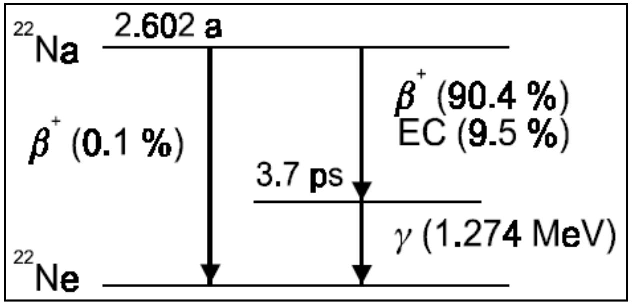
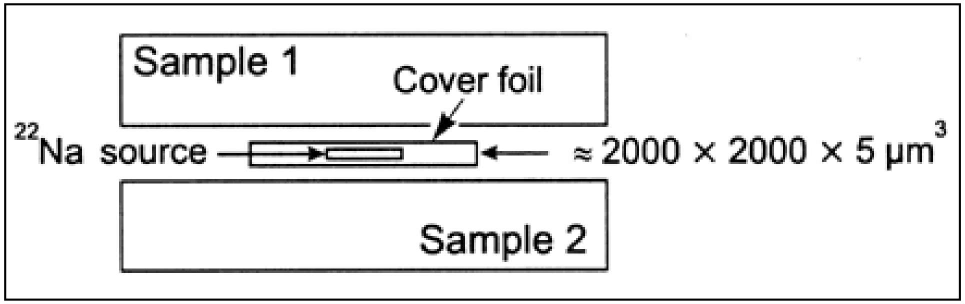
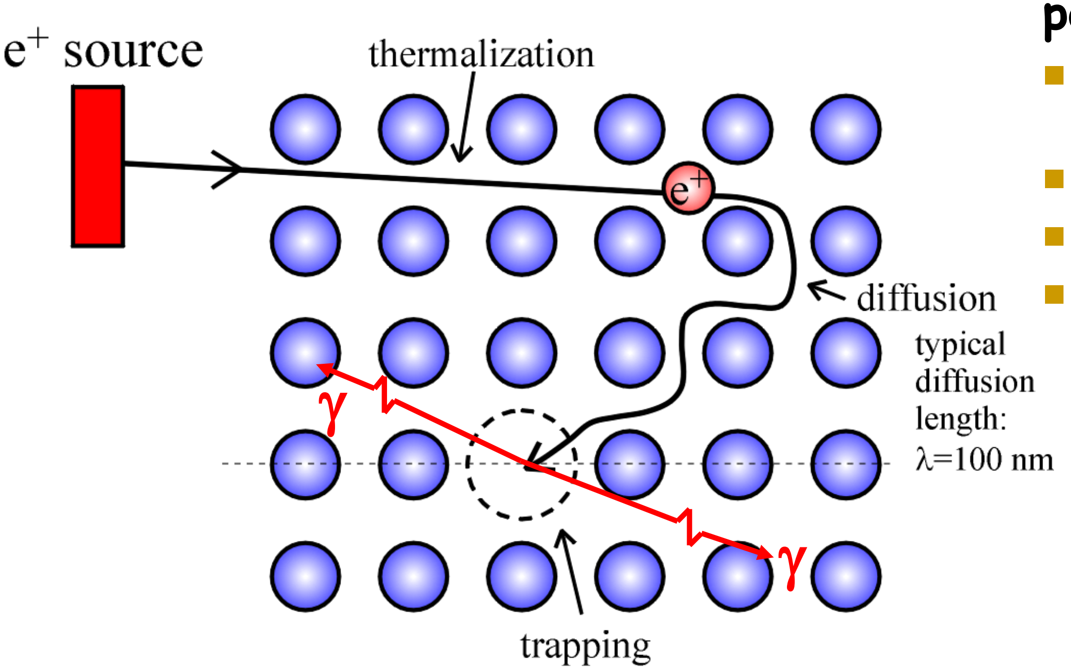
# Porosimetry by Means of Positron Annihilation

