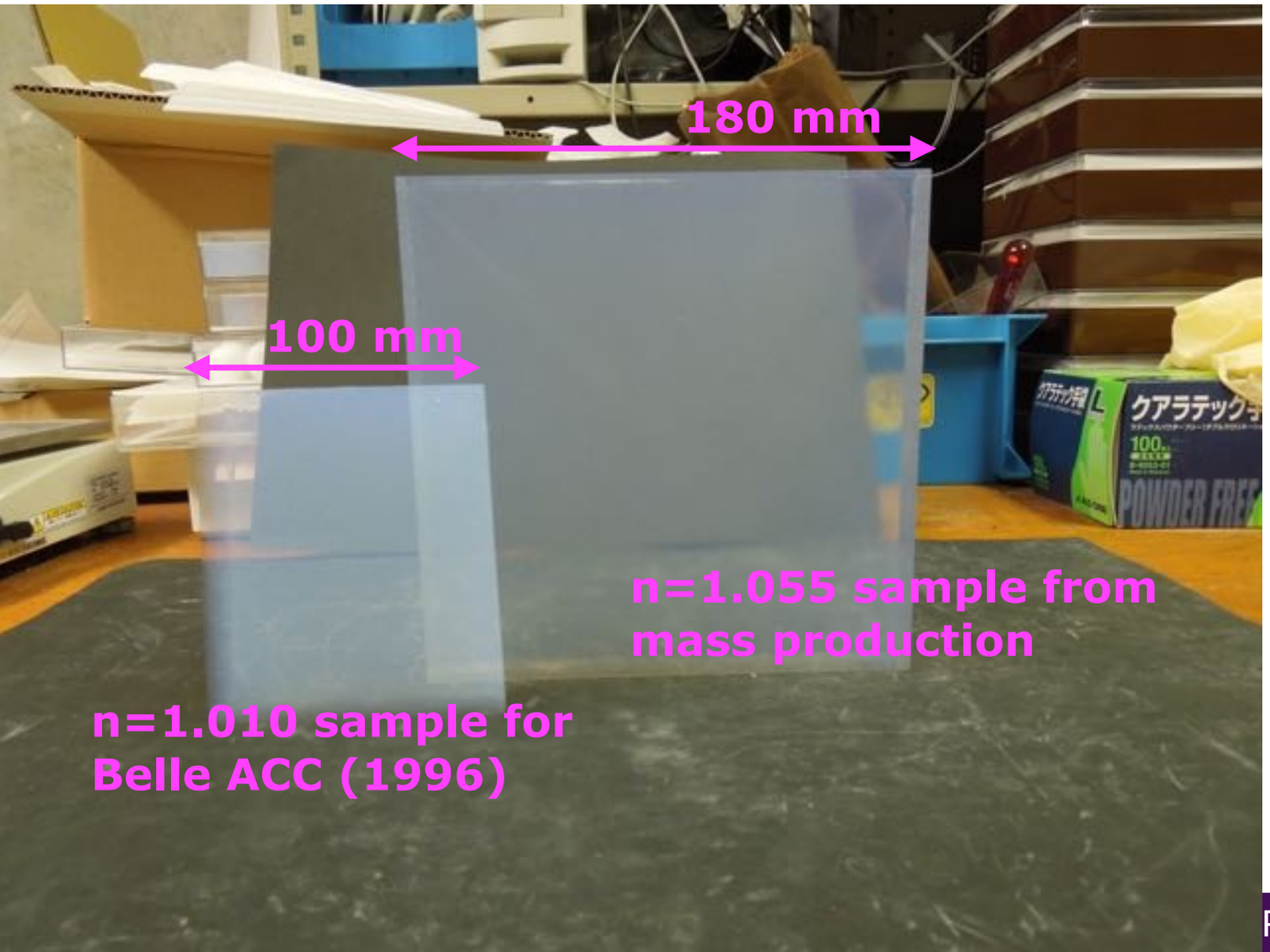
Small chips found in some tiles



If missing area > 0.4 % w.r.t. whole surface (~1.0 cm^2), the sample is removed from candidates.

