Jet Propulsion Laboratory
California Institute of Technology

Porosity Characterization of Mesoporous Aerogels Using Positron Annihilation Spectroscopy, Nitrogen Adsorption and Molecular Diffusion

Mihail P. Petkov and Steven M. Jones
NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, U.S.A.

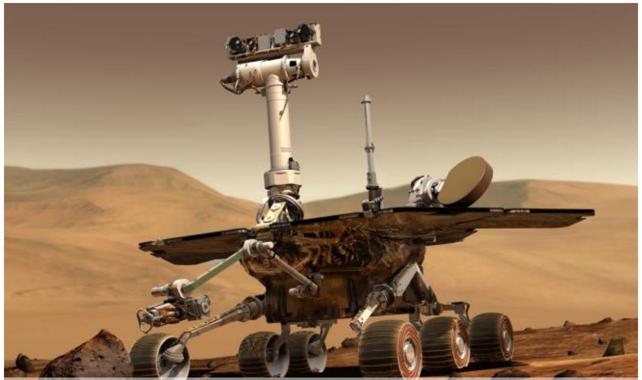
Outline

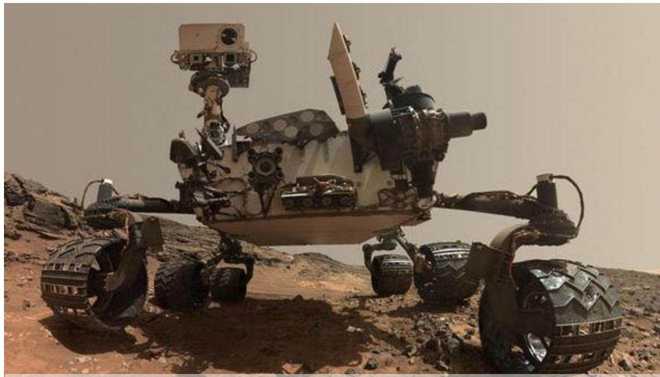
- JPL aerogels: past, present and future
- Porosity and microstructure govern virtually all material properties
- Methods for characterization: pros and cons
  - Density
  - Pore size & size distribution
  - Pore morphology
  - Intrinsic surface
  - Adsorption centers
- Summary

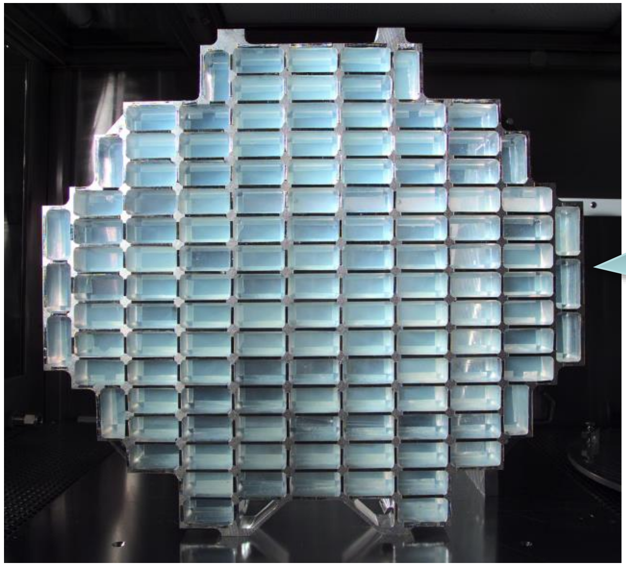
JPL Aerogels: Past

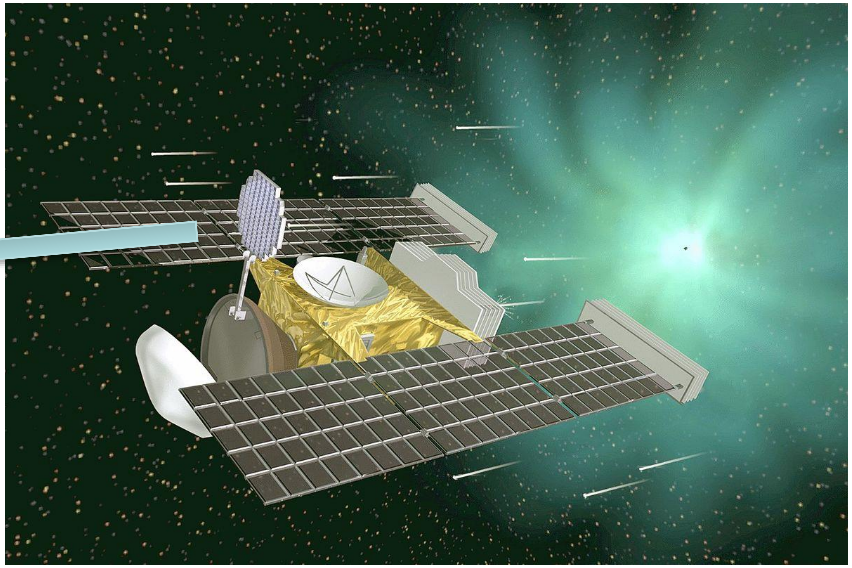
Mars Rovers and Landers: Thermal insulation


Pathfinder / Sojourner 1997


Spirit & Opportunity 2003-present


Curiosity 2012-present


Stardust Collector


Stardust: Collecting comet particles
Flyby Wild 2 on January 2, 2004

JPL Aerogels: Present & Future

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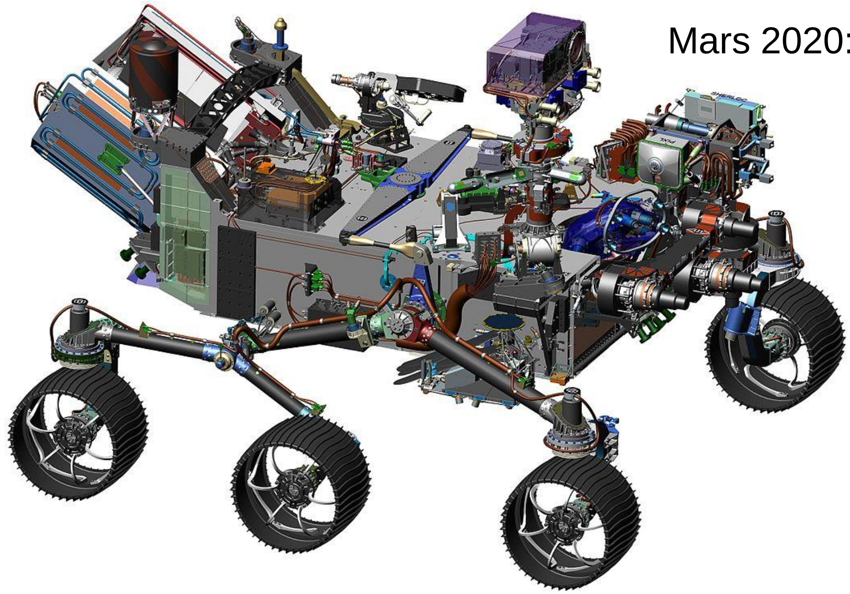
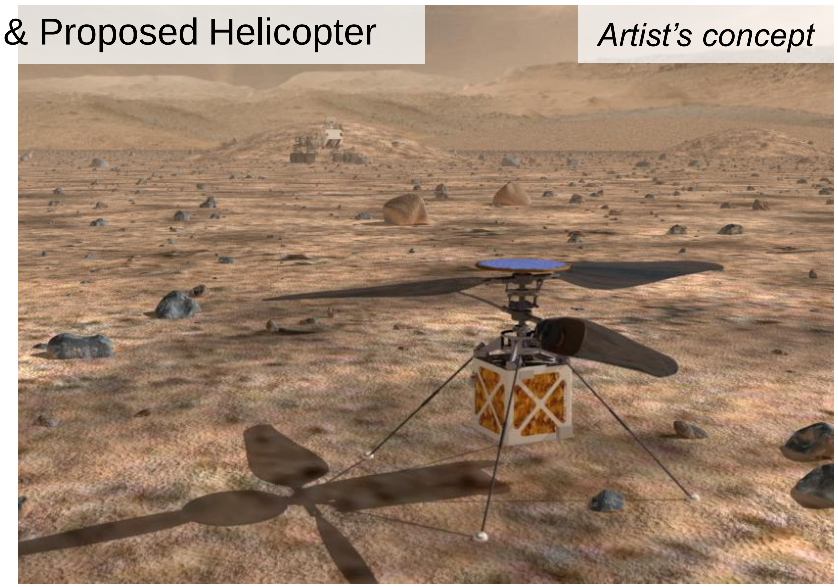


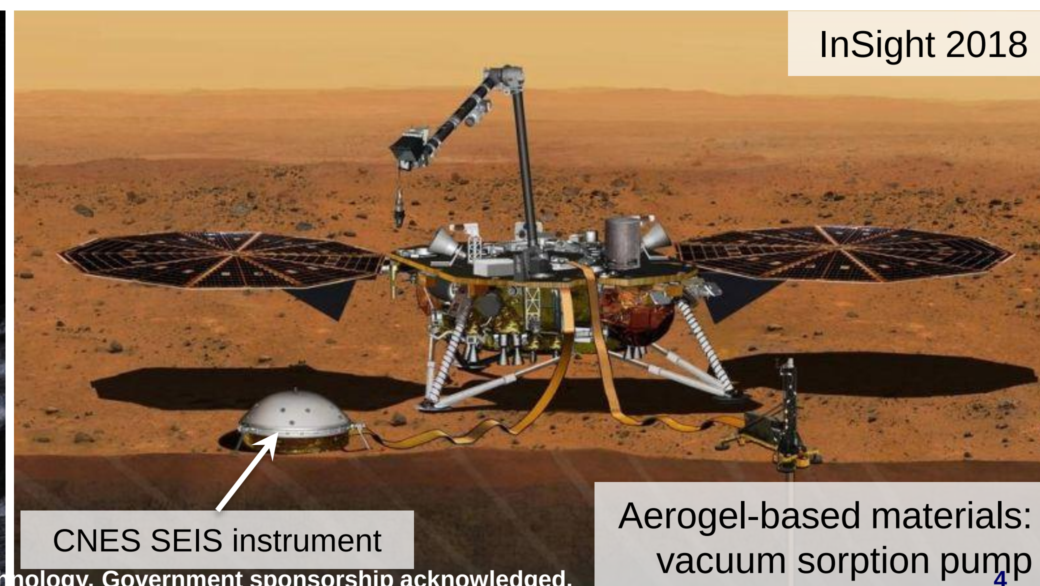


Mars 2020: Rover & Proposed Helicopter

Artist's concept

Potential: Europa Lander

Artist's concept



InSight 2018

CNES SEIS instrument

Aerogel-based materials: vacuum sorption pump

JPL Aerogels: Mission Need

- What we have learned from prior applications:
  - Thermal insulation is an excellent space application!
  - Unique alternative uses:
    - Stardust (1999-2006): Similar sample return concept proposed for particles collected form Mars atmosphere (SCIM)
    - InSight (2018-2020+): Getters for vacuum maintenance

- R&D: Feasible applications for NASA missions
  - Composites for instrument-specific thermal insulation
  - Passive adsorbers for environmental sampling
    - Enormous surface area, fast molecular kinetics, chemi- and physisorption facilitating media, targeted adsorption, etc.
    - Volatile organics "concentrator" media in optical detection schemes
  - Others?

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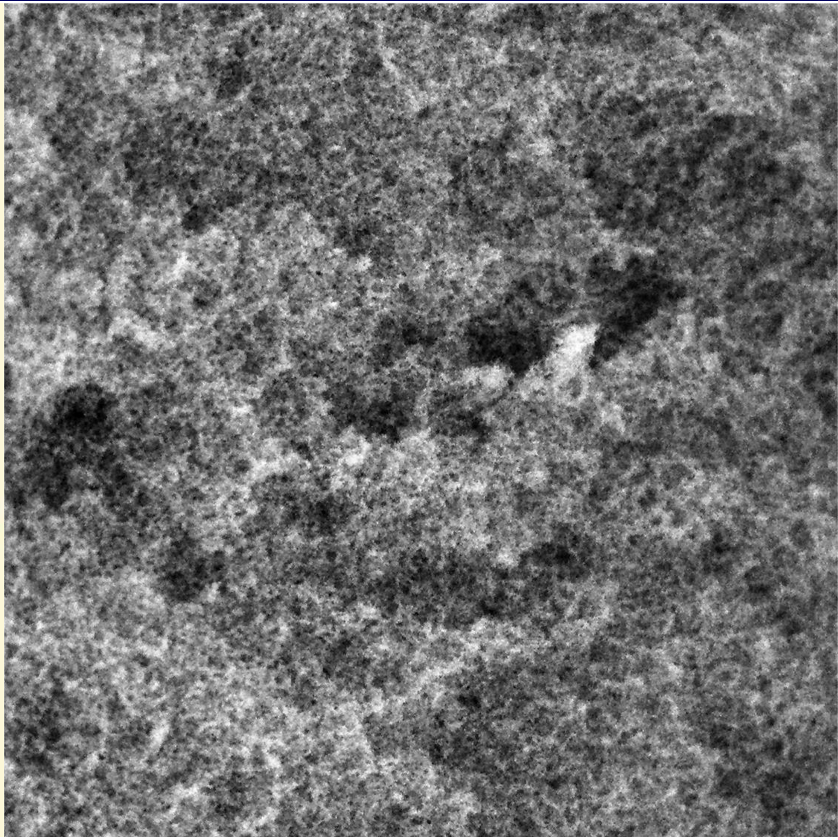
Silica Aerogel Synthesis at JPL