**R. Krause-Rehberg, Dept. of Physics, University Halle**

# Positron Annihilation Lifetime Spectroscopy - PALS



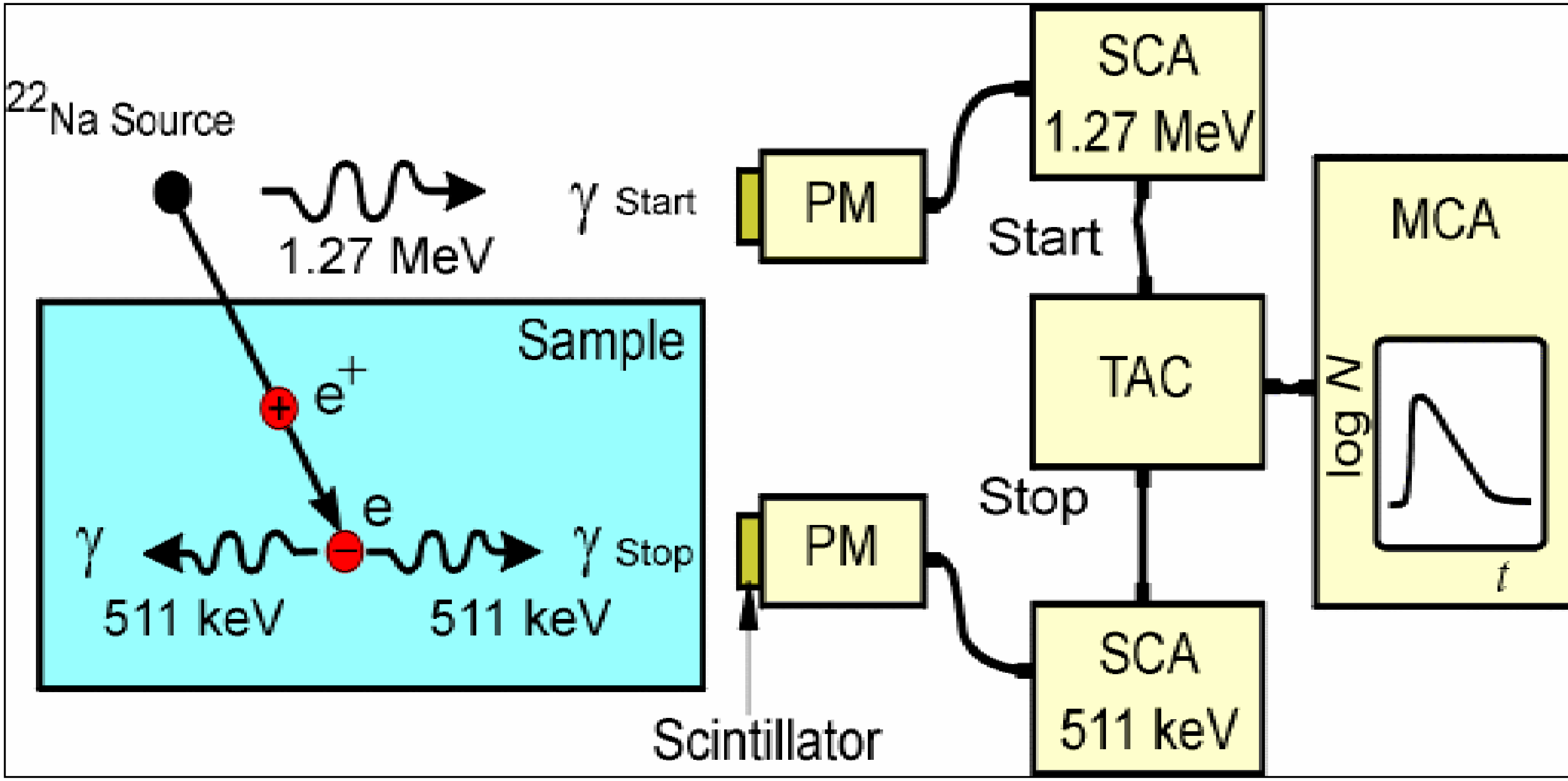

**positrons:**

- thermalize (reach thermal energies)
- diffuse
- being trapped
- and annihilate

**When trapped in vacancies:**

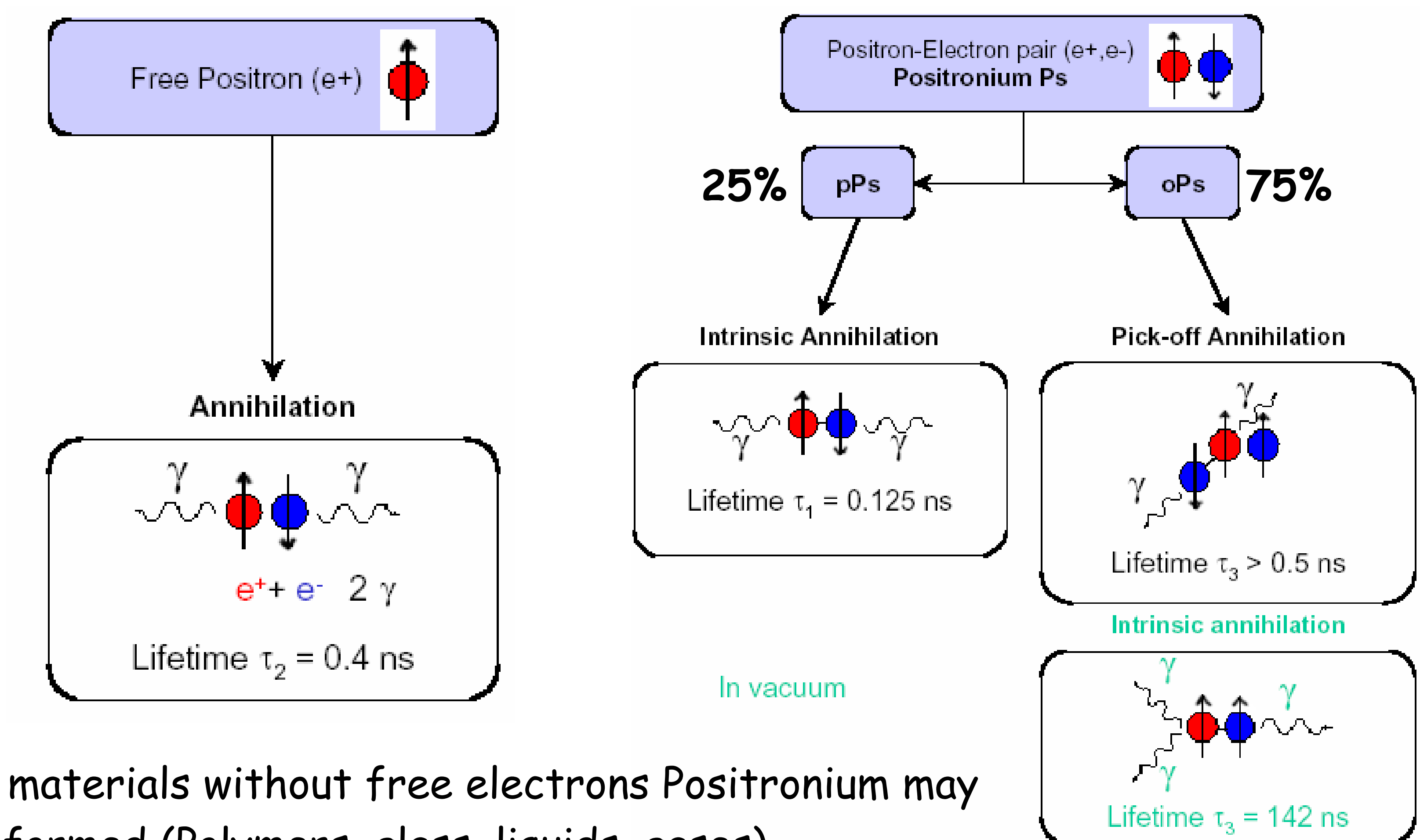
- Lifetime increases due to smaller electron density in open volume

# Measurement of Positron Lifetime



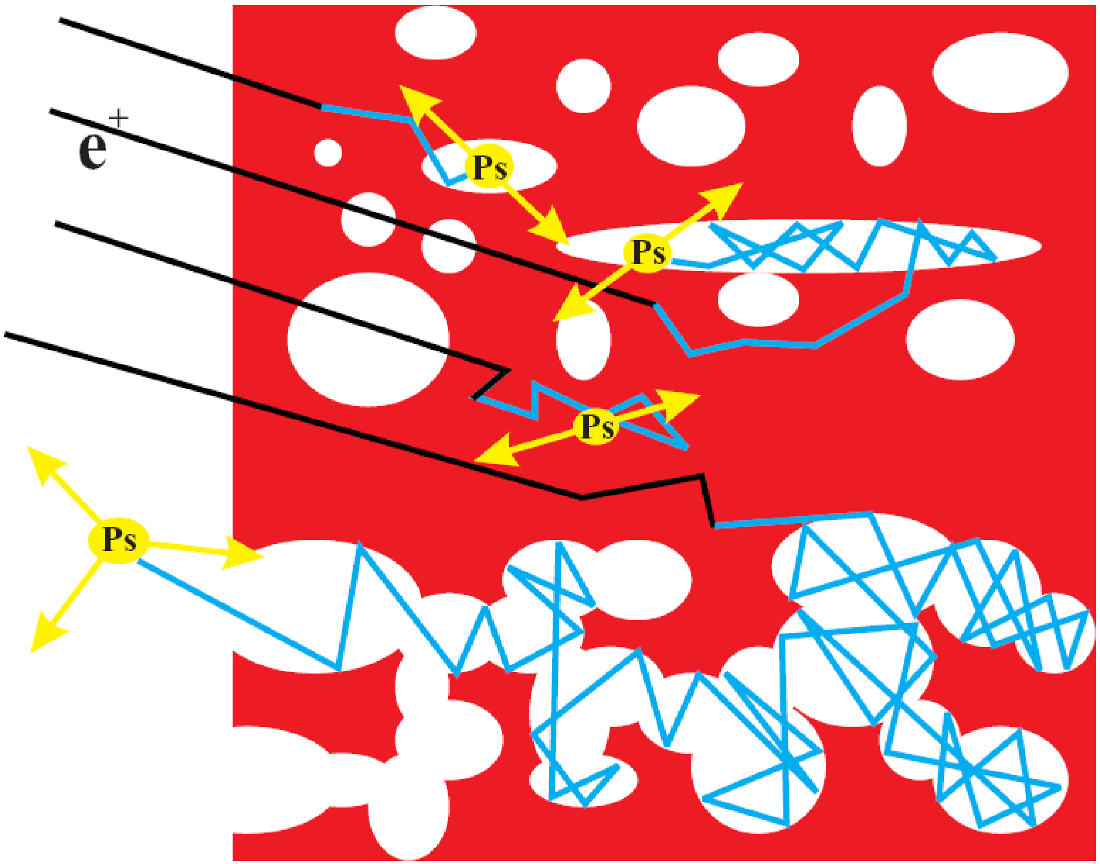

- Positron lifetime: time between 1,27 MeV and 0,511 MeV quanta

# Principles of PALS: ortho-Positronium




- In materials without free electrons Positronium may be formed (Polymers, glass, liquids, gases).

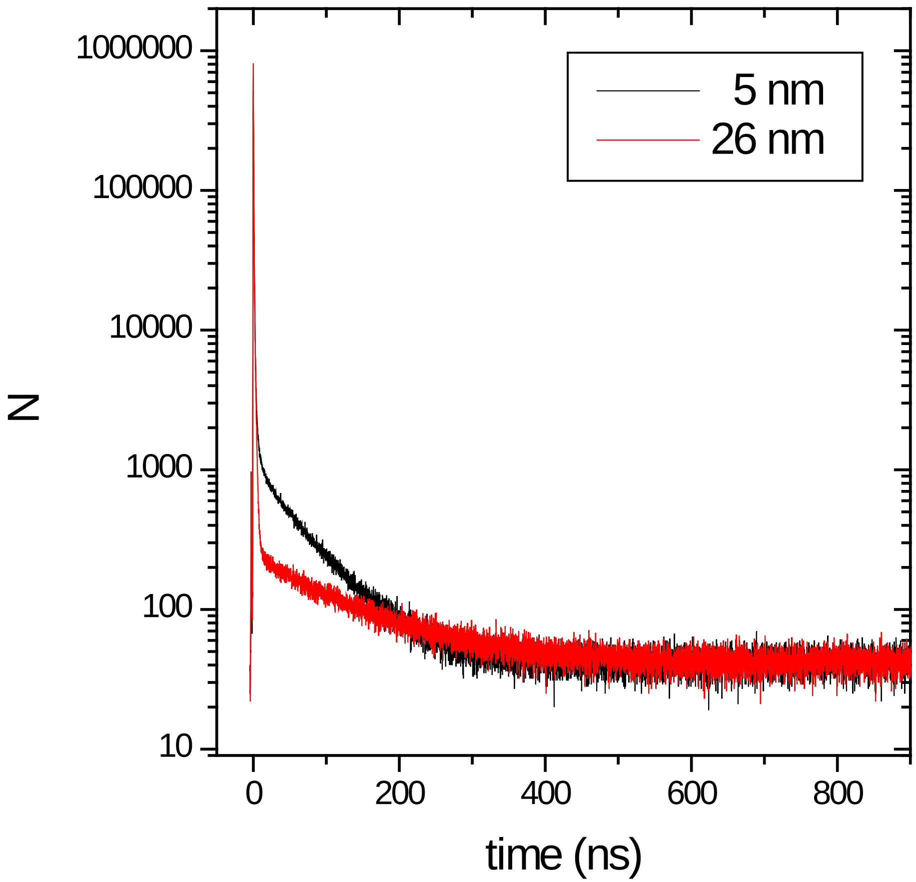
# Principles of PALS: pick-off Annihilation




**pick-off annihilation:**

- o-Ps is converted to p-Ps by capturing an electron with anti-parallel spin
- happens during collisions at walls of pore
- lifetime decreases rapidly
- lifetime is function of pore size 0.5 ns ... 142 ns
- lifetime can be extracted from spectra