New Aerogel Tile

- Large tile of 180×180×20 mm^3 with no cracks
  - Optimization of pressure control in supercritical drying process.
  - 3 times longer duration from operating point to atmospheric pressure introduced by Chiba university group.



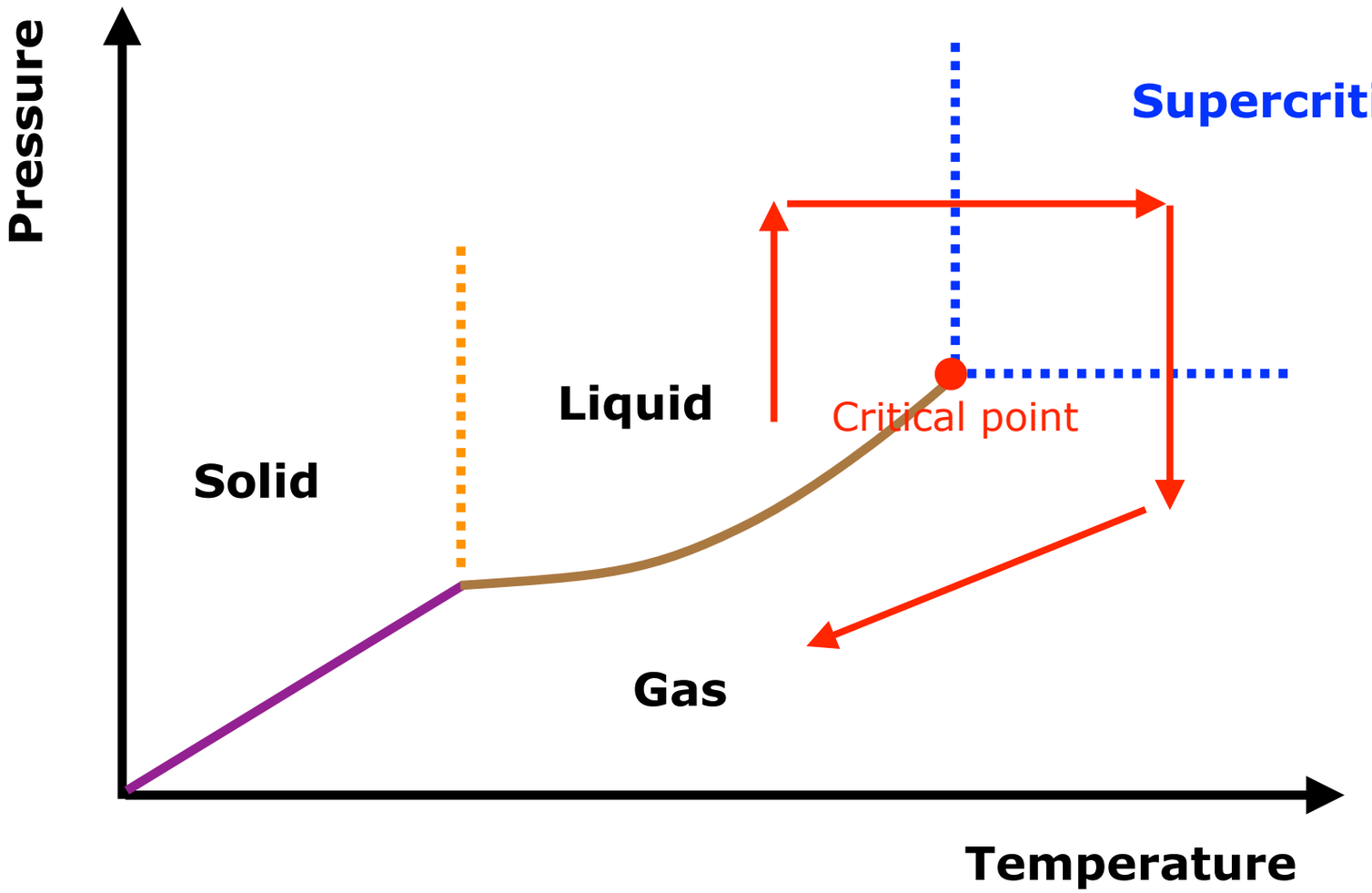
Crack-free yield ~ 87%

Drawback is to need more time for tile production.