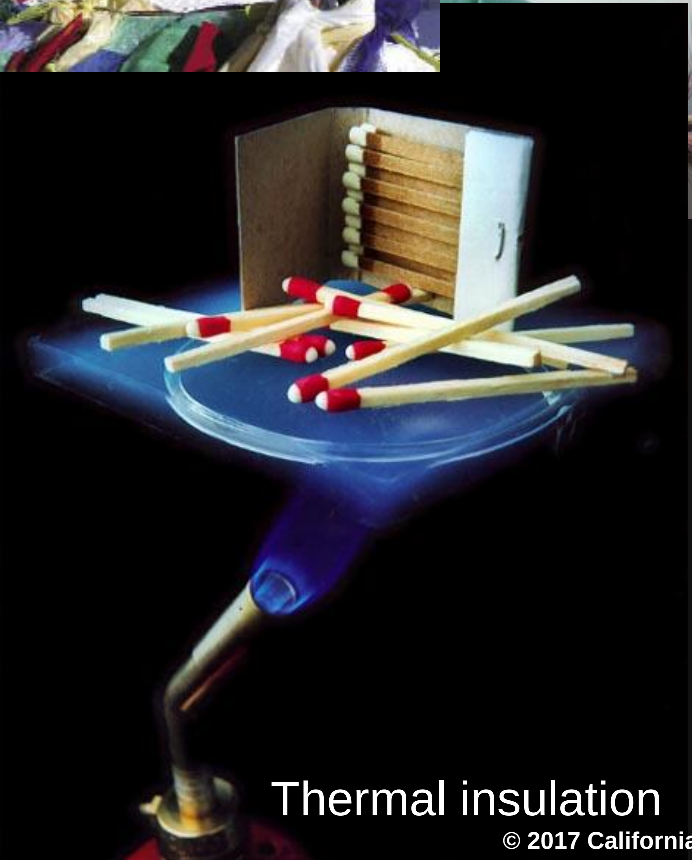
T.M. Tillotson, L.W. Hrubesh *"Transparent ultra low-density silica aerogels prepared by a two-step sol-gel process"*, *J.Non-Cryst.Solids* **145** (1992) 44

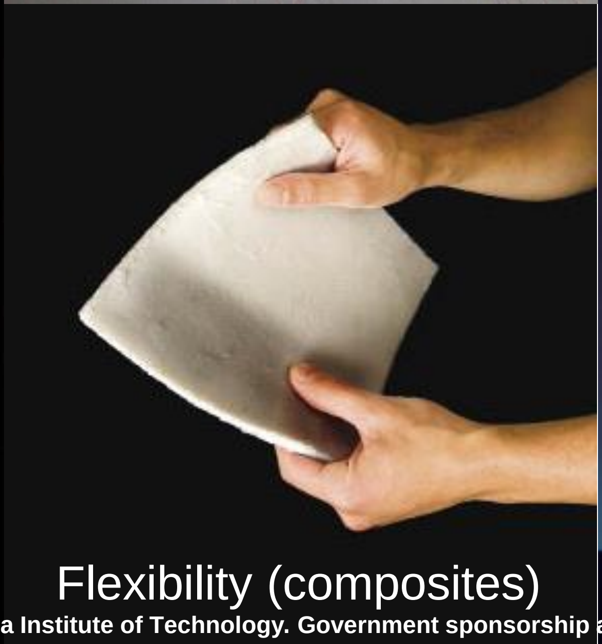


Scanning electron microscope image of a 25 mg/cm^3 silica aerogel sample. Image seize is 10x10 μm^2.

- Typical uniform density range: 20-250 mg/cm^3
  - Linear gradient density capability (NASA Stardust Discovery mission)
- Other materials: alumina, germania, hafnia, titania, zirconia, vanadia, etc.
- Composite materials (carbon, zeolites, magnetic particles, fiber-reinforced etc.)

Key Aerogel Properties





Aerogel Properties (Cont'd)

- Least dense solid (*Guinness World Records*):
  - 2002: *"JPL's aerogel makes record books as lightest solid"*
    https://www.space.com/1913-jpl-aerogel-record-books-lightest-solid.html
  - 2013: *"Graphene aerogel is the new world's lightest substance"*, Zhejiang University
    http://www.guinnessworldrecords.com/world-records/least-dense-solid
  - Highly porous materials: >99.9% porosity attainable
- Translucency / transparency and color:
  - Material and structure dependent:
    - The first-ever SnO_2 aerogels were first reported to be transparent, but that property has not been replicated (chemistry dependence?)
    - SiO_2 aerogels are usually transparent / translucent; very-low-density material turns translucent (large pores)
    - Al_2O_3 aerogels (usually white) were recently made transparent
    - Various type aerogels have produced a large variety of colors

Aerogel Properties (Cont'd)

- Thermal conductivity and aerogel microstructure:
  - Solid component: Filament morphology
  - Gas component: Porosity morphology
  - Radiative component: Additives (e.g., carbon)
- Strength:
  - Shear strength (poor): Structural additives (fibers)
  - Compressive strength: Filament interconnectivity
  - *Deficient understanding of relationship with microstructure*
- Flexibility:
  - Poor flexibility of inorganic aerogels
  - Flexible composites combine fibers and aerogels pellets
  - Monolithic flexible organic aerogels have been fabricated
- Molecular adsorption:
  - Capacity: Intrinsic surface, bond density
  - Kinetics: Porosity, morphology

Microstructure and Properties

- Key aerogel microstructure characteristics determine virtually all properties:
  - Pore size, size distribution and connectivity
  - Solid microstructure: filament morphology
  - Intrinsic surface: total area and surface chemistry
- Microstructure characterization:
  - No universal characterization methodology exists
    - Surface area, porosity, density are usually measured
  - Characterization of many properties is complicated:
    - Weight: by water adsorption
    - Volume: by matrix elasticity and shrinkage
    - Surface area: by sorbent and matrix relaxation
    - Porosity: by probing species (interaction with matrix)
      by deficiencies of experimental techniques

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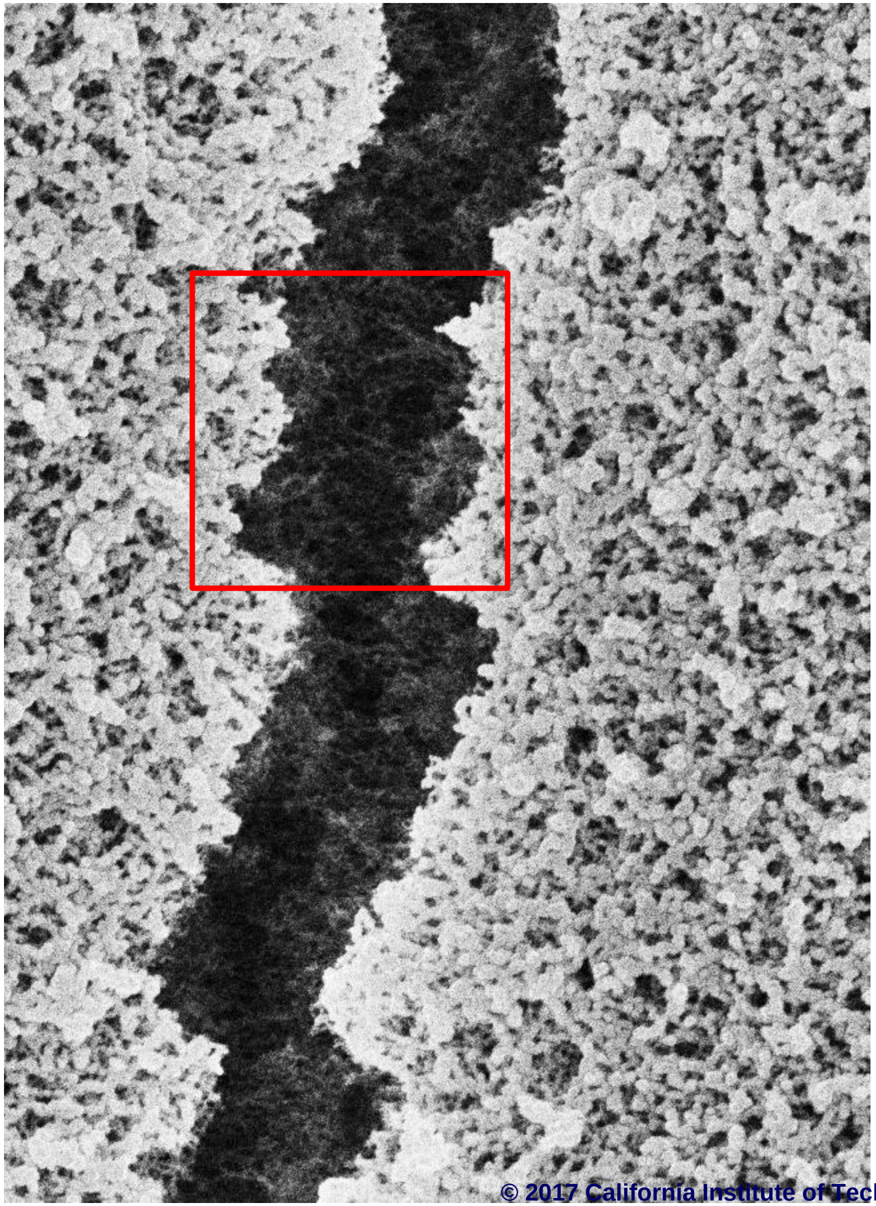
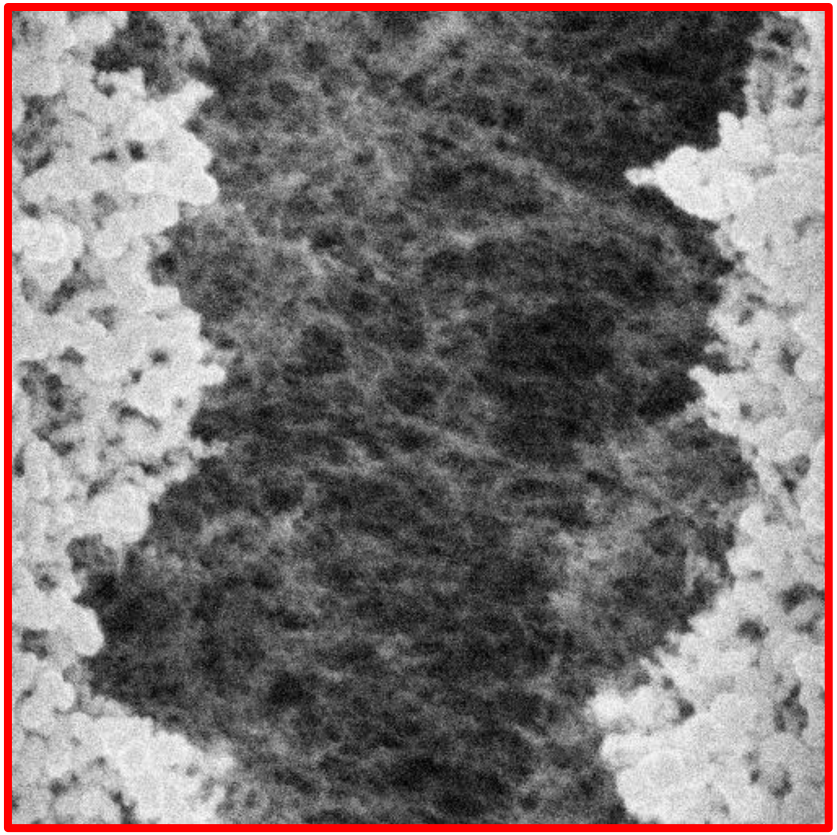
Scanning Electron Microscopy:
Microstructure and Porosity Visualization

SEM Imaging Artifacts

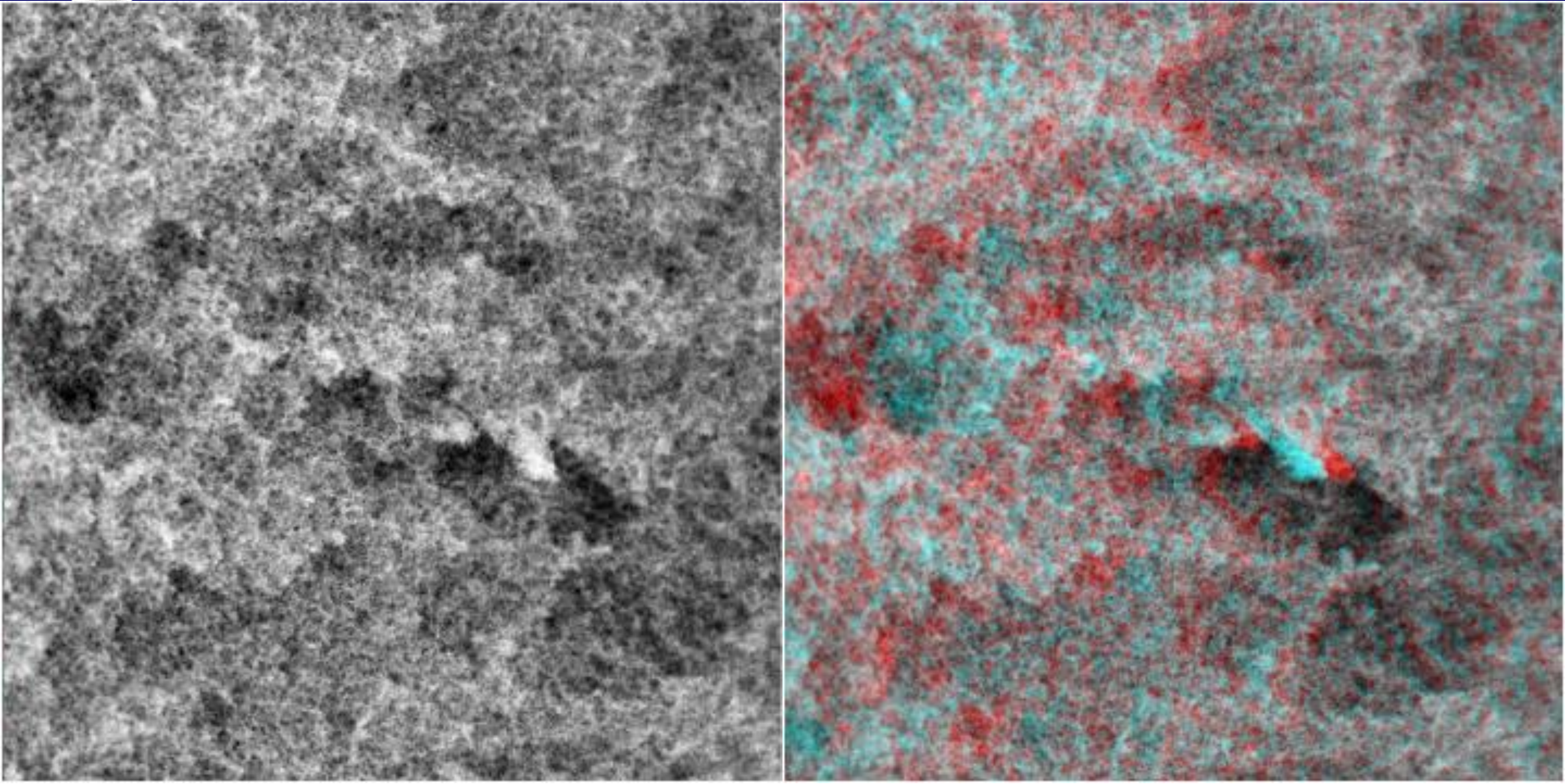




Sample preparation creates artifacts that can mislead the structural analysis:

- Au/Pd sputter-coated aerogel surface creates the appearance of a globular structure (left) whereas, in reality, aerogels have filament structure (right)

SEM Imaging: Microstructure and Porosity



1 μm   1 μm

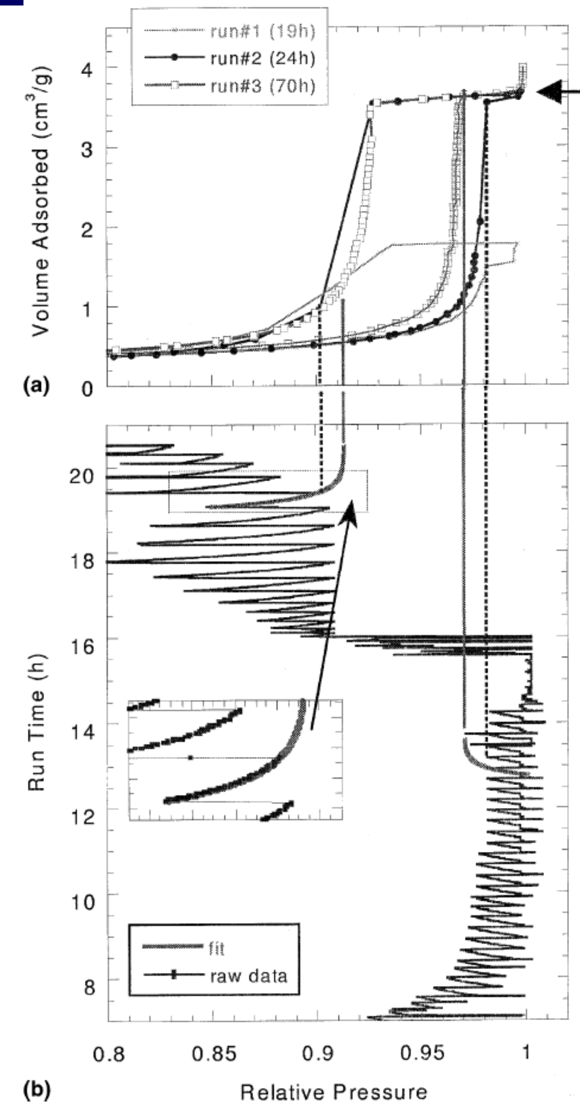
Scanning electron microscope images (10μm×10μm) of the microstructure of a 25 mg/cm^3 silica aerogel, magnified 20,000 times. The anaglyph (right) reveals more detailed depth information than a standard SEM image of the same area (left).

Nitrogen Adsorption:

Specific Surface Area (BET) & Pore Size Distribution (BJH)

Gas Adsorption Artifacts

- Nitrogen adsorption techniques are commonly used:
  - Surface area: Brunauer-Emmett-Teller (BET)
  - Pore size distribution: Barrett-Joyner-Halenda (BJH)
- Deficient relaxation times often cause gas adsorption techniques to yield erroneous pore side distribution
  - Proper relaxation allowance for mm^3-sized granules may require >100 of hours for one measurement
  - Crushing compliant materials into granules to facilitate faster adsorption may change the pore size distribution
  - Producing small granules in the desired size may have different sorption properties due to “skin effects”



G. Reichenauer and G.W. Scherer
J. Non-Cryst. Solids **285** (2001) 167

N_2 / CO_2 Adsorption

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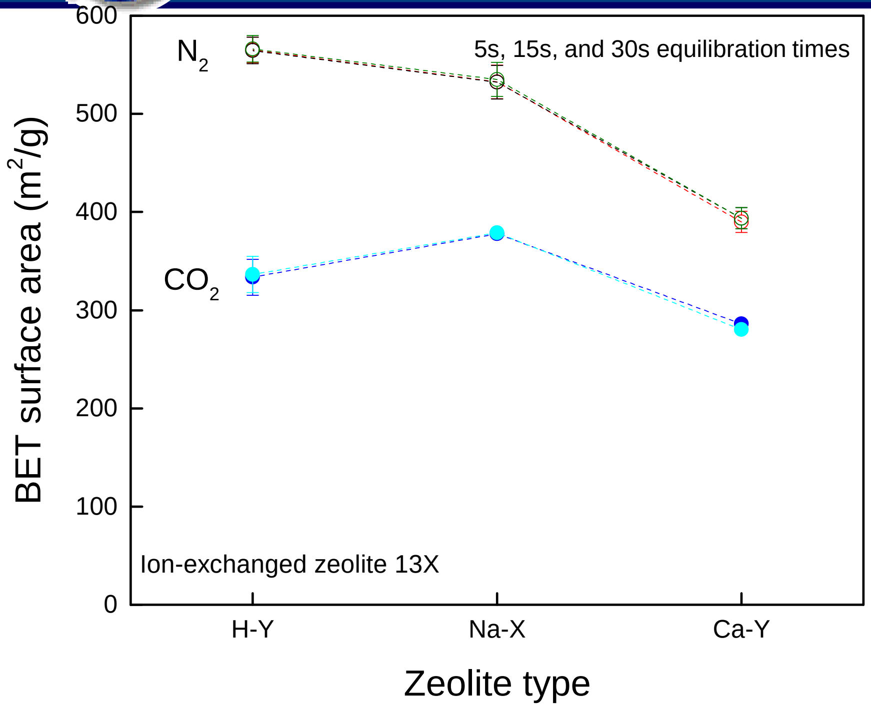
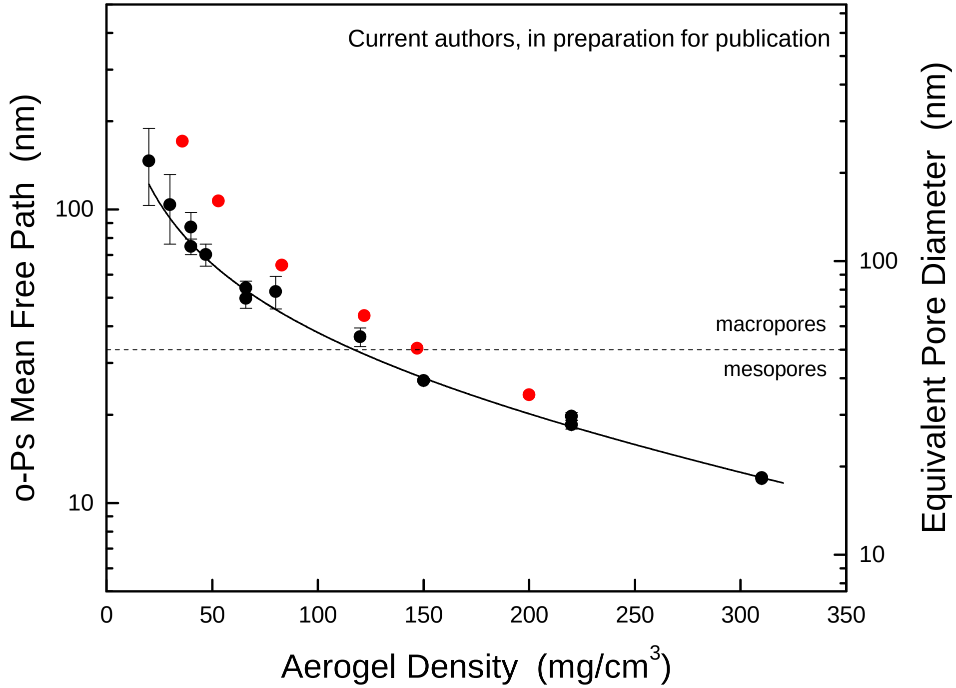


BET surface area data for zeolite-loaded aerogel (ZLA) composites with different ion-exchanged 13X zeolites. Mean free path (MFP) can be calculated as 4V/S and related to pore shape through morphology models.

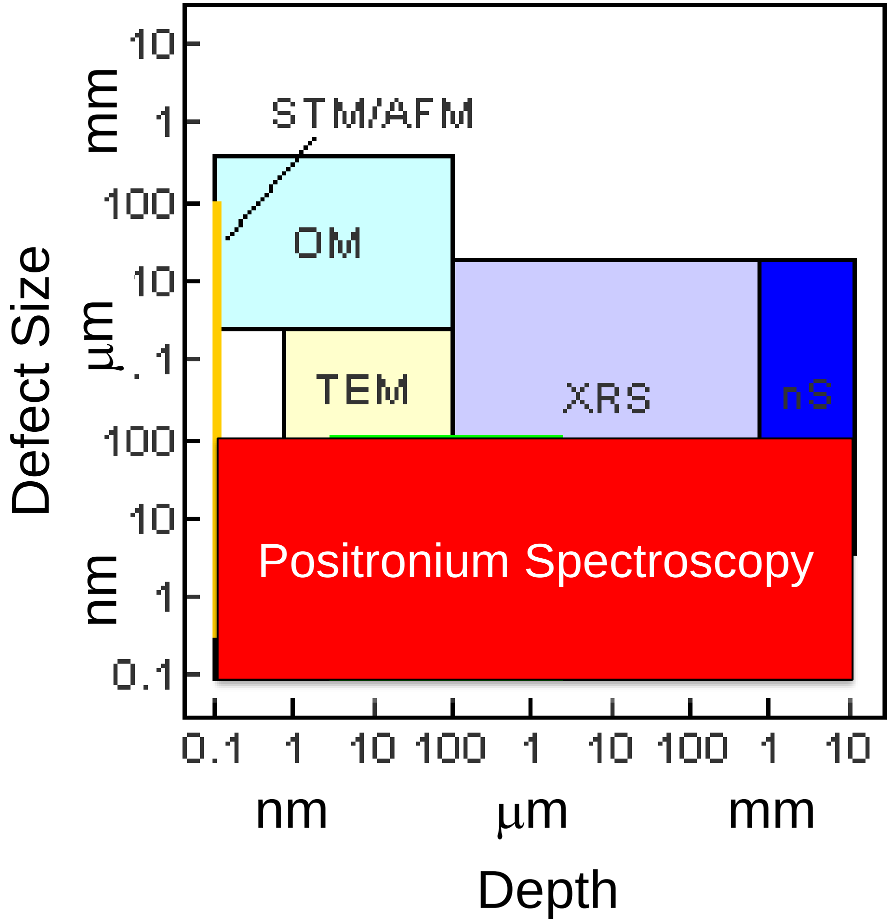


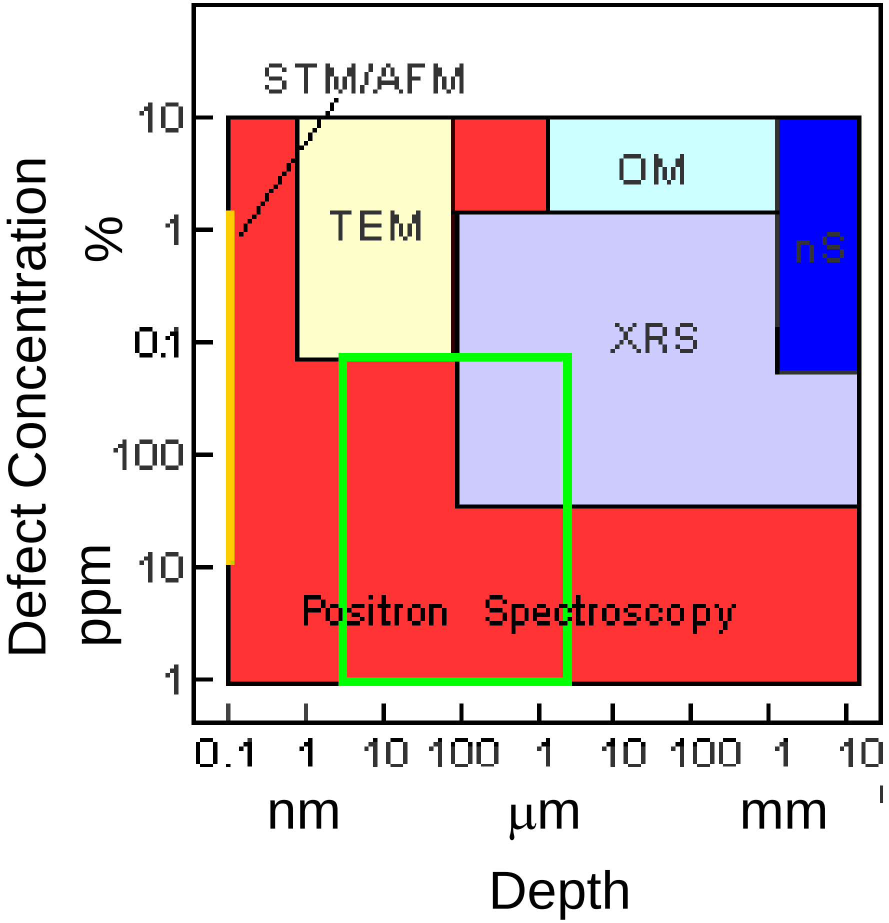
MFP in silica aerogel as a function of sample density. The PALS MFP (●) is calculated from models, that for N_2 adsorption (●) is calculated as 4V/S. The PALS data encompass four different sets of samples.

- The BET method yields consistent surface area results for different equilibration times. Suitable for mean free path (MFP) estimation. MFP = 4V/S
- MFP is an invariant. Conversion to pore size depends on assumed shape.
- BET MFP from N_2 adsorption is a good macro- and mesopores characteristic.
- N_2 adsorption is not suitable for micropores (Kelvin equation breakdown)

Positron Annihilation Spectroscopy (PAS):
Pore Size & Size Distribution

PAS: Sensitivity of the Positron Probe

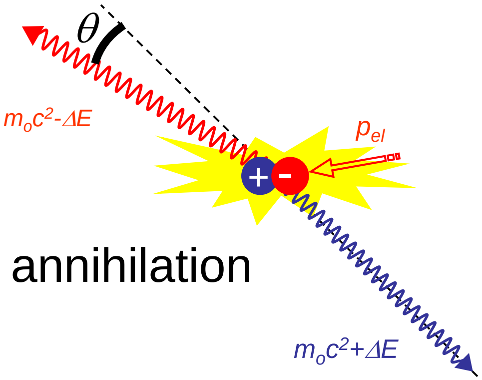




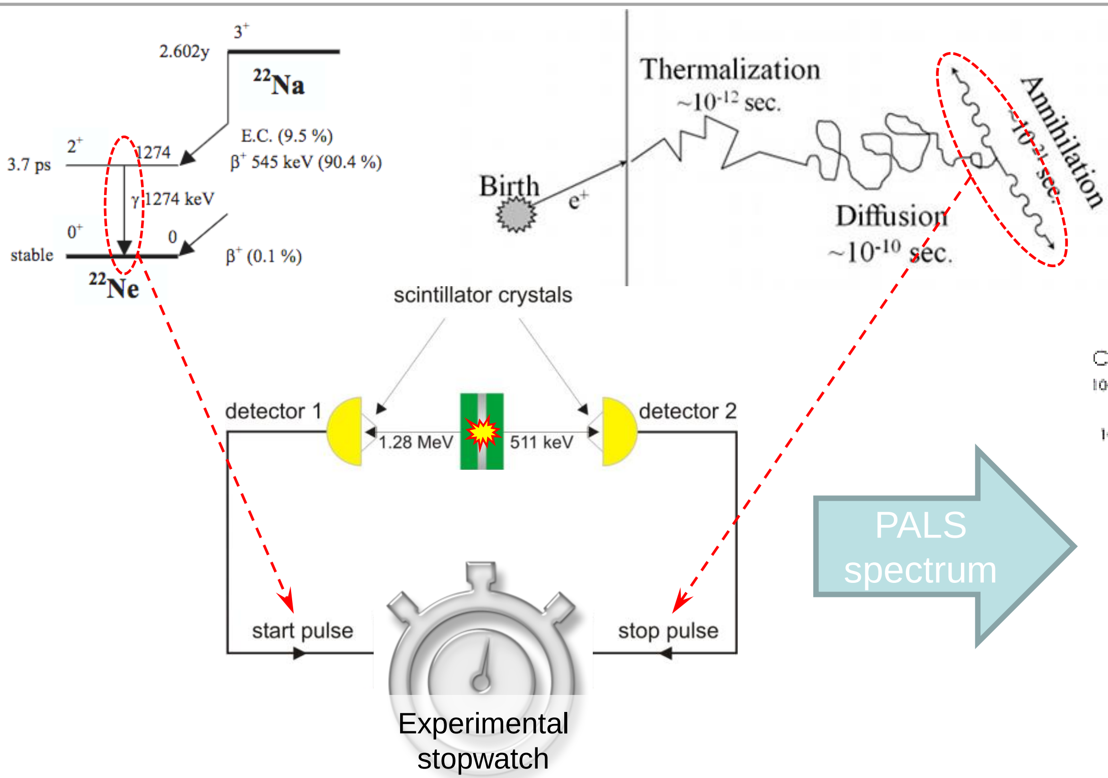
LLNL e^+ site: http://www-phys.llnl.gov/H_Div/Positrons/PositronMaterials.html

- Positrons are the most sensitive probe for point defects (vacancies, clusters, voids), dislocations, grain boundaries
- Positronium (e^+-e^- atom) is the most sensitive probe for micro- and mesopores

PAS Techniques



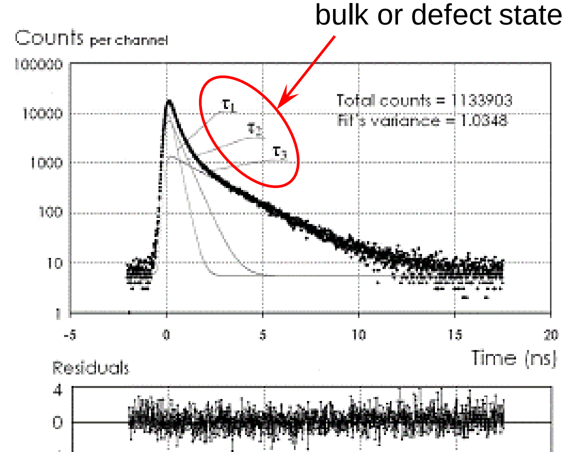
- Doppler Broadening (DB) of the annihilation line:
  - A "measure" of transverse **electron momentum** manifested in the red- and blue-shifted photons
- Angular Correlation of the Annihilation Radiation (2D-ACAR)
  - A "measure" of longitudinal **electron momentum** manifested in the deviation angle from 180º



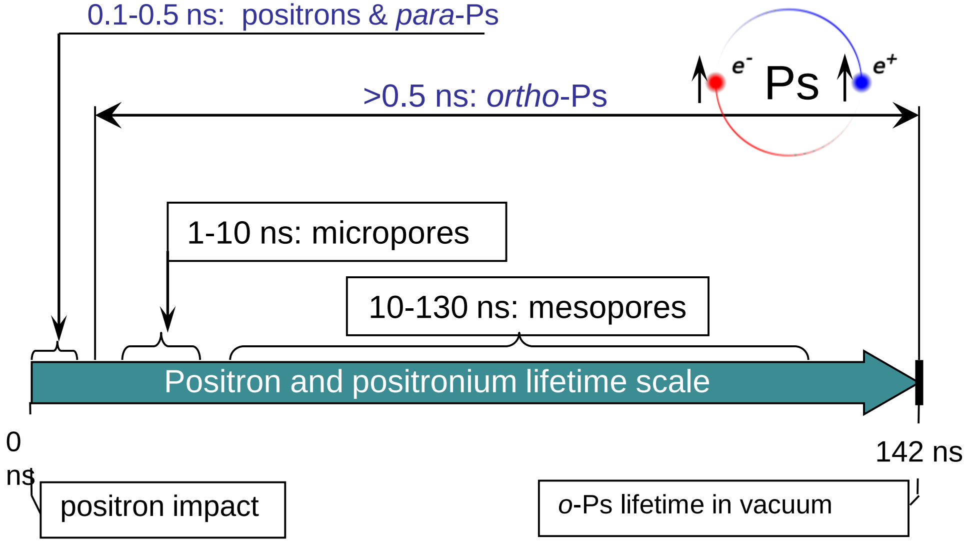
Positron Annihilation Lifetime Spectroscopy (PALS)

electron density

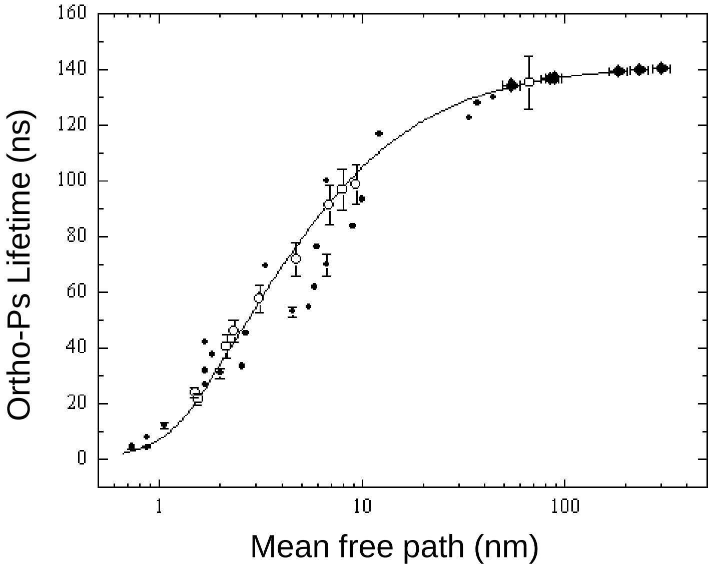
Each lifetime component represents bulk or defect state in the material

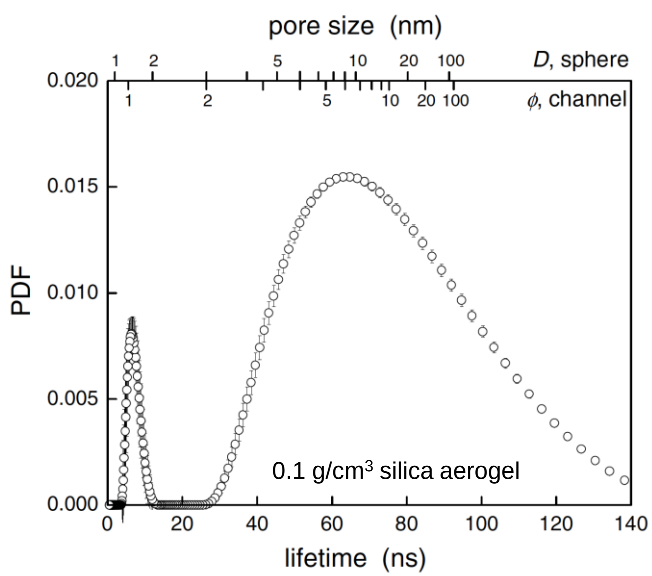


PALS: Time Scale for Porosity



K. Ito *et al.*, *J. Phys. Chem. B*, **103**, 4555 (1999)
D.W. Gidley *et al.*, *Appl. Phys. Lett.*, **70**, 1282 (2000)

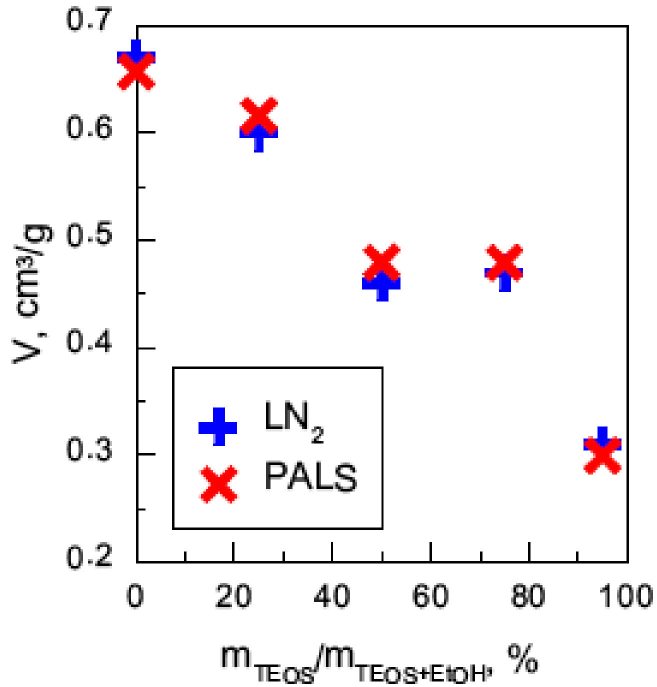




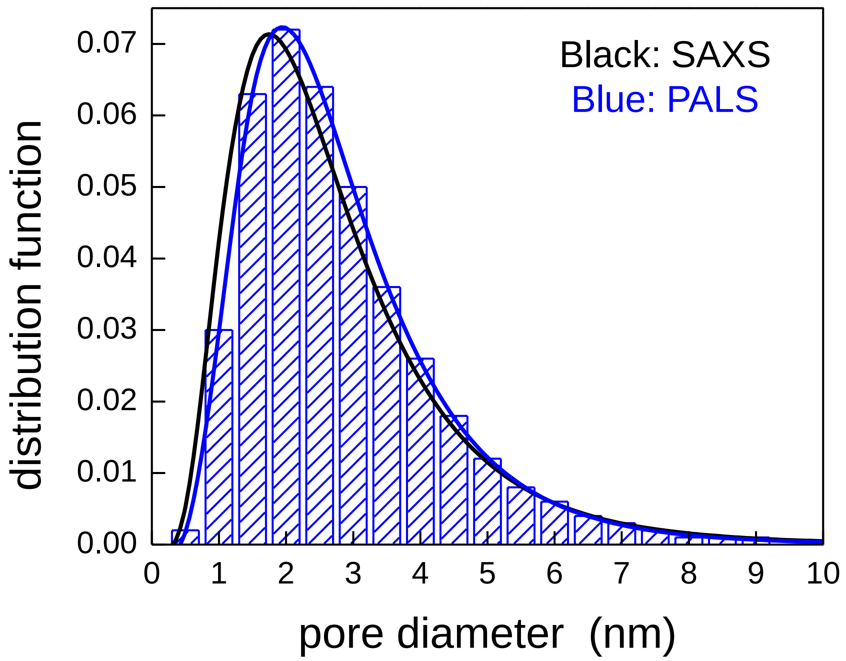
I. Mincov et al., *J. Non-Cryst. Sol.* **350**, 253 (2004)

- Ortho-positronium (o-Ps) mean free path (MFP) is a measure of pore size
  - Size correlation established with different techniques
  - Size distribution derivation capabilities
- O-Ps intensity is a measure of pore density

Comparison: PALS Vs. Other Techniques



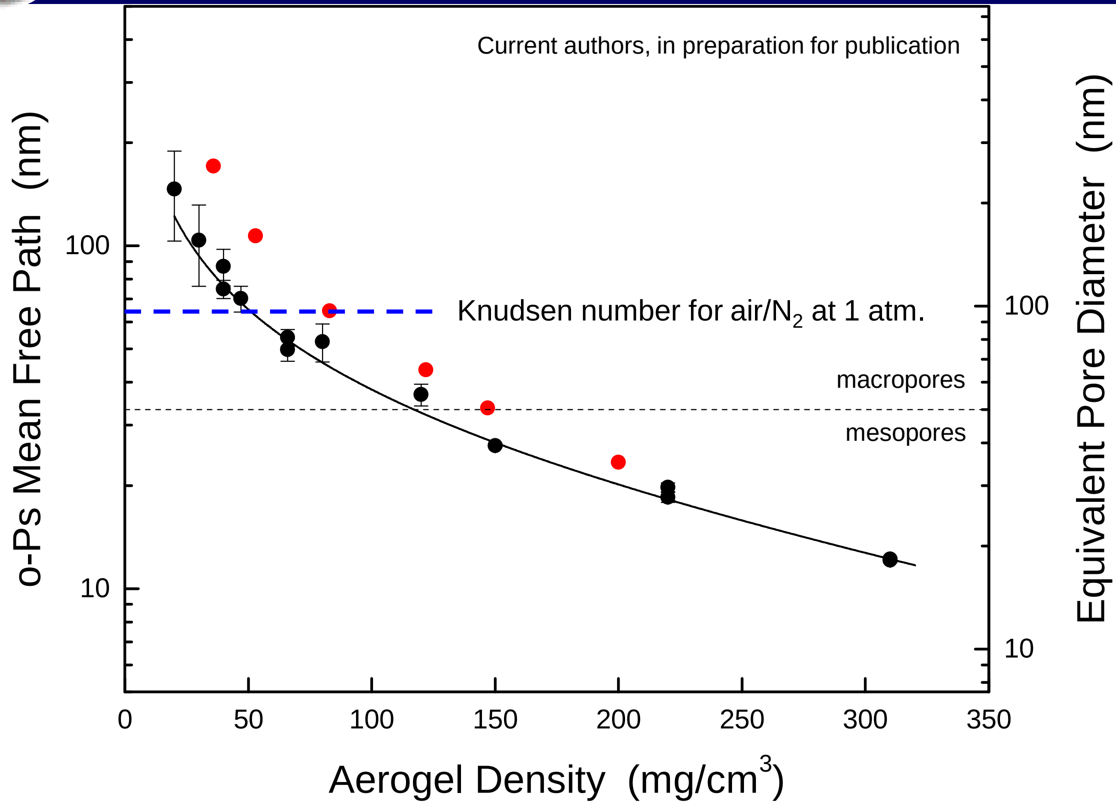
Total pore volume determined by nitrogen adsorption and PALS after R. Zaleski *et al.*, *Adsorption* **22** (2016) 745.



SAXS-PALS pore size distribution comparison for a methyl-silsesquioxane porous low-k dielectric

- No technique derives pore size directly. Most measure MFP and correlate with size through assumed pore shape shape (usually using 4V/S).
- Comparison of PAS results with more conventional techniques:
  - SAXS / SANS: Superb
  - N_2 adsorption (BET): Excellent
  - SEM / TEM: Very good

Porosity Results: PALS & N_2 Adsorption



MFP in silica aerogel as a function of sample density. The PALS MFP (●) is calculated from models, that for N_2 adsorption (●) is calculated as 4V/S. The PALS data encompass four different sets of samples.

Imperfect correlation between PALS and N_2 adsorption:

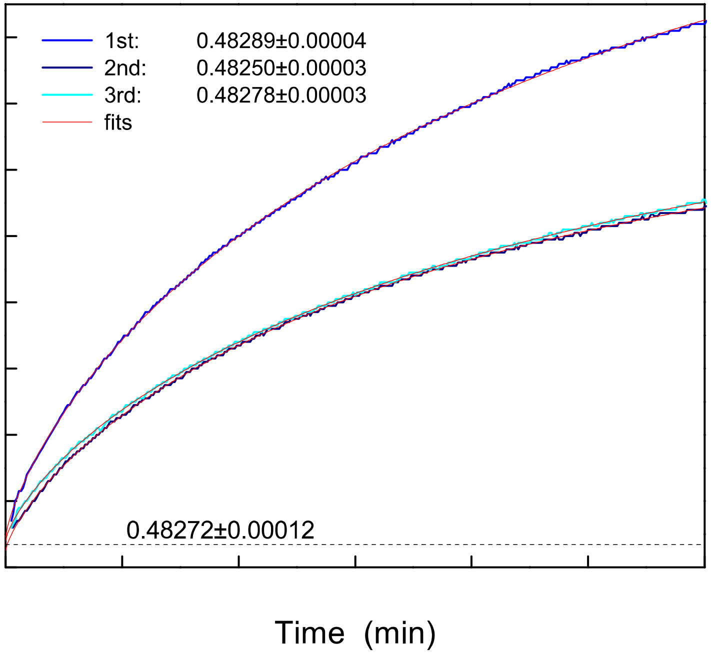
- Unknown sample shape effect for N_2 adsorption, unknown equilibration time
- Decreased PALS sensitivity for macropores?
- Changes around Knudsen diffusion regime?

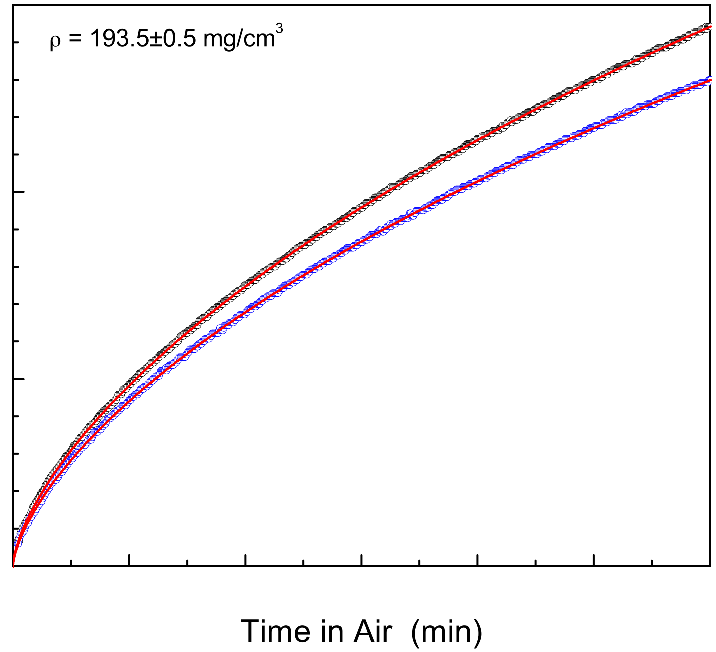
Molecular Diffusion:

Kinetics, Capacity and… Morphology?

“Can one hear the shape of a drum?” Mark Kac

Dry Weight, Density and Water Adsorption





Atmospheric moisture adsorption in hydrophilic silica aerogel with different density. The samples were dried at 350 °C in dry N_2 atmosphere. Hydrophobic aerogel also adsorbs moisture with ~1/10 of this capacity.

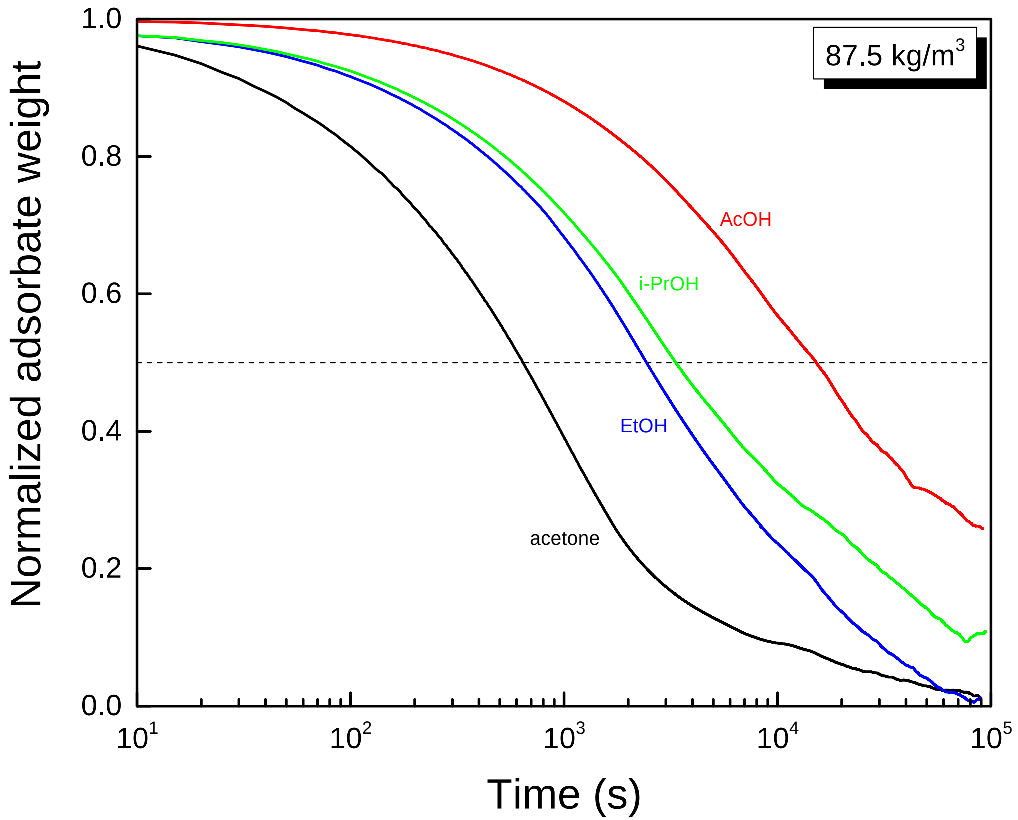
- Dry weight obtained through heat treatment in dry N_2 and analysis of diffusion kinetics
- Density obtained with the glass bead method
- Adsorption modeled using a Kohlrausch dependence:

$$W = W_{dry} + \Delta W \cdot \left(1 - e^{-\left(\frac{t}{t_0}\right)^{\beta}} \right)$$

Kohlrausch exponent (β)

Kohlrausch time (t_0)

Dry Weight, Density and Water Adsorption



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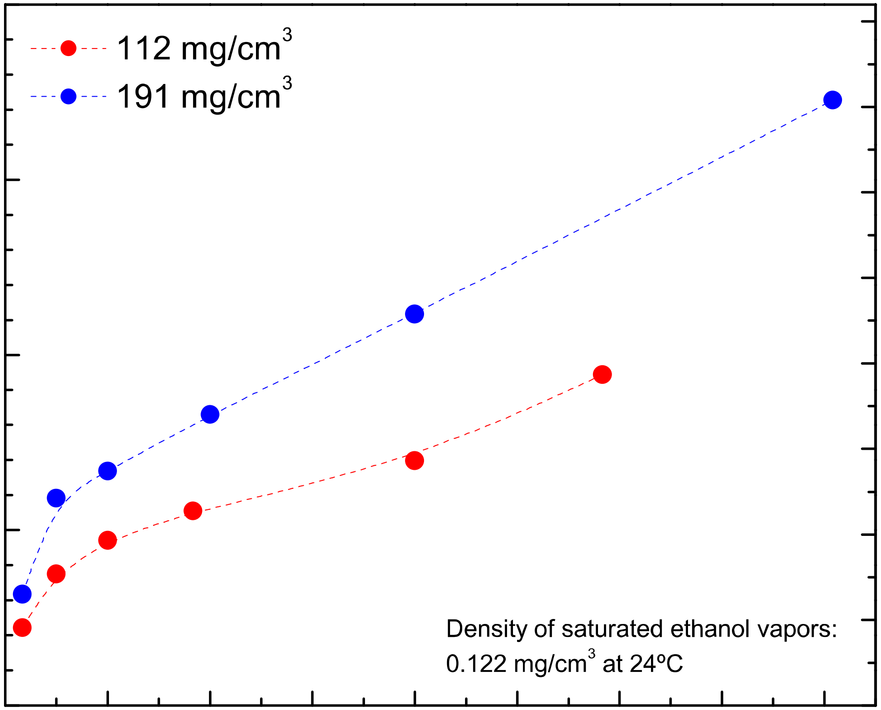
Ethanol Adsorption Versus Exposure Time

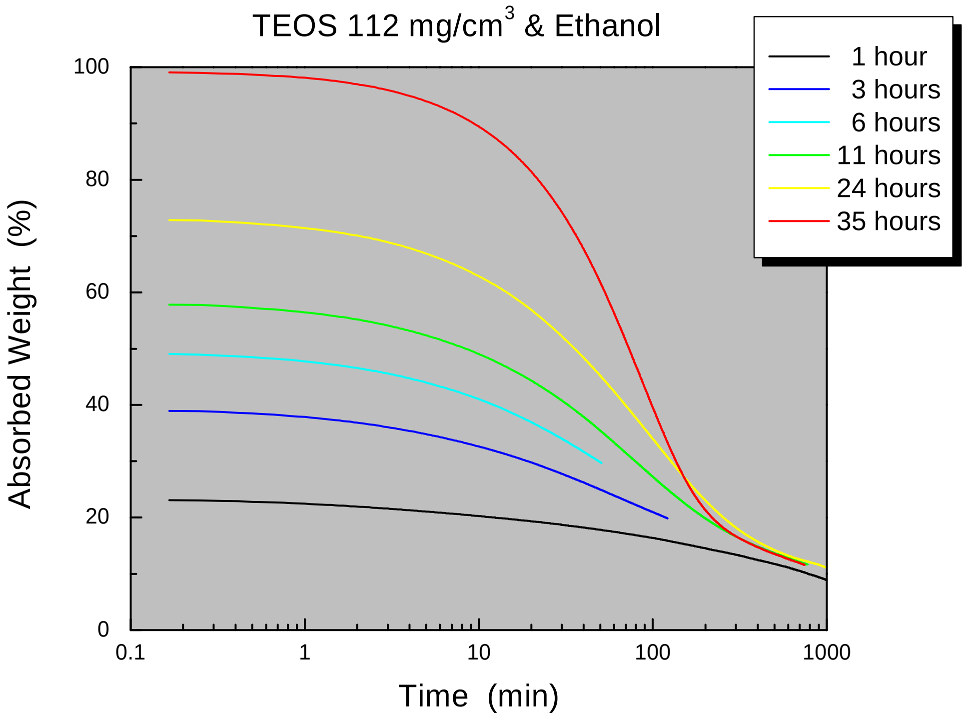


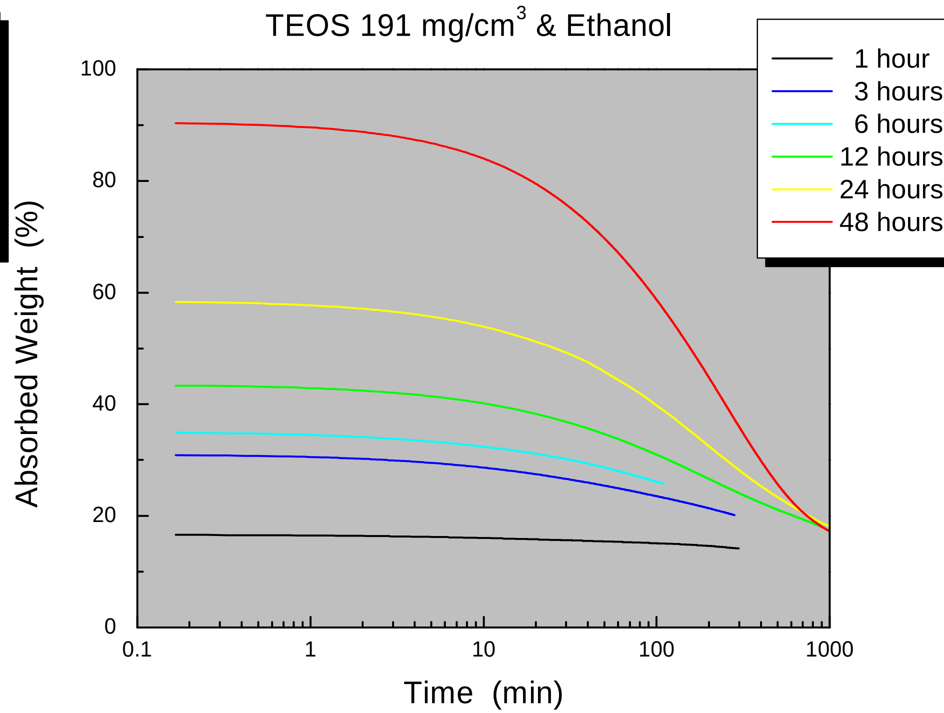
Absorption time (h)

Dried silica aerogel samples were placed in a desiccator, containing liquid ethanol in dry N_2 atmosphere. Adsorbed amount of ethanol was calculated from extrapolation of desorption measurements.

- No saturation of ethanol adsorption was observed prior to initiation of sample collapse under capillary pressure
- Fast initial adsorption attributed to sample surface area
- Slower subsequent adsorption attributed to ethanol-on-ethanol adsorption

Ethanol Desorption Measurements

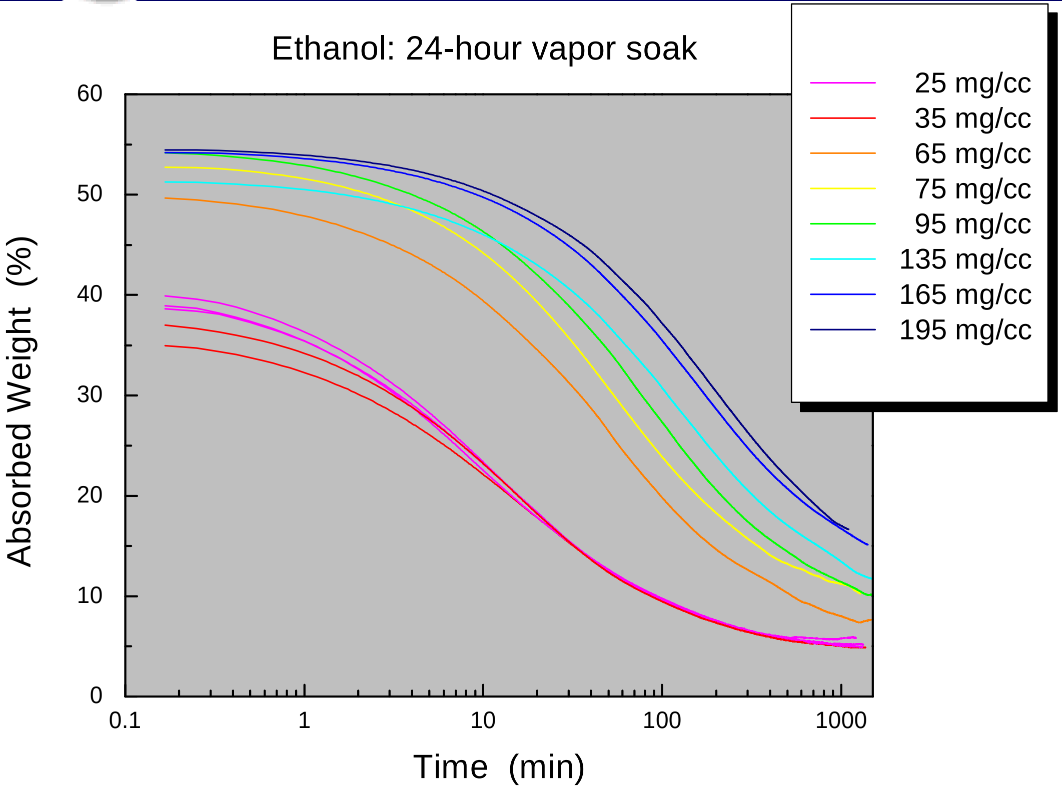


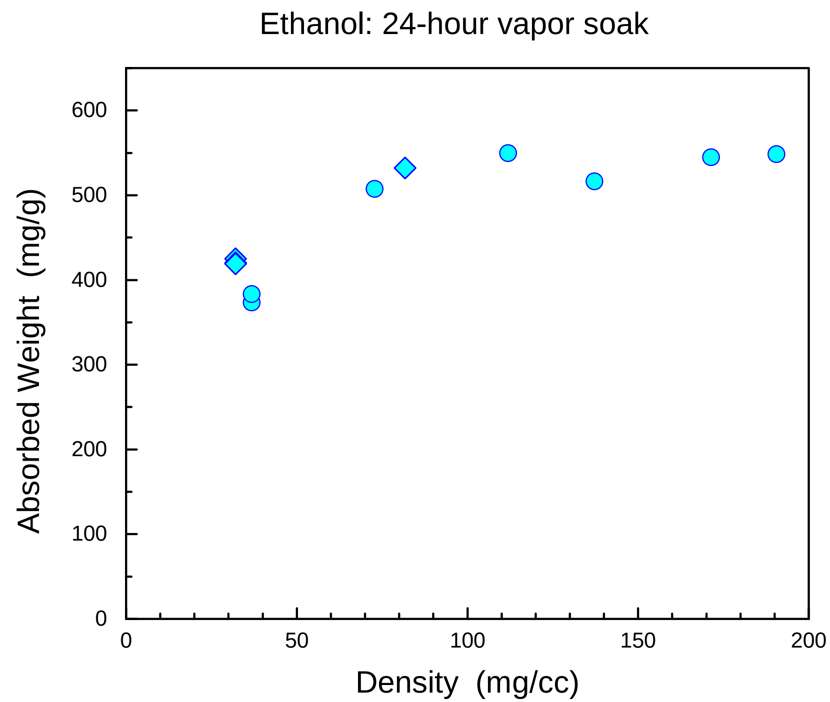


Sample weight change due to ethanol desorption from silica aerogels with density of 112 mg/cm^3 (left) and 191 mg/cm^3 (right). The adsorption times are given in the respective legends.

- Silica aerogels are capable of adsorbing ethanol in large quantities of the order of the sample mass, in some cases more than 2.5X by weight.
- Ethanol adsorption eventually leads to pore collapse due to capillary pressure of the formed liquid inside the pores.

Ethanol Desorption
After 24-Hour Soaking in Saturated Vapors





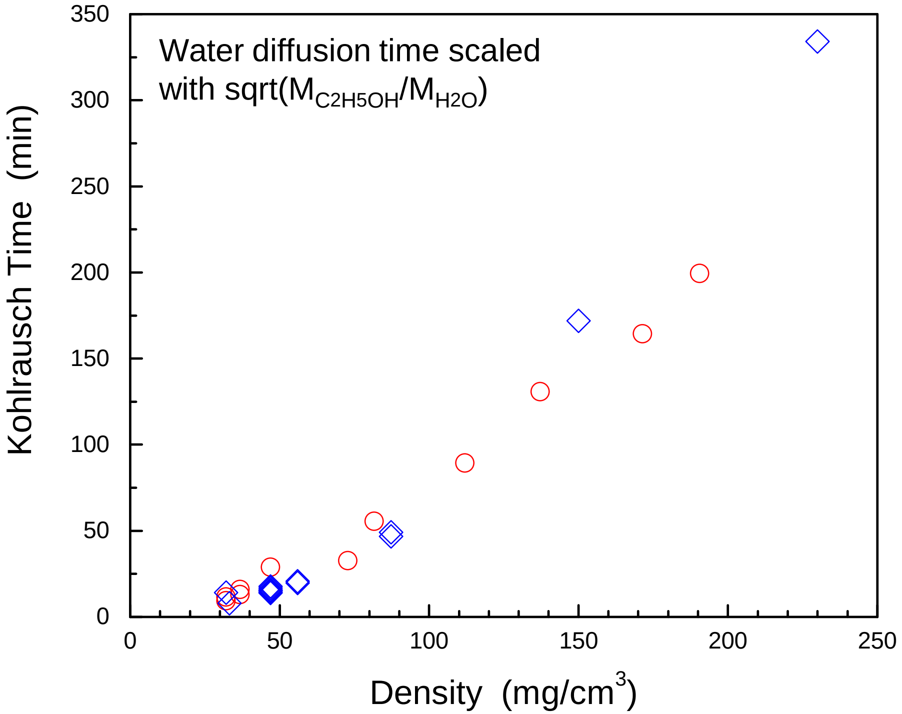
- Ethanol adsorption versus desorption kinetics:
  - Ethanol adsorption competes with ambient moisture; initial weight loss dominant
- Adsorption can be carried in an isolated setup with inert N_2 environment
- Desorption modeled by a Kohlrausch dependence:

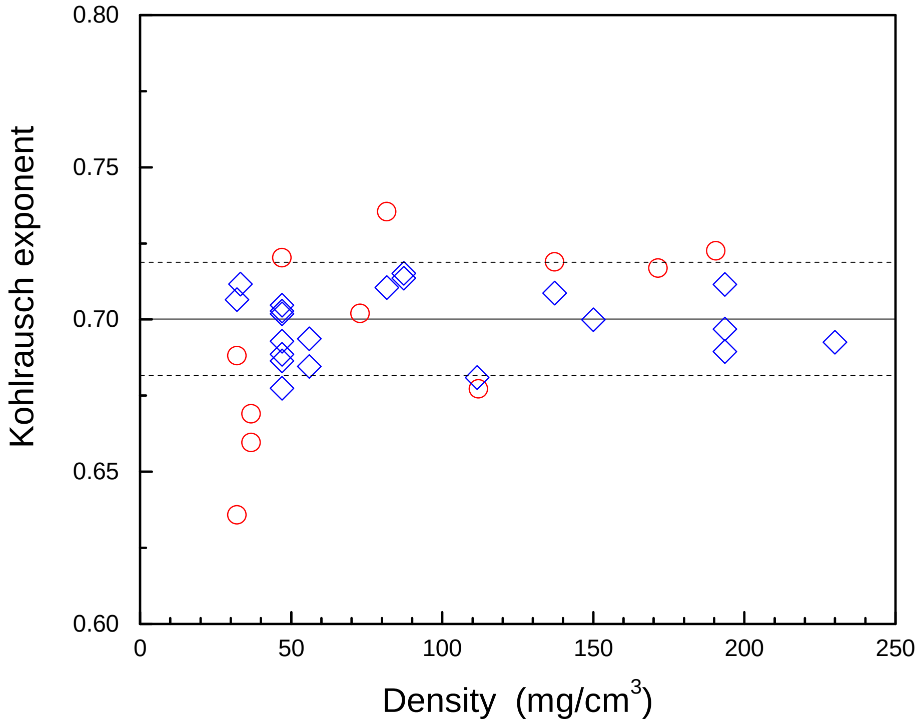
$$W = W_{dry} + \Delta W \cdot e^{-\left(\frac{t}{t_0}\right)^{b}}$$

Kohlrausch exponent

Kohlrausch time

Kohlrausch Analysis:
Ethanol Desorption & Water Adsorption





- Different processes – adsorption and desorption – same kinetic model
- Different species – water and ethanol – similar diffusion-scaled Kohlrausch time
- Kohlrausch exponent as a characteristic of the aerogel microstructure:
  - Practically independent of aerogel density
  - Independent of adsorbate species (tested with water, ethanol, chlorosilanes)
- *Hypothesis*: **Kohlrausch parameters are directly related to tortuosity**

Kohlrausch Behavior and Tortuosity

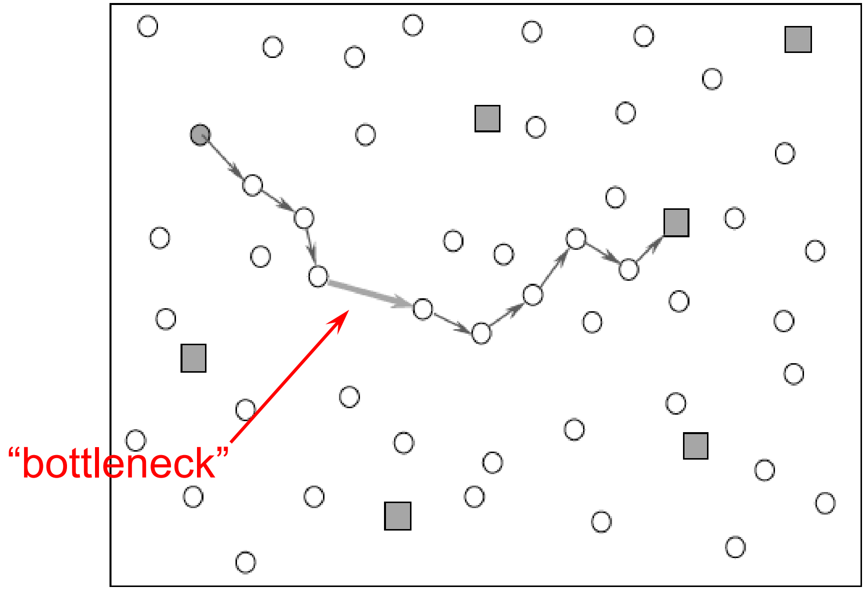
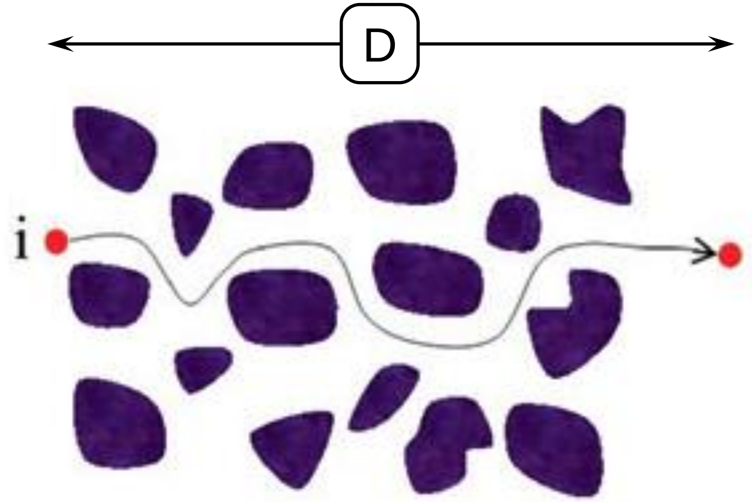


Illustration of the origin of Kohlrausch relaxation in dielectrics due to hopping transport.
B. Sturman *et al.*, *Phys. Rev. Lett.* **91** (2003) 176602

Diffusion in porous media

- L: actual particle path length
- D: projected travelled distance

Tortuosity = L/D

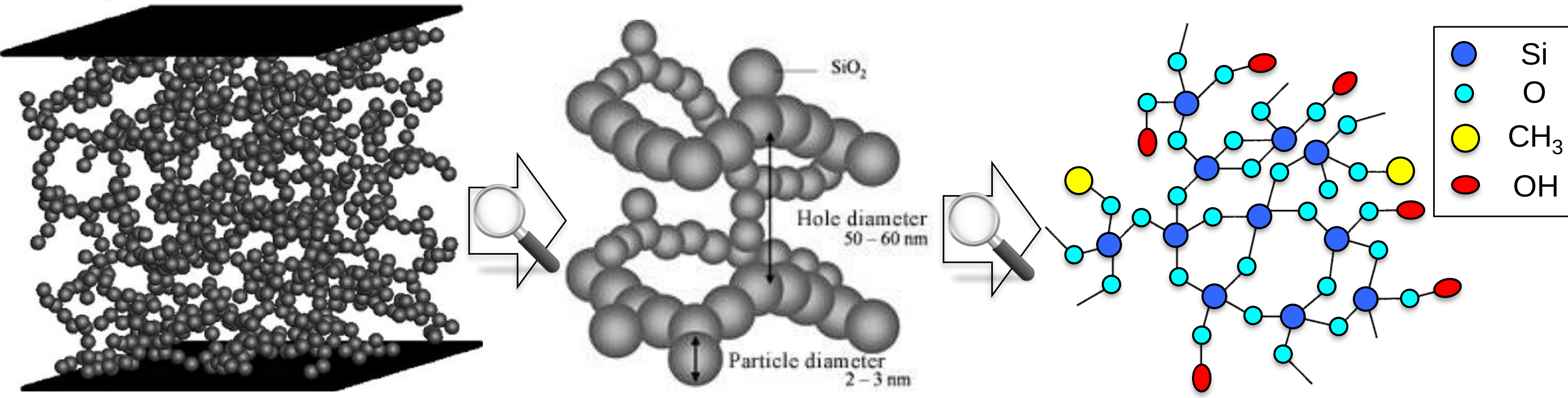


- Hopping transport in random media gives rise to Kohlrausch behavior
- The Kohlrausch exponent is governed by the "bottleneck" (longest traverse)
- Tortuosity, characterizing diffusion in porous media, scales with path length
- Magnitude and probability for longest traverse scales with path length
  - > **Kohlrausch parameters are a measure for tortuosity (morphology)**

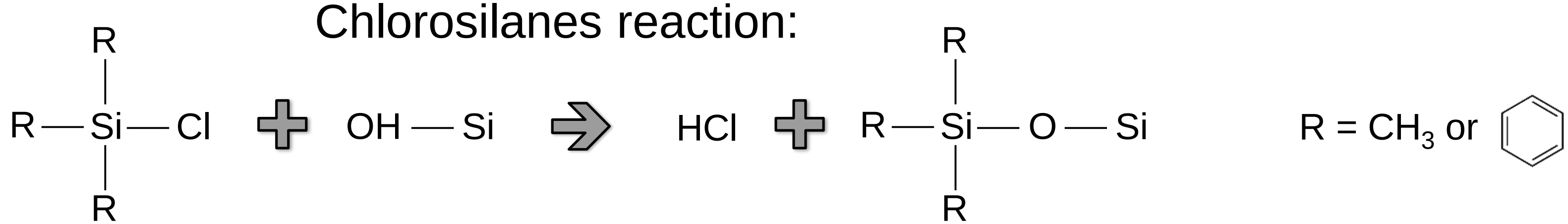
Chemisorption:

Adsorption Site Density

Chlorosilanes Chemisorption



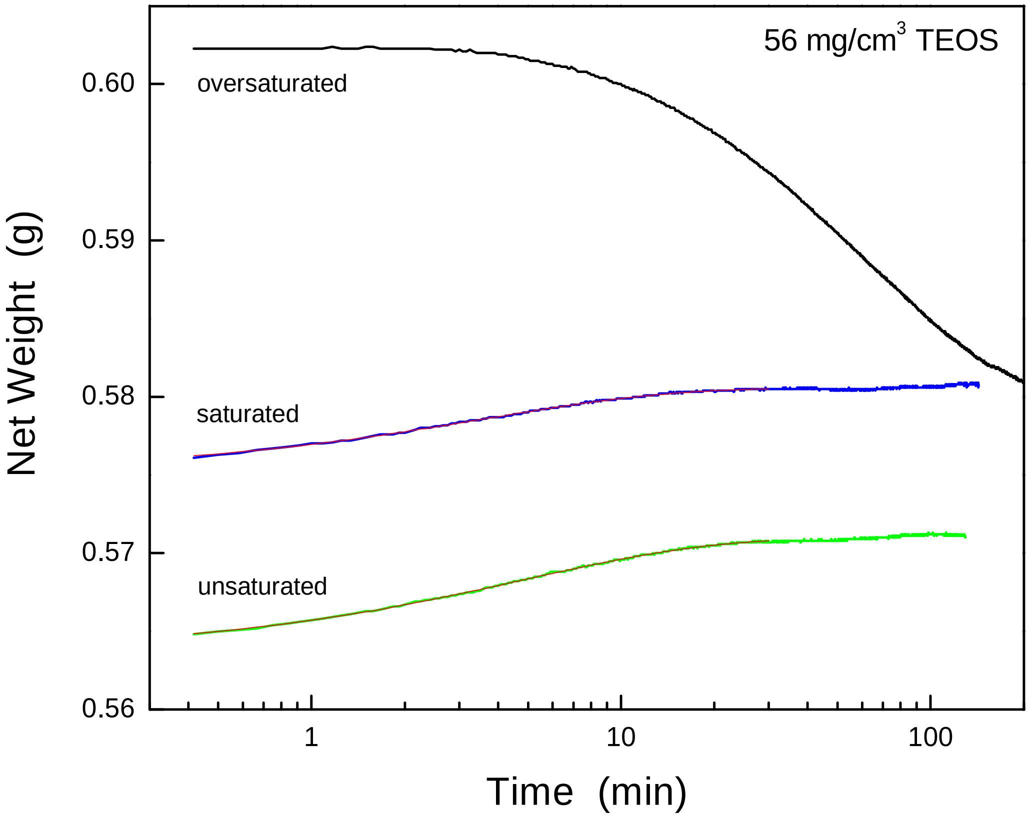
Chlorosilanes reaction:



- Chlorosilanes bind chemically to the silica network (irreversible chemisorption)
- The formed Si-O-Si bonds are stable at drying temperatures (350 °C)
  - Facilitates saturation tests in an incremental accumulation approach
- Chlorosilane type can be varied to change molecular size without changing the reaction (trimethyl, dimethyl-phenyl, methyl-diphenyl, triphenyl chlorosilanes)
  - Trimethyl-chlorosilane: high vapor pressure at RT, small size (high diffusion rate)

TMCS Adsorption in Aerogels: Saturation

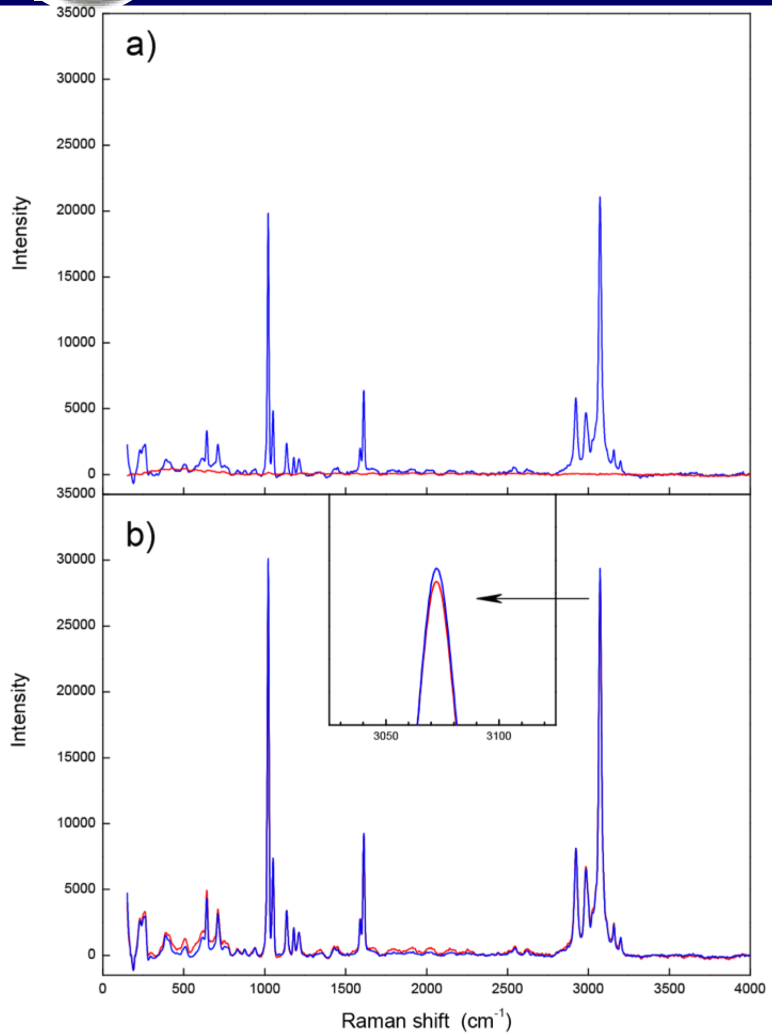
M.P. Petkov *et al.*, *J. Supercritical Fluids*, **106** (2015) 100



Weight gain measurements of one aerogel sample exposed to TMCS multiple times. Unsaturated adsorption (green) is easily discernable. Excessive TMCS diffuses out of oversaturated samples (black). At identical lab conditions, the sample weight at t=0 will approximate the same value (blue), indicating saturation of the chemisorption.

- Process:
  1. Drying aerogel in N_2 at 350 °C
  2. Exposure of aerogel to TMCS in saturated vapors in a bell jar at ambient conditions
  3. Weight gain measurement at t=0
  4. Repeat 1-to-3 until saturation is reached (no further wait gain)
- TMCS does not physisorb efficiently on silica surface; weight gain due to subsequent water adsorption is evident.
- Density of hydroxyl groups in the as-produced sample is calculated from the weight gain at saturated chemisorption.

Adsorbate Uniformity at Saturation



Bulk and surface Raman spectra of unsaturated (top) and saturated with TMCS sample (bottom)

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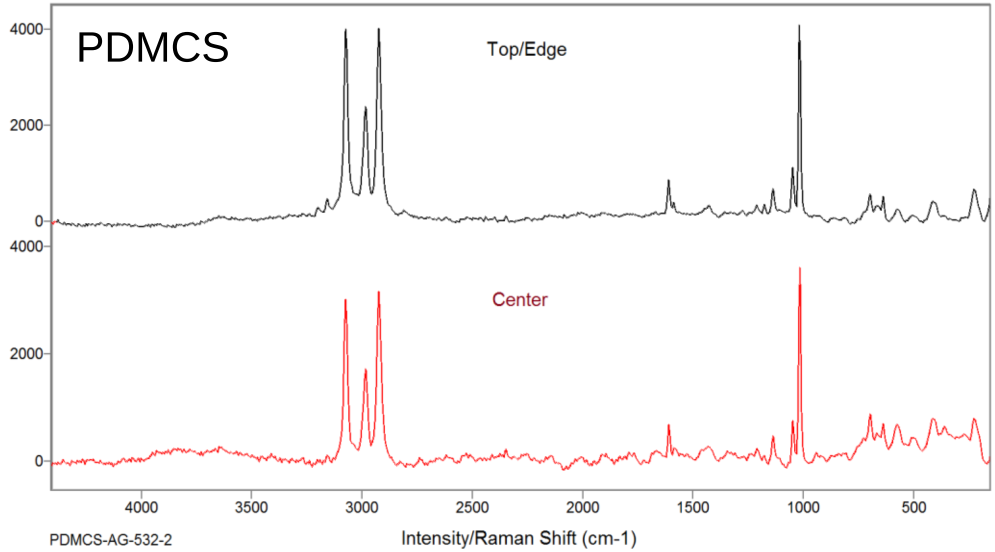
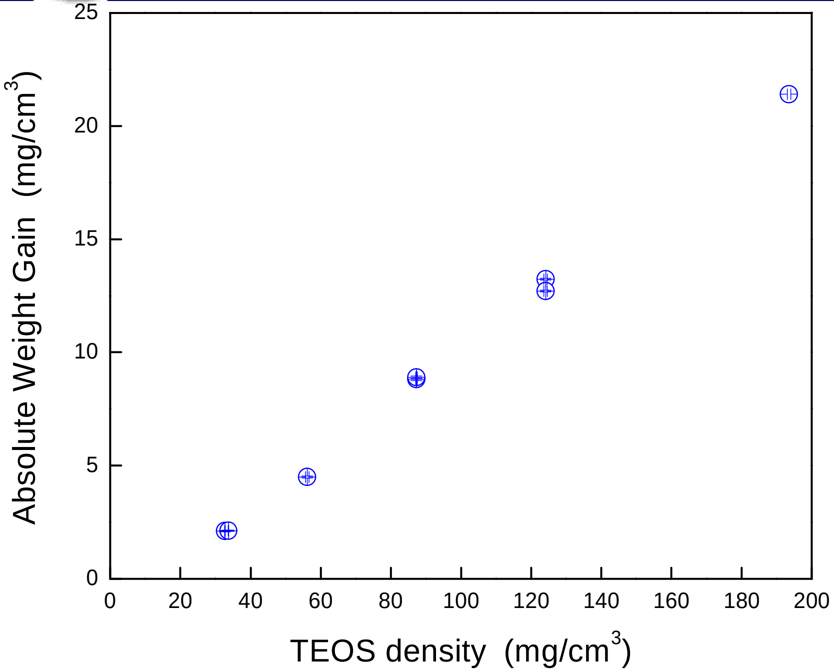


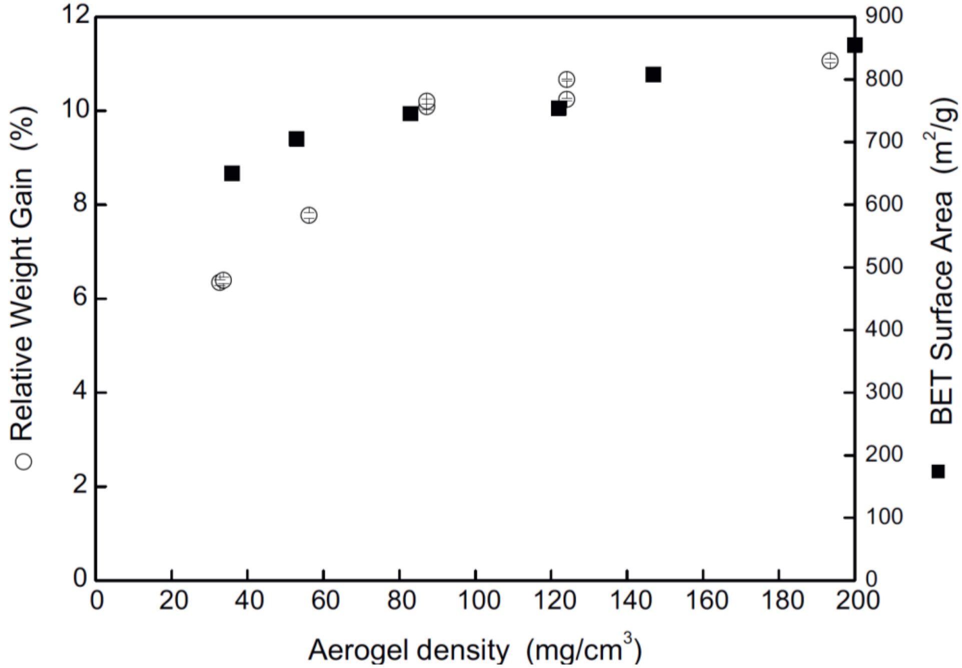
Surface and bulk Raman spectra of saturated with phenyl-dimethyl-chlorosilane (PDMCS) sample.

- Saturated samples exhibit uniform distribution of adsorbent throughout the sample volume
- Sol-gel kinetics imply random distribution of bond centers available to adsorbate
- Bond site density measured through weight gain due to TMCS adsorption is proportional to the intrinsic surface area

Saturated TMCS Adsorption



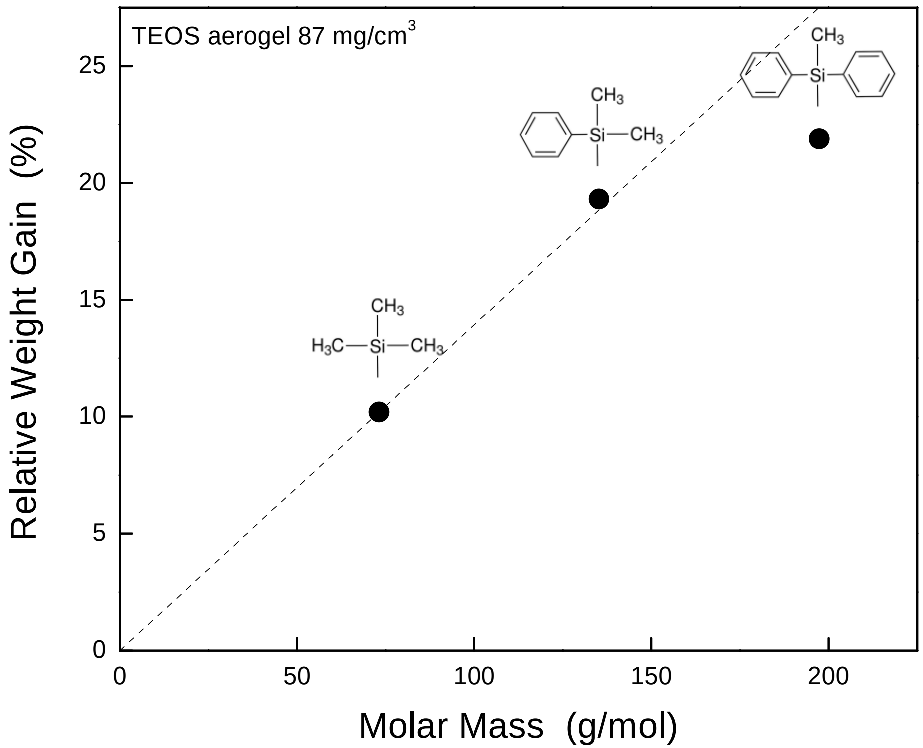
Absolute weight gain due to TCMS adsorption in TEOS aerogel as a function of sample density.



Relative weight gain as a function of sample density.

- Absolute weight gain increases with density, indicating increased intrinsic surface area
- Relative weight gain saturates for >100 mg/cm^3 density, implying similar microstructure for higher TEOS density
- **BET comparison relates N_2-measured surface area to weight gain from TMCS adsorption**

Hydroxyl Group Density Calculation



Maximum attained relative weight gain in 87 mg/cm^3 TEOS aerogel after saturation in trimethyl-chlorosilane, phenyl-dimethyl-chlorosilane and diphenyl-methyl chlorosilane as a function of the adsorbate molar mass. The dashed line is based on the TMCS result alone (not a fit).

- Heavier chlorosilanes have significantly lower vapor pressure, which hinders the experiment
- Linear scaling of the weight gain with the molar mass indicates identical density of bond sites
  - The entire pore volume may not be accessible by larger molecules, or vapor pressure and temperature conditions limit saturation
- OH^- density estimate: 0.76 nm^{-2}
  - Silica surface: 7.8 nm^{-2}
- OH^- density combined with BET is an alternative measure of surface area

Outline

- JPL aerogels: past, present and future
- Porosity and microstructure govern virtually all material properties
- Methods for characterization: pros and cons
  - Density
  - Pore size & size distribution
  - Pore morphology
  - Intrinsic surface
  - Adsorption centers
- Summary

Summary

- Demonstrated a new simple method for measuring the intrinsic surface area based on:
  - Choice of adsorbent (e.g., TMCS), which bonds to the silica network and ***not*** physisorb on itself
  - Measurement of adsorbed mass translates to bond site density
  - Comparison with BET to obtain scaling factor
  - *All you need is a microbalance!*
- Process characteristics:
  - Self-limiting saturated adsorption, very high repeatability
  - Uniformity of TMCS coverage throughout the sample volume
  - Relative ease of working with TMCS due to high vapor pressure
- Relevance to our goals: Direct measurement of bond site density relevant to large organic molecules
- Future plans:
  - Expanding the study to a variety of adsorbates
  - Investigation of adsorption in functionalized TEOS aerogel

Outline

- Motivation: ***Is there a qualitative transition in the microstructure as a function of density?***
- Porosity and microstructure:
  - – Pore size and size distribution
  - – Porosity microstructure – in search of a better description
- Adsorption/desorption through weight measurements
  - – Adsorption kinetics (water, ethanol, chlorosilanes, benzene)
  - – Desorption kinetics (ethanol)
  - – Similarities governed by the microstructure
- Summary

Summary

- Adsorption and desorption of species as methods for probing aerogel microstructure:
  - Kohlrausch (stretched exponential) analysis applied to both cases
    - Indicates obstructed diffusion
  - Characteristic Kohlrausch time comparable between species through diffusion-scaling ($\sim 1/\sqrt{M}$) and identical Kohlrausch exponent, $\beta = 0.70$, for different adsorbates
    - Both infer obstructed diffusion governed by the aerogel microstructure
  - Kohlrausch exponent independent on aerogel density
    - Implies a scale-invariant structure on a typical pore size dimension, scalable through a single linear parameter (e.g., MFP or pore size)
    - Characterization of the gelation process
    - *Proposal*: Kohlrausch exponent is directly related to tortuosity
- Areas of interest for future studies:
  - Expanding the range of adsorbates in aerogel with identical density
  - Comparison of different aerogels (alumina, germania, zirconia, hafnia)
  - Kohlrausch exponent studies in materials with defined tortuosity