# Principles of PALS: typical spectrum

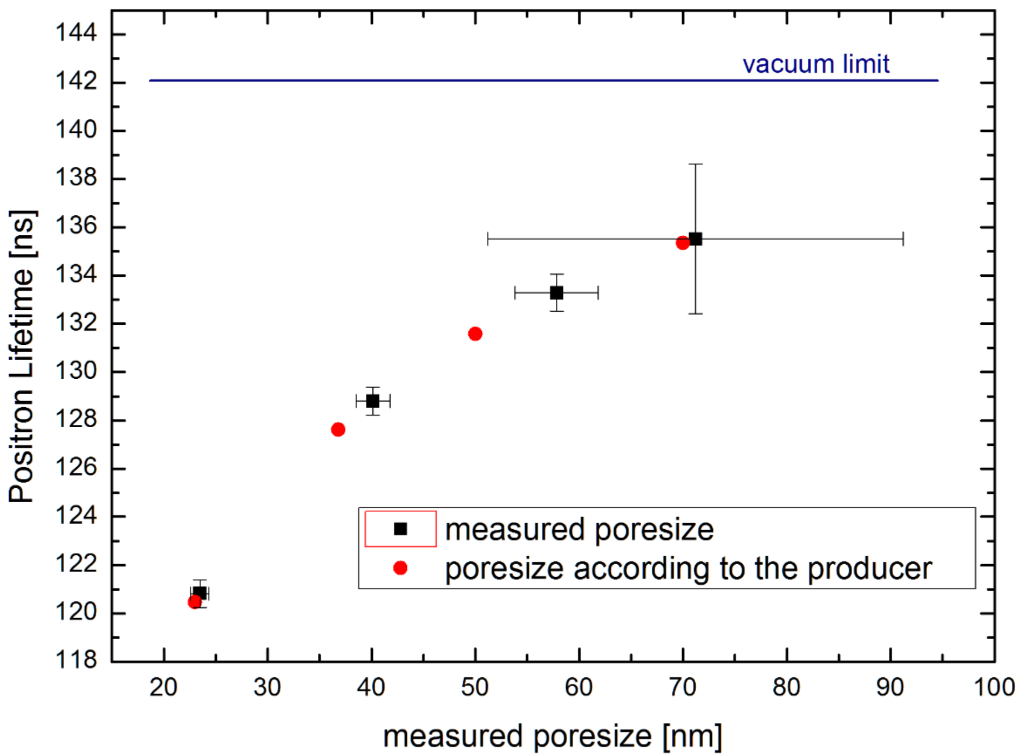



**typical lifetime spectrum for porous glass:**

- 4 exponential decay components
- p-Ps -> 0.125 ns
- free positrons ~ 0.5 ns
- o-Ps in amorphous region of glass ~ 1.5 ns
- o-Ps in pores

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$

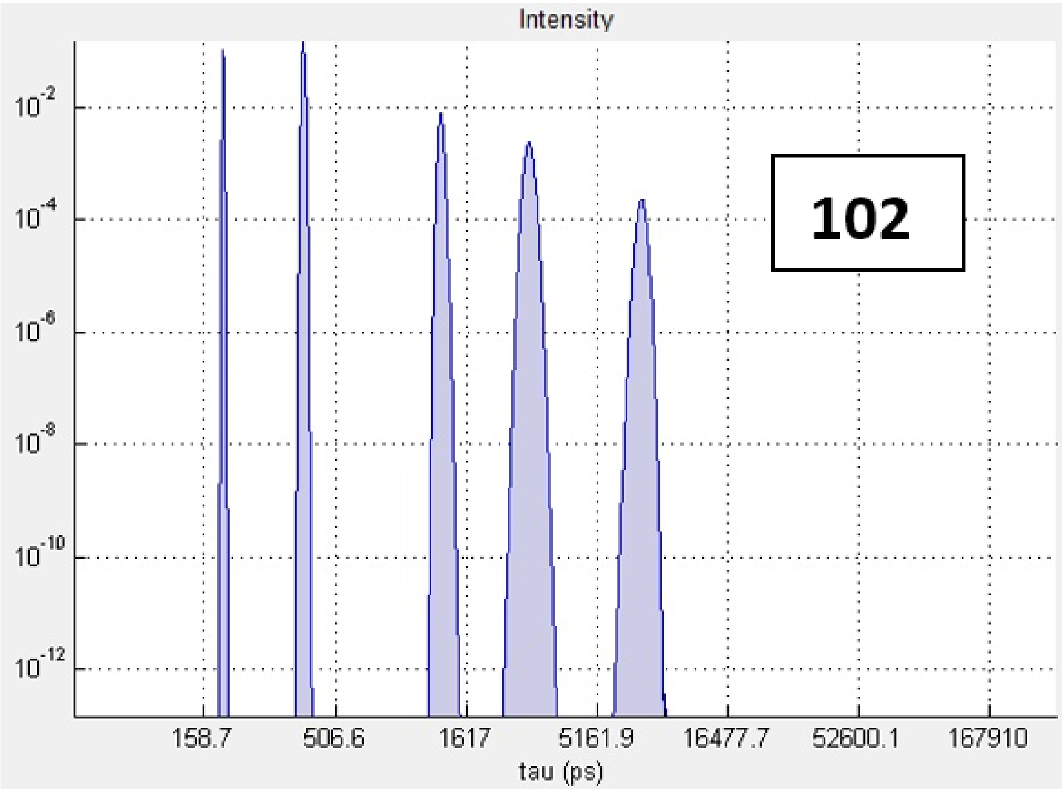
# PALS: detection limits




- lower detection limit: open volume of 3Å diameter
- e.g. open volume between polymer chains

- upper limit: 60 nm diameter
- physical limit: vacuum lifetime of o-Ps = 142 ns
- upper limit depends also on corresponding intensity

# New Analysis Technique: MELT



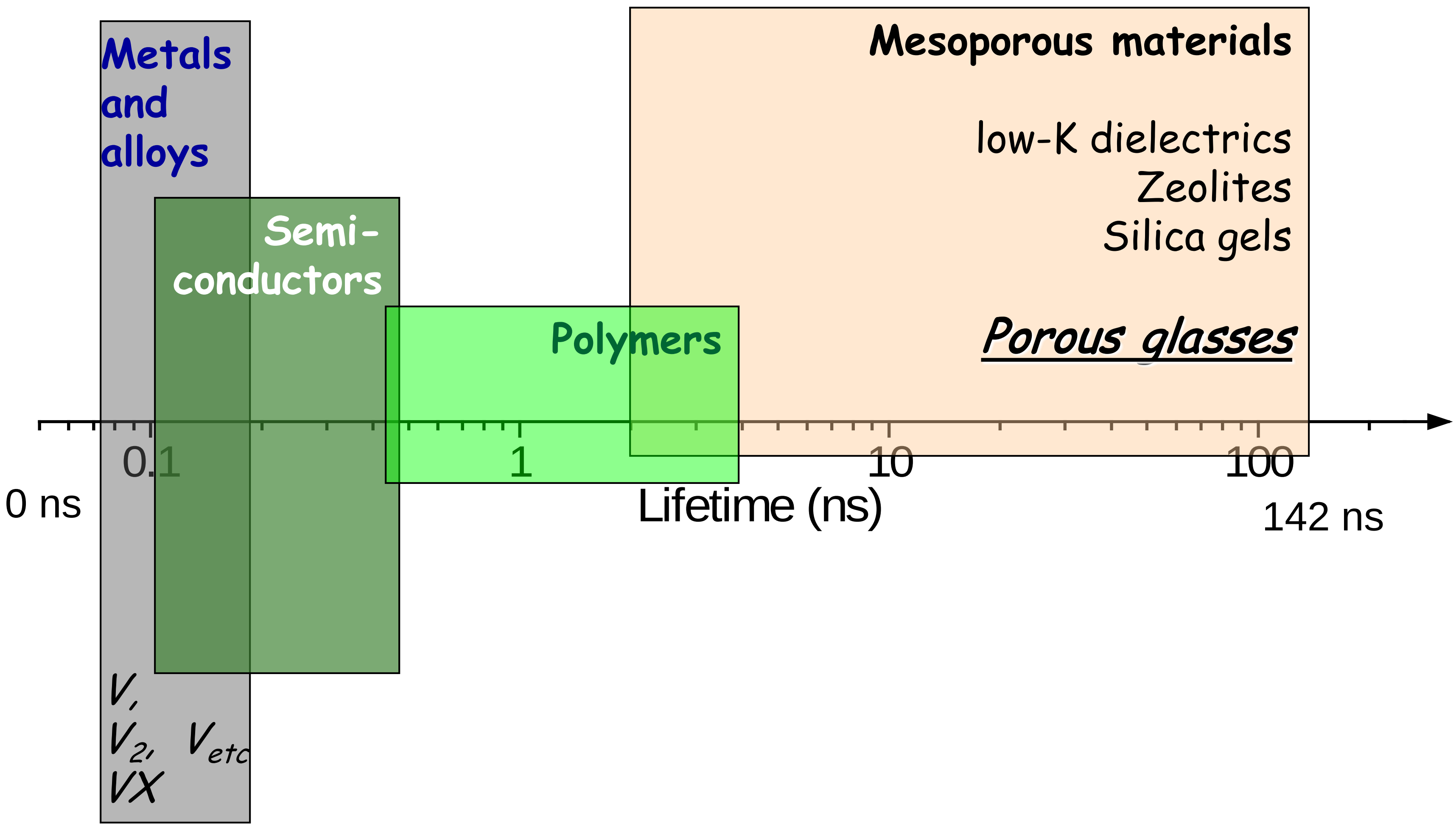

porous polymer

**MELT = Maximum Entropy for Lifetime Analysis**

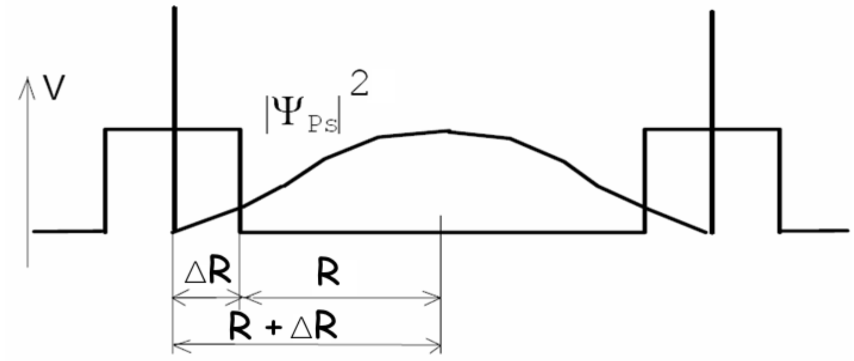
- number of components must not be known
- output is intensity versus lifetime
- pore size distribution can be determined
- disadvantage: very high statistics necessary (> $10^7$ counts)


A. Shukla et al., 1997, Materials Science Forum, 255-257, 233

# Principles of PALS: typical lifetimes



# The TE model




- Annihilation rate: $$\frac{1}{\tau_{o-Ps}} = \lambda_{o-Ps}$$ $$= \lambda_{2\gamma} + \lambda_{3\gamma}$$ $$= \lambda_{2\gamma}^{0}(P) + \lambda_{3\gamma}^{0}(1-P) \cong \lambda_{2\gamma}^{0}(P)$$ $$\lambda_{2\gamma}^{0} = \frac{\lambda_S + 3\lambda_T}{4} = \lambda_A \approx 2ns^{-1}$$
- Pore size < 1 nm -> $\lambda_{3\gamma}$ neglected, only pick off annihilation

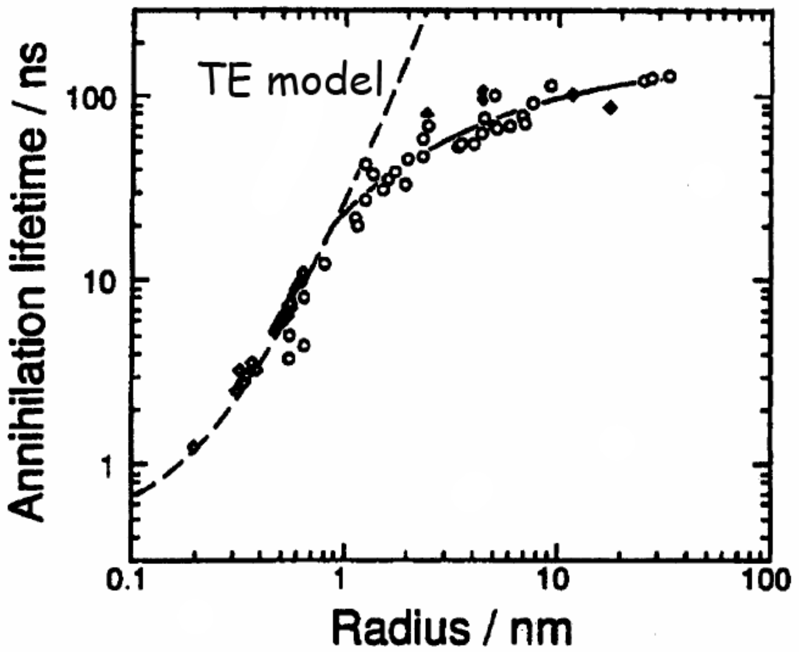
$$\lambda_{TE}(R) = \lambda_A \left[ 1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi} \sin\left( \frac{2\pi R}{R+\Delta R} \right) \right]$$

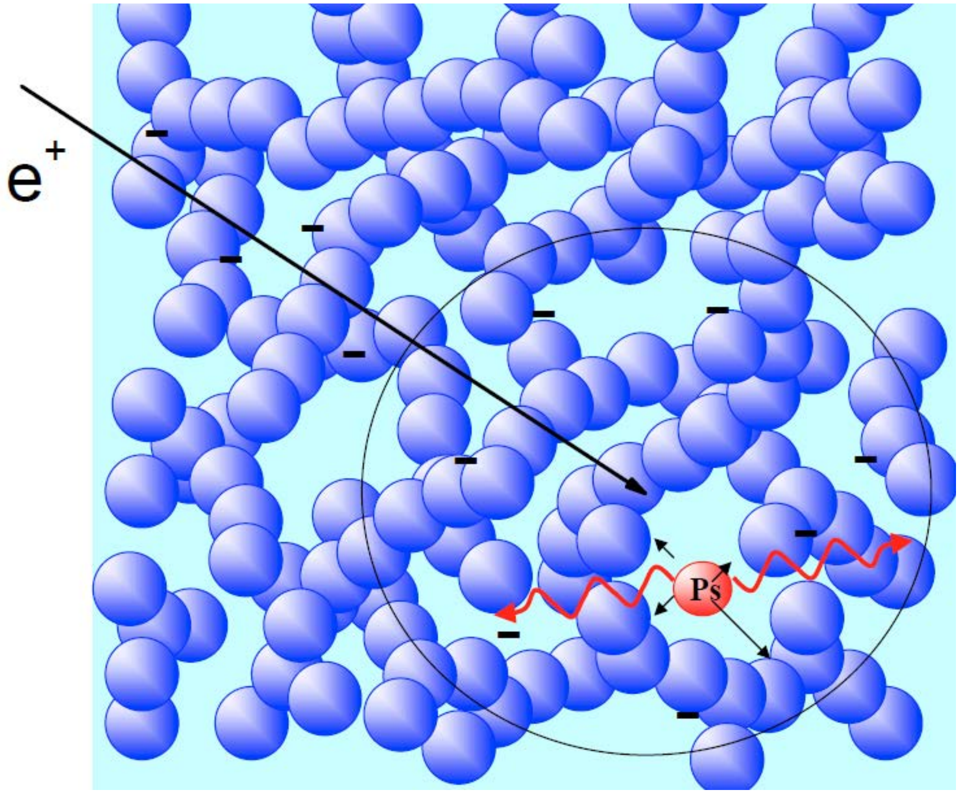
- $\Delta R$ = 0.166 nm determined by Eldrup and Jean
- Pore size > 1 nm ->$\lambda_{3\gamma}$ cannot be neglected, temperature dependence of o-Ps lifetime (excited states)

Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499-5510. / Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51-58.

# The TE model

- TE model valid for r > 2nm
- very successful for open-volume characterization in polymers

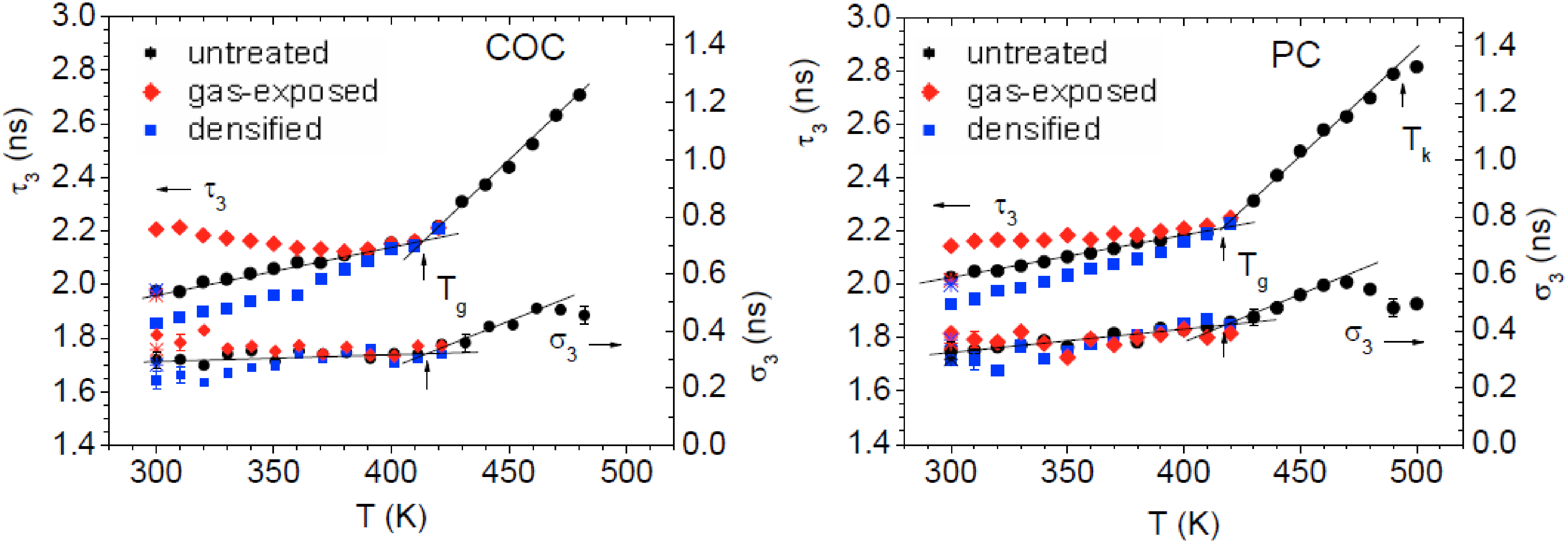




Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499-5510. / Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51-58.

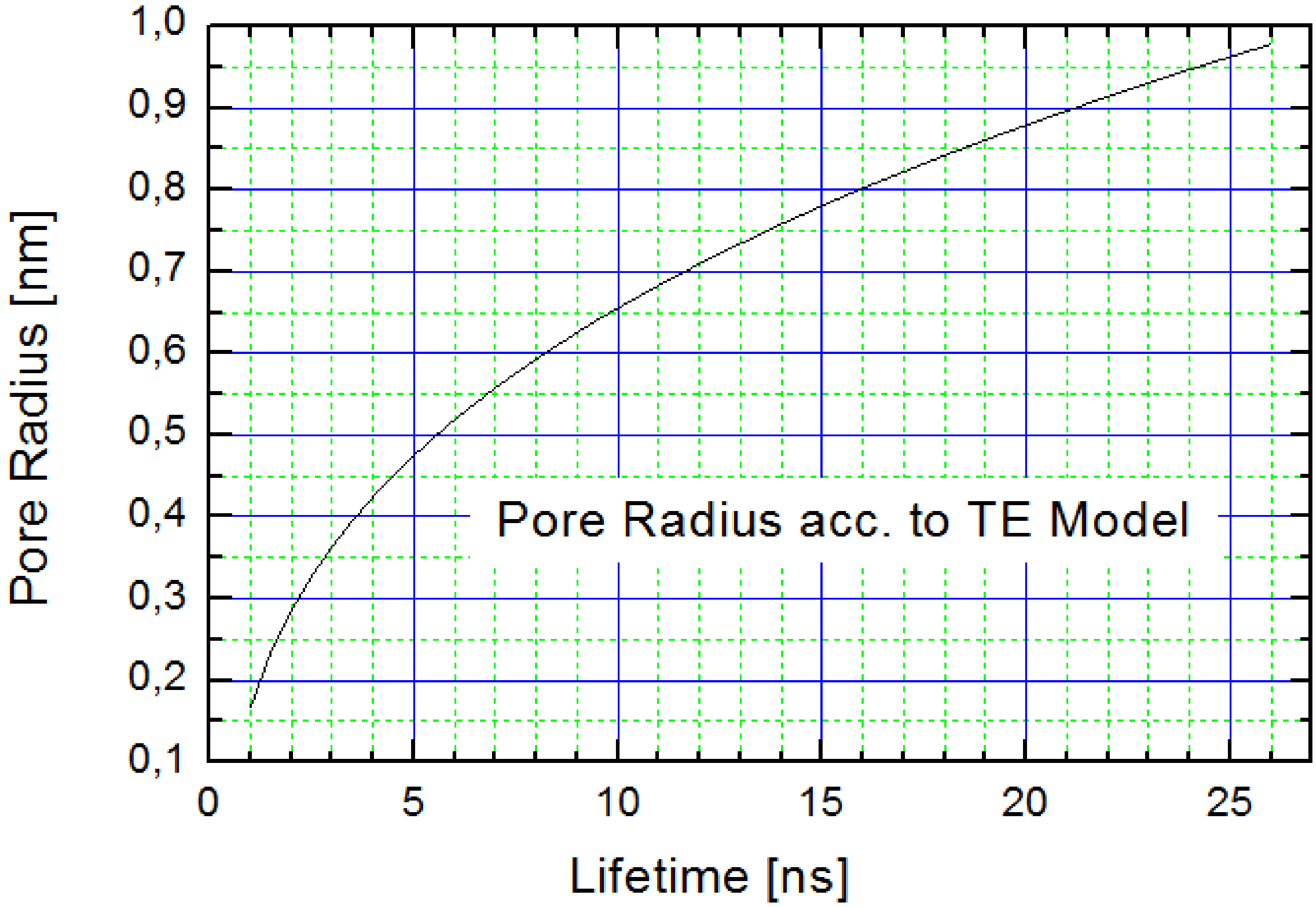
# Polymer research




PALS study of different polymers under $CO_2$ gas exposure and pressure densified (200 MPa)

G. Dlubek et al., Macromol. Chem. Phys. 2008, 209, 1920–1930 and e-Polymers 2007, no. 108

# The TE model (valid until 1 nm radius)





Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499-5510. / Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51-58.

# Polymer research

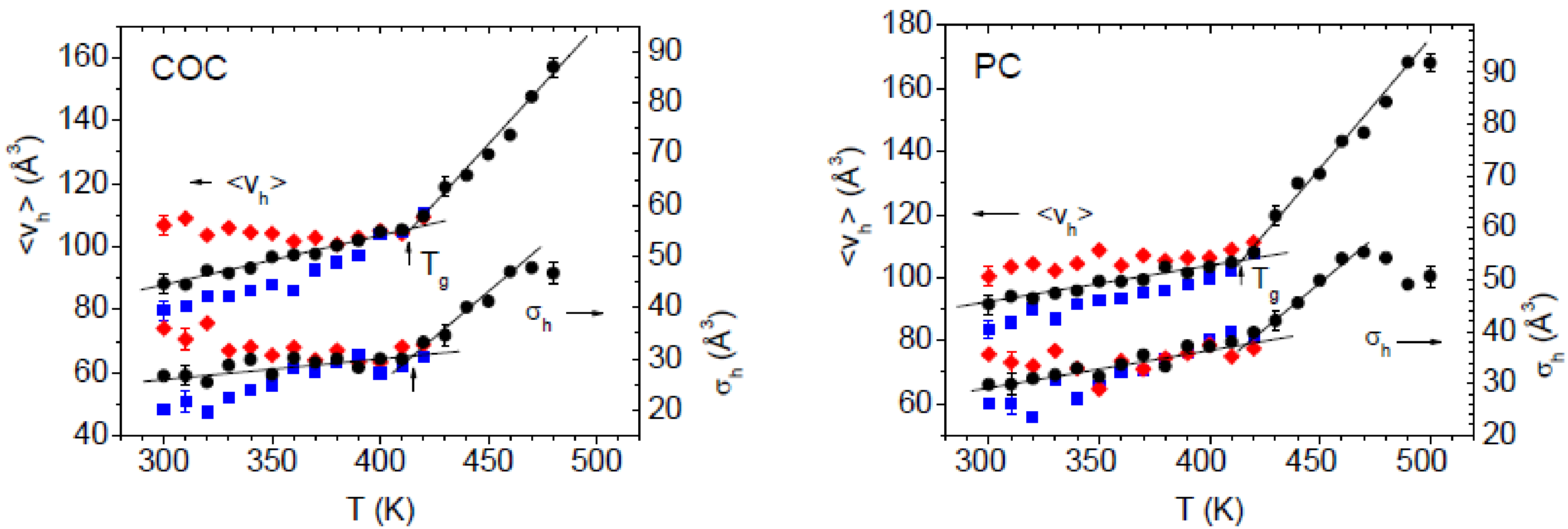



**Fig. 5.** The mean, $\langle v_h \rangle$, and the mean dispersion, $\sigma_h$, of the hole volume as a function of temperature $T$ for untreated (black), densified at 200 MPa (blue), and $CO_2$ gas-exposed and degassed (red) COC and PC.

G. Dlubek et al., Macromol. Chem. Phys. 2008, 209, 1920–1930 and e-Polymers 2007, no. 108

# Polymers under confinement conditions

| Sample | $\tau_1$ (ns) | $I_1$ (%) | $\tau_2$ (ns) | $I_2$ (%) | $\tau_3$ (ns) | $I_3$ (%) | $\tau_4$ (ns) | $I_4$ (%) |
|---|---|---|---|---|---|---|---|---|
| Reference $PSiO_2$ empty | 0.1194 ±0.0021 | 30.6 | 0.510 ±0.0047 | 27.28 ±0.66 | 1.652 ±0.0022 | 28.23 ±0.75 | 85.799 ±0.362 | 13.88 ±0.43 |

≈10 nm diameter

####### After filling the sample with polymer.

- Three component decomposition is very good (Variance= 1.13).

All component are free

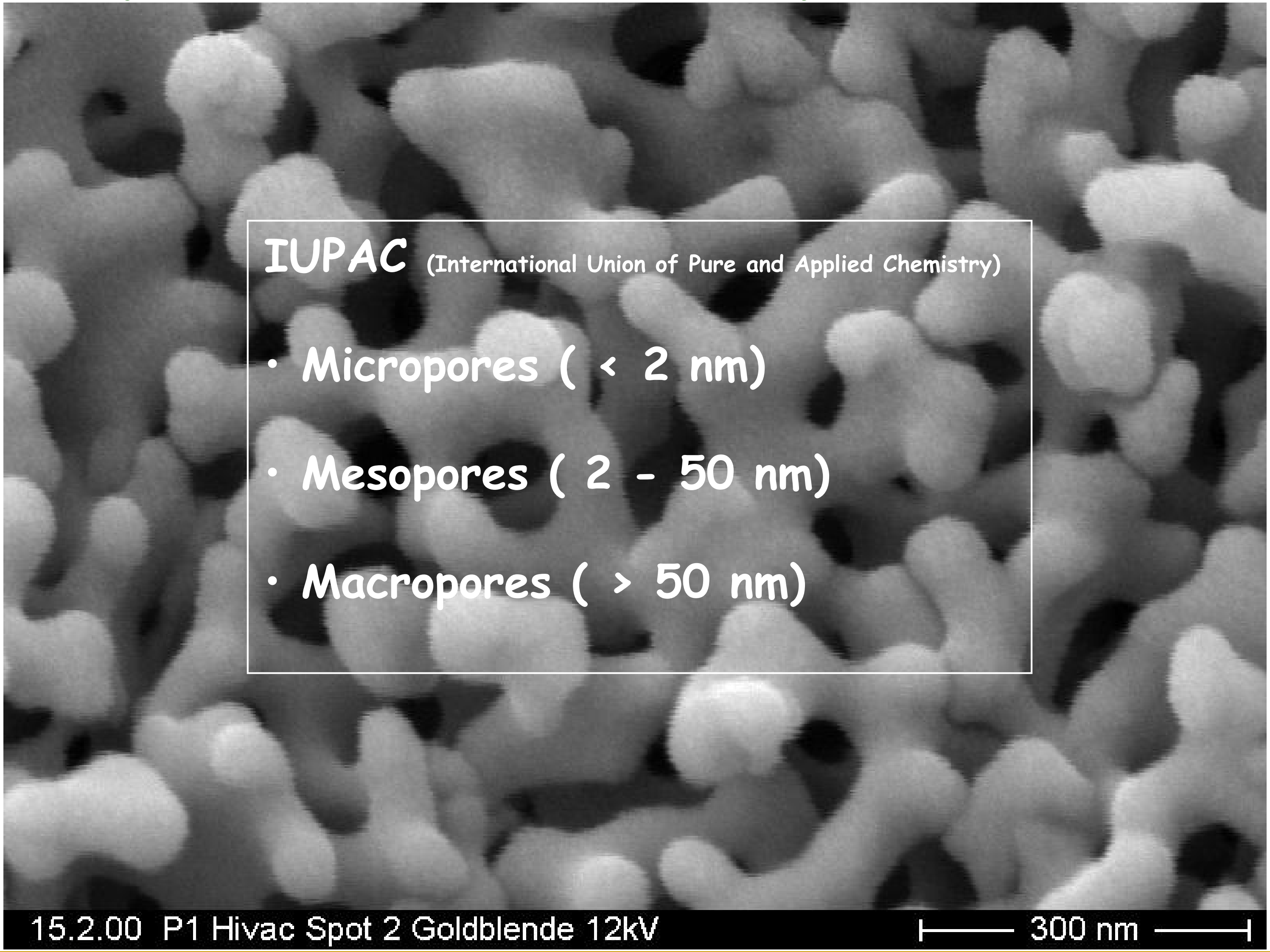
| Sample | $\tau_1$ (ns) | $I_1$ (%) | $\tau_2$ (ns) | $I_2$ (%) | $\tau_3$ (ns) | $I_3$ (%) |
|---|---|---|---|---|---|---|
| PMPS in $PSiO_2$ | 0.1555 ±0.0016 | 35.8 | 0.6477 ±0.0027 | 27.31 ±0.56 | 2.740±0.002 9 | 36.88 ±0.404 |

polymer filled pores

Wycliffe Kiprop Kipnusu
University of Leipzig,
Faculty of Physics and Earth Science
Institute of Experimental Physics I
Division of ''Molecular Physics''
Linnestraße 5,
04103 Leipzig, Germany

- experiments planned to observe open volume in polymer under confinement
- shift of glass temperature?
- experiment just running…

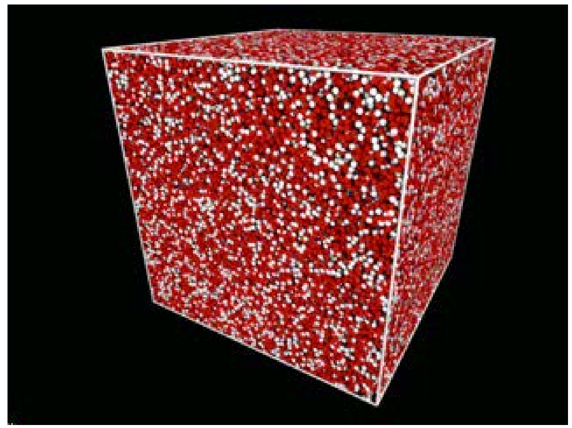
# Mesopores - Controlled pore glasses



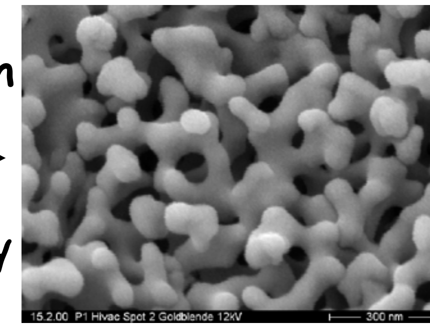
# Controlled pore glasses - CPG

**VYCOR-Process**

*alkali borosilicate glass* → **T** (*530 - 710°C*) →



→ **Extraction** (*HCl/NaOH*) →

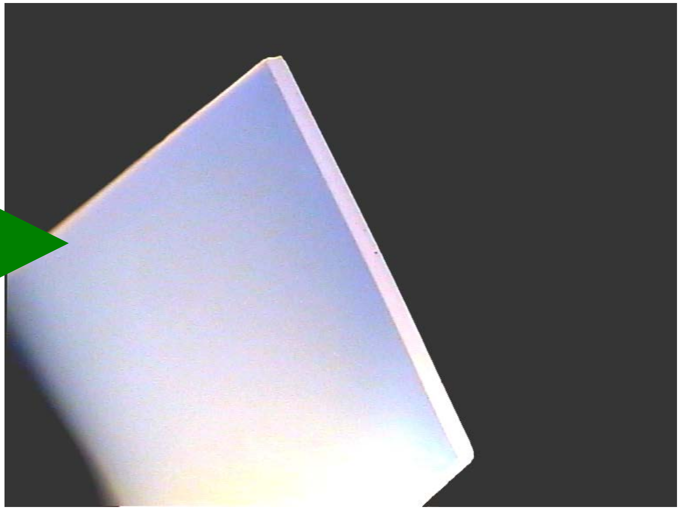



## *$d_p$ 1 to 110 nm*

- spinodal phase separation
- decomposition is initiated by heat treatment
- alkali rich borate phase <-> pure silica
- alkali phase soluable in acid -> silica network
- pore size depends on basic material
- shape depends on duration and T of heat treatment

F. Janowski, D. Enke in F. Schüth, K.S.W. Sing, J. Weitkamp (Eds.), *Handbook of Porous Solids*, WILEY-VCH, Weinheim, **2002**, 1432-1542.

# Controlled pore glasses - CPG



**porous microspheres:**

- 100 µm

**porous membranes:**

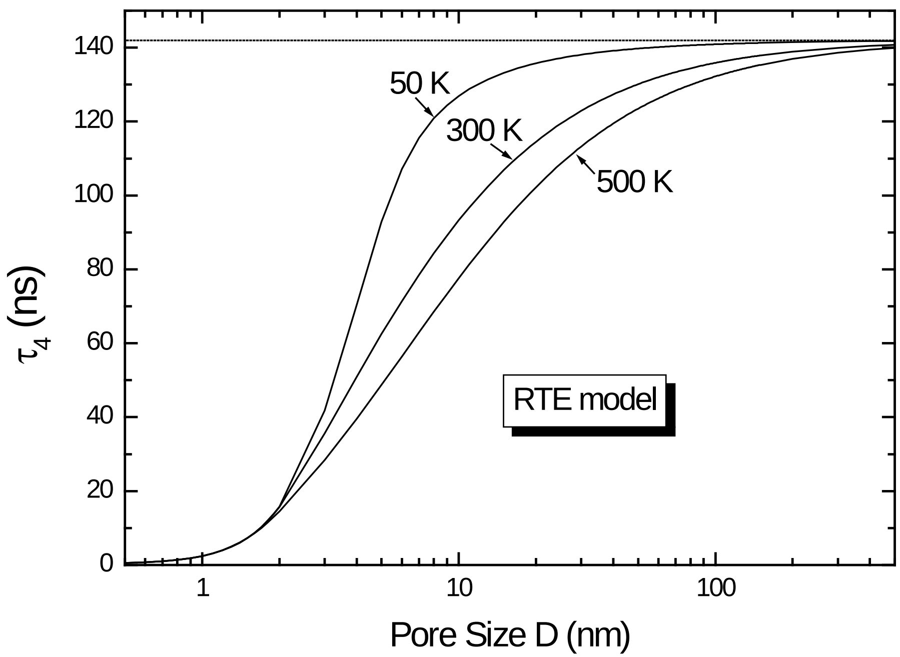
- 20 x 20 x 0.2 mm

DE-Patent 19848377 A1

# Model for R > 1 nm - RTE

- Rectangular TE model = RTE model (for 3D cubic pores):

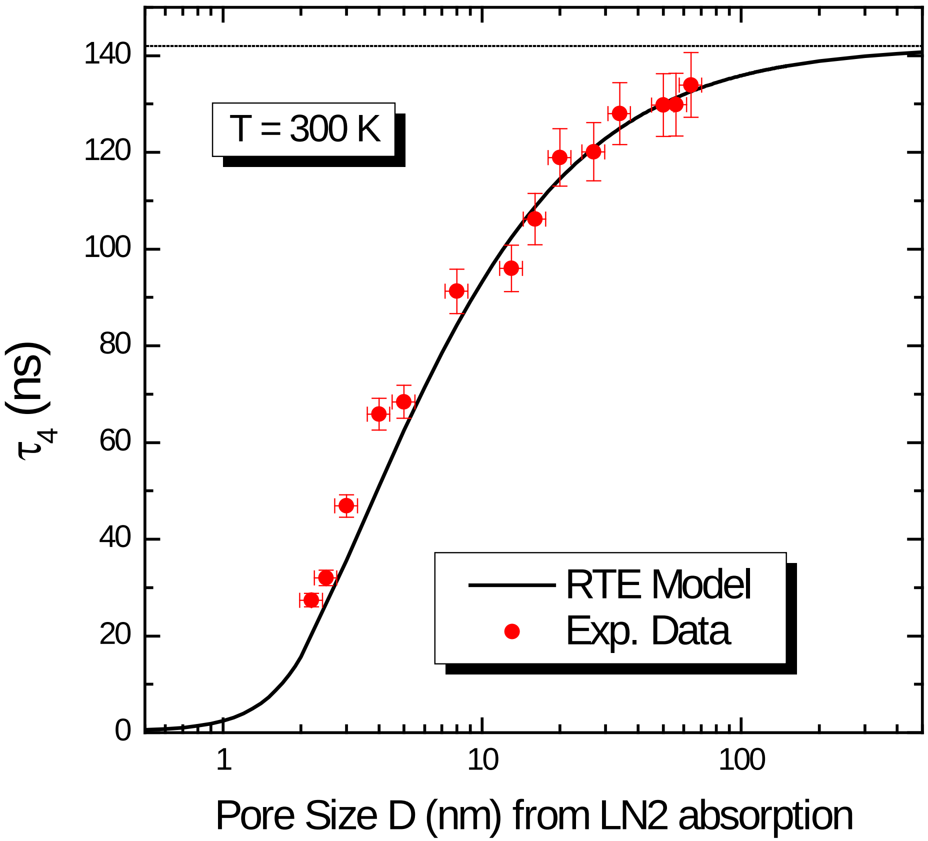
$$\lambda_{RTE}(D,T) = \lambda_A - \frac{\lambda_S - \lambda_{3\gamma}}{4}\left[1 - \frac{2\delta}{D} + \frac{\sum_{i=1}^{\infty} \frac{1}{i\pi}\sin\left(\frac{2i\pi\delta}{D}\right) e^{\left(\frac{-\beta i^2}{D^2 kT}\right)}}{\sum_{i=1}^{\infty} e^{\left(\frac{-\beta i^2}{D^2 kT}\right)}}\right]^3$$




- Boltzmann statistics ascribes explicit temperature dependence to the lifetime
- Rectangular geometry -> prevention of complicated Bessel functions
- $\delta$= 0.18 nm analogous to TE model

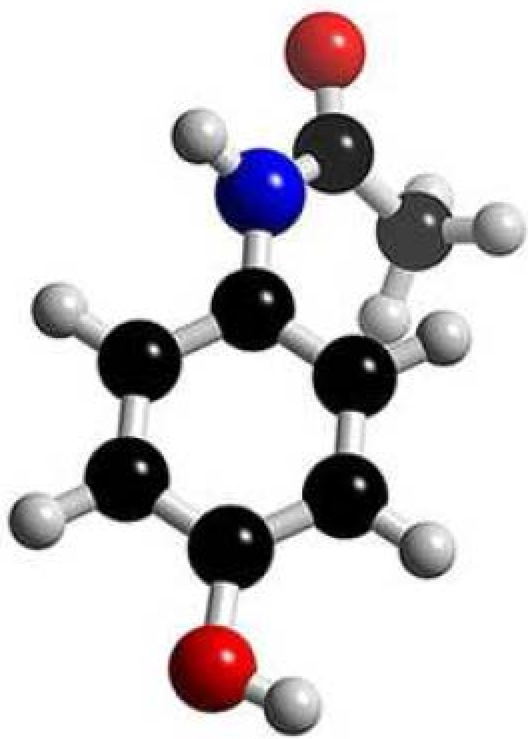
D. W. Gidley, T. L. Dull, W. E. Frieze, J. N. Sun, A. F. Yee, *J. Phys. Chem. B* **2001**, *105,* 4657.

# The experiments at room temperature



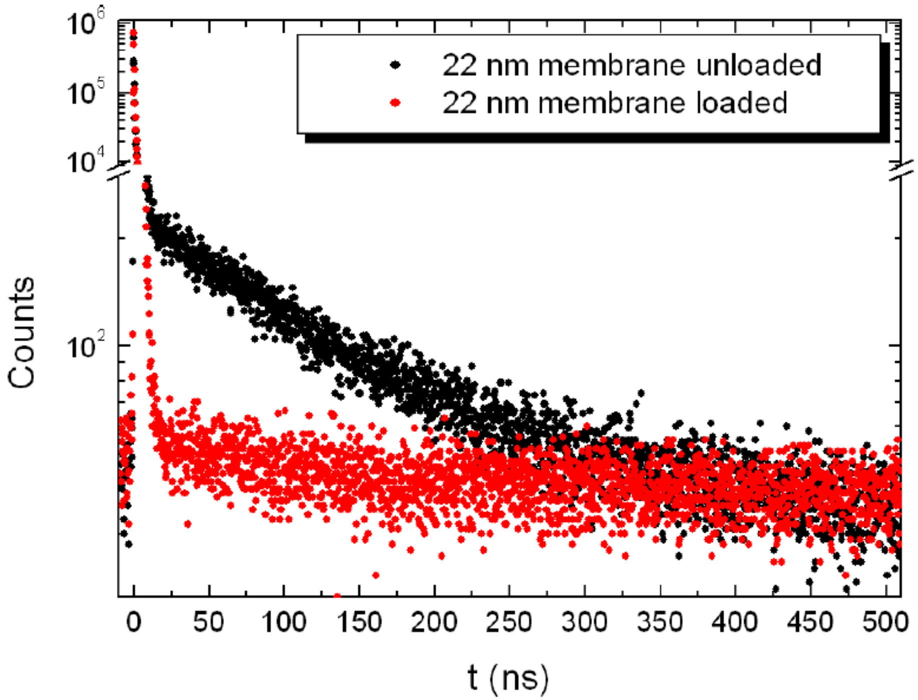

- we measured porous glass in a broad pore size range
- pore size obtained by $N_2$-adsorption method
- for T=300 K general agreement to the RTE model
- calibration curve for the correlation of o-Ps lifetime and pore size

# Loading of Mesopores by Drugs



- CPG membranes have been loading with Acetaminophen ($C_8H_9NO_2$) – also known as Paracetamol
- different pore sizes were studied
- filling by dropping membrane in hot melt of drug
- degree of filling can be studied with positrons

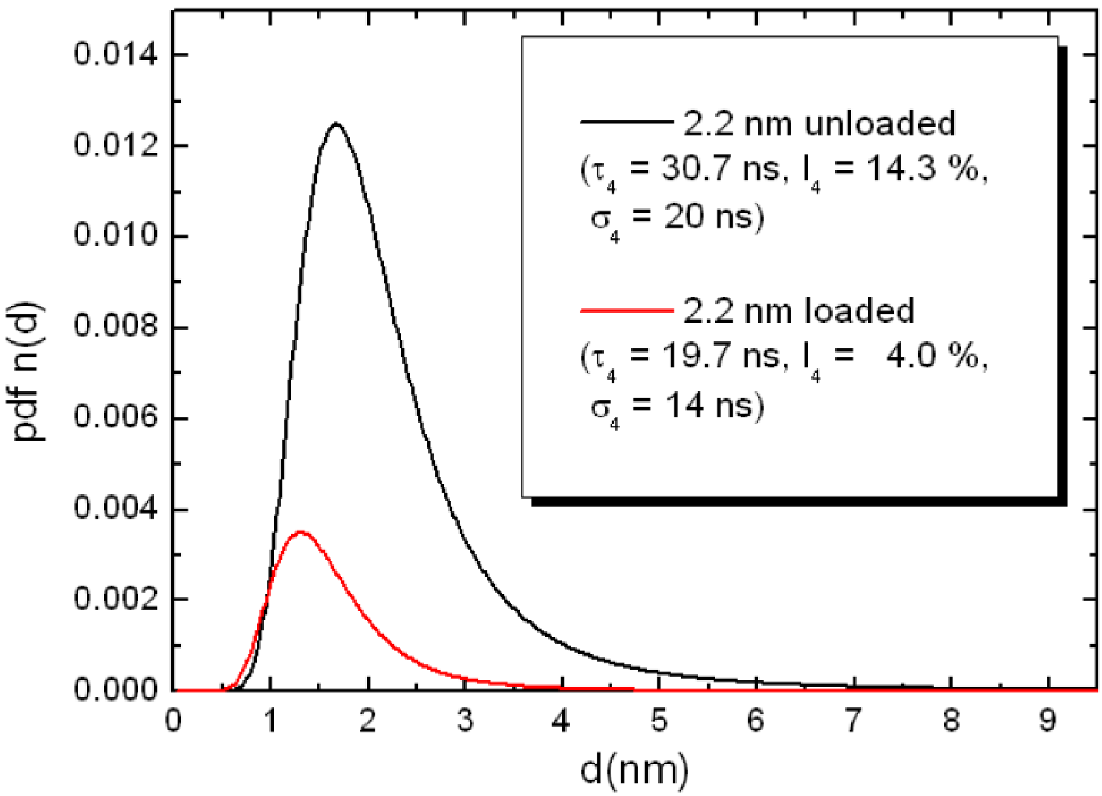
# Loading of Mesopores by Drugs




- Filling almost complete for large pores (22 nm)
- lifetime spectra show much smaller intensity for long-lived component
- remaining pores are smaller

| Probe | Membrandicke | vor Bel.: $\tau_4$ und $I_4$ | | nach Bel.: $\tau_4$ und $I_4$ | |
|---|---|---|---|---|---|
| 22 nm | 300 $\mu$m | 121 ns | 6,2 % | 111 ns | 0,5 % |
| 9,3 nm | 300 $\mu$m | 98 ns | 7,8 % | 58 ns | 0,9 % |
| 3 nm | 500 $\mu$m | 47 ns | 11,7 % | 52 ns | 5,0 % |
| 2,2 nm | 300 $\mu$m | 30,7 ns | 14,3 % | 19,7 ns | 4,0 % |

# Loading of Mesopores by Drugs




- pdf = probability density function
- Example: membrane with 2.2 nm pore
- distribution of pore sizes is shifted to smaller values
- 30.7 ns corresponds to 2.2 nm and 19.7 ns -> 1.5 nm

# Small pores in the wall of larger pores

Microporous and Mesoporous Materials 182 (2013) 136–146

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

ELSEVIER


## Transformation of porous glasses into MCM-41 containing geometric bodies

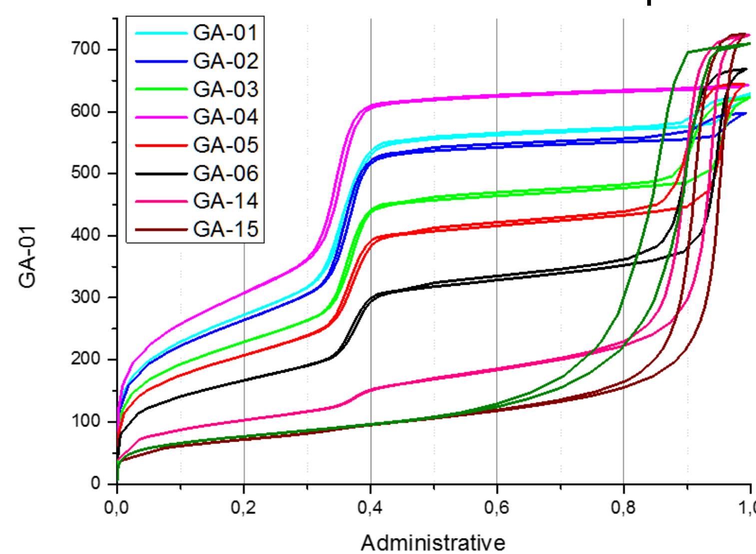
CrossMark

Hans Uhlig [a,*], Marie-Luise Gimpel [a], Alexandra Inayat [b], Roger Gläser [a], Wilhelm Schwieger [b], Wolf-Dietrich Einicke [a], Dirk Enke [a]

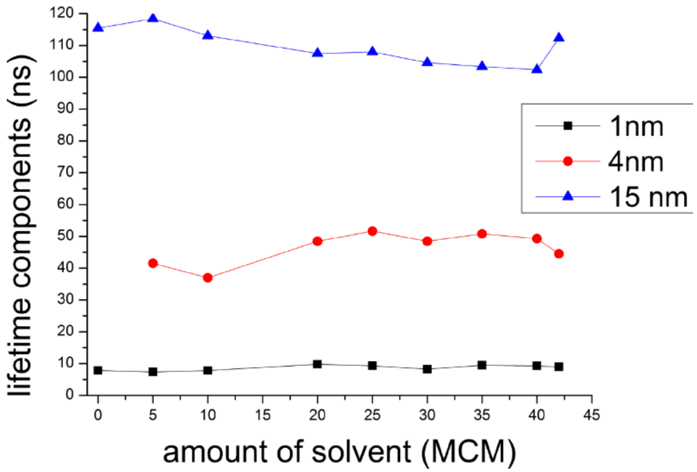
[a] University of Leipzig, Institute of Chemical Technology, Linnéstr. 3, 04103 Leipzig, Germany
[b] University of Erlangen-Nuremberg, Institute of Chemical Reaction Engineering, Egerlandstr. 3, 91058 Erlangen, Germany

| Sample | Amount of tenside solution in ml | new sample name |
|---|---|---|
| GA-01 | 40 | MCM-40 |
| GA-02 | 35 | MCM-35 |
| GA-03 | 30 | MCM-30 |
| GA-04 | 42 | MCM-42 |
| GA-05 | 25 | MCM-25 |
| GA-06 | 20 | MCM-20 |
| GA-14 | 10 | MCM-10 |
| GA-15 | 5 | MCM-05 |

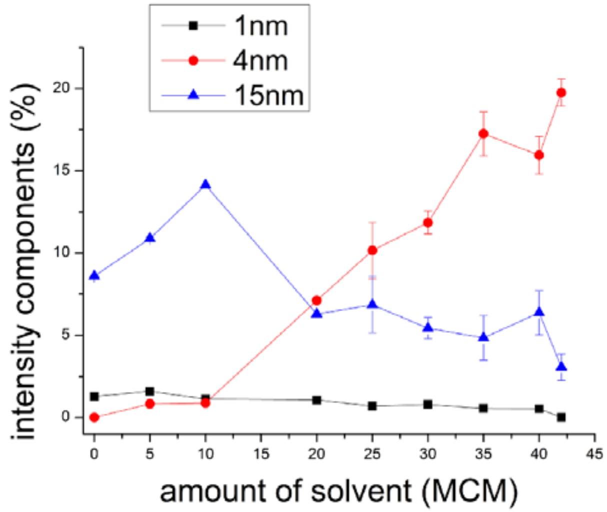
LN2 adsorption

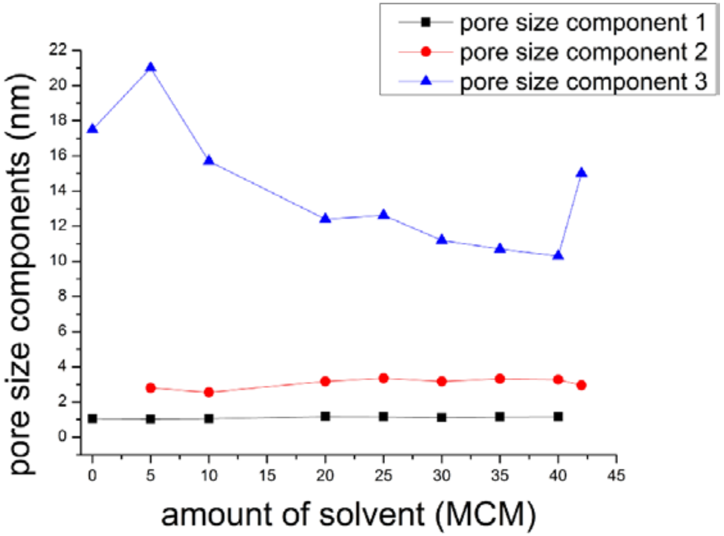


# Small pores in the wall of larger pores



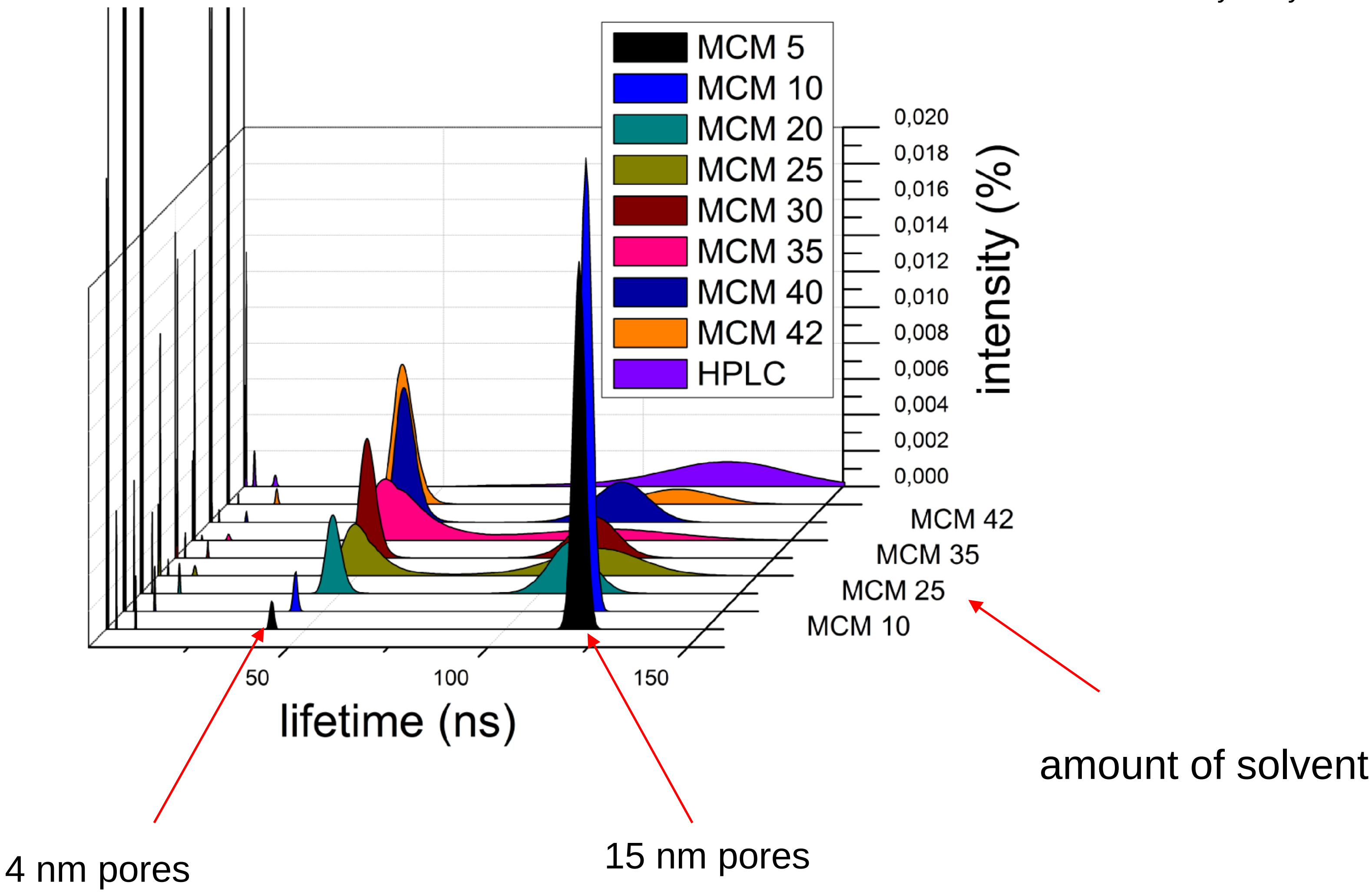

- solvent (MCM) was added into a larger pore system
- large pores: 15 nm
- small pores are formed in the walls: 4 nm