M.Tabata et al., The Journal of Supercritical Fluids, Vol.110, April 2016, Pages 183-192

Supercritical Drying

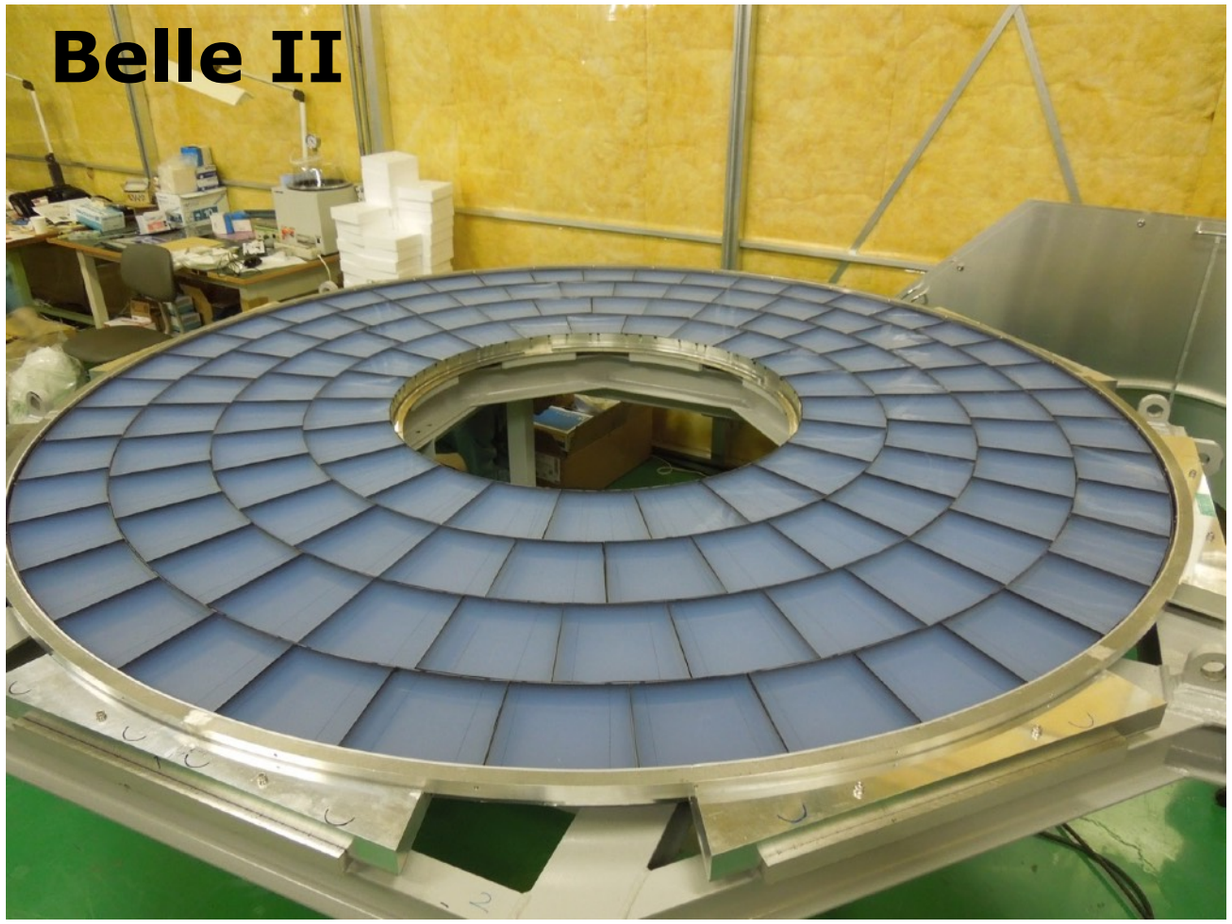
Phase diagram

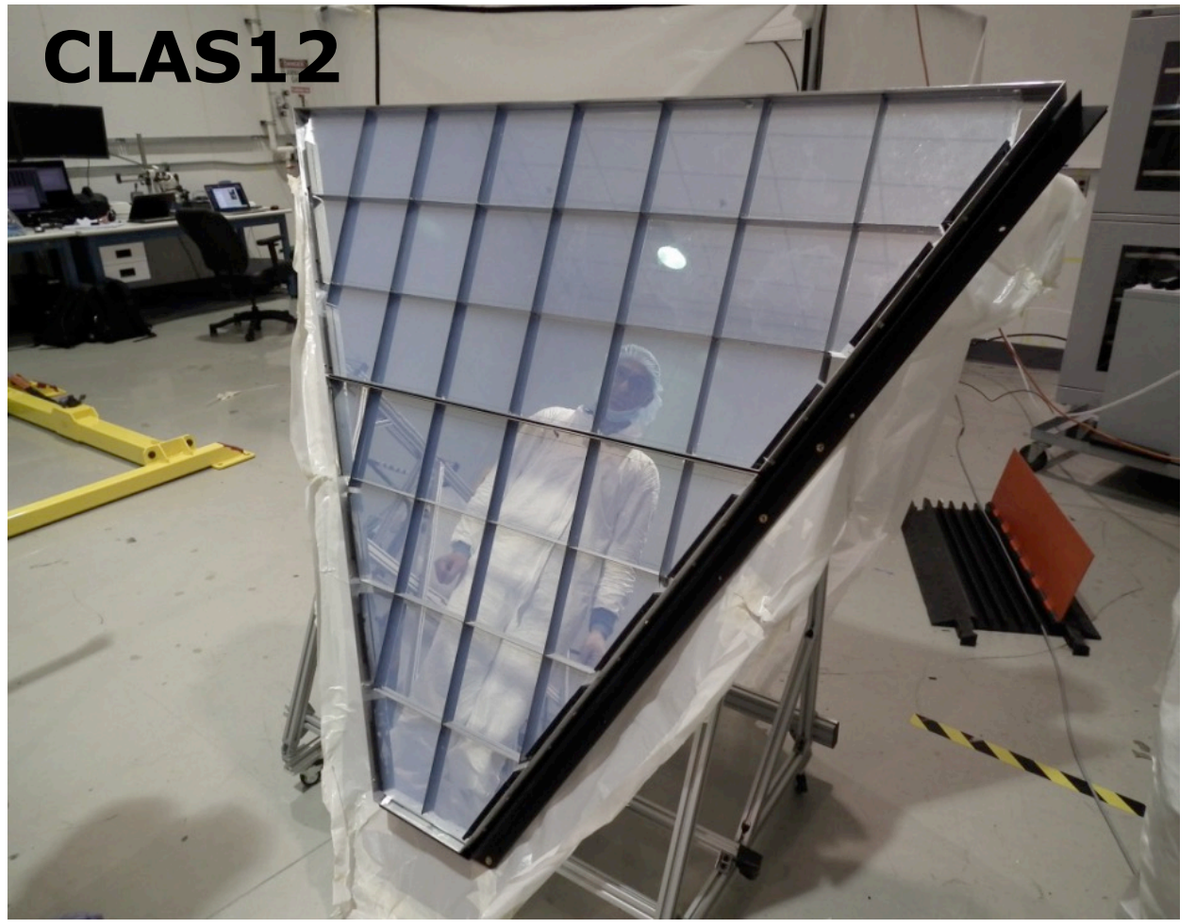


Drying through supercritical region, instead of passing through liquid-gas boundary.

Boundary Effect

- Aerogel tile has certain dimensions. To cover whole radiator area we need to spread tiles.





In both cases tile-to-tile is isolated via black sheet so that Cherenkov photons do not go through the neighboring tiles.

Passing through? Simulation capability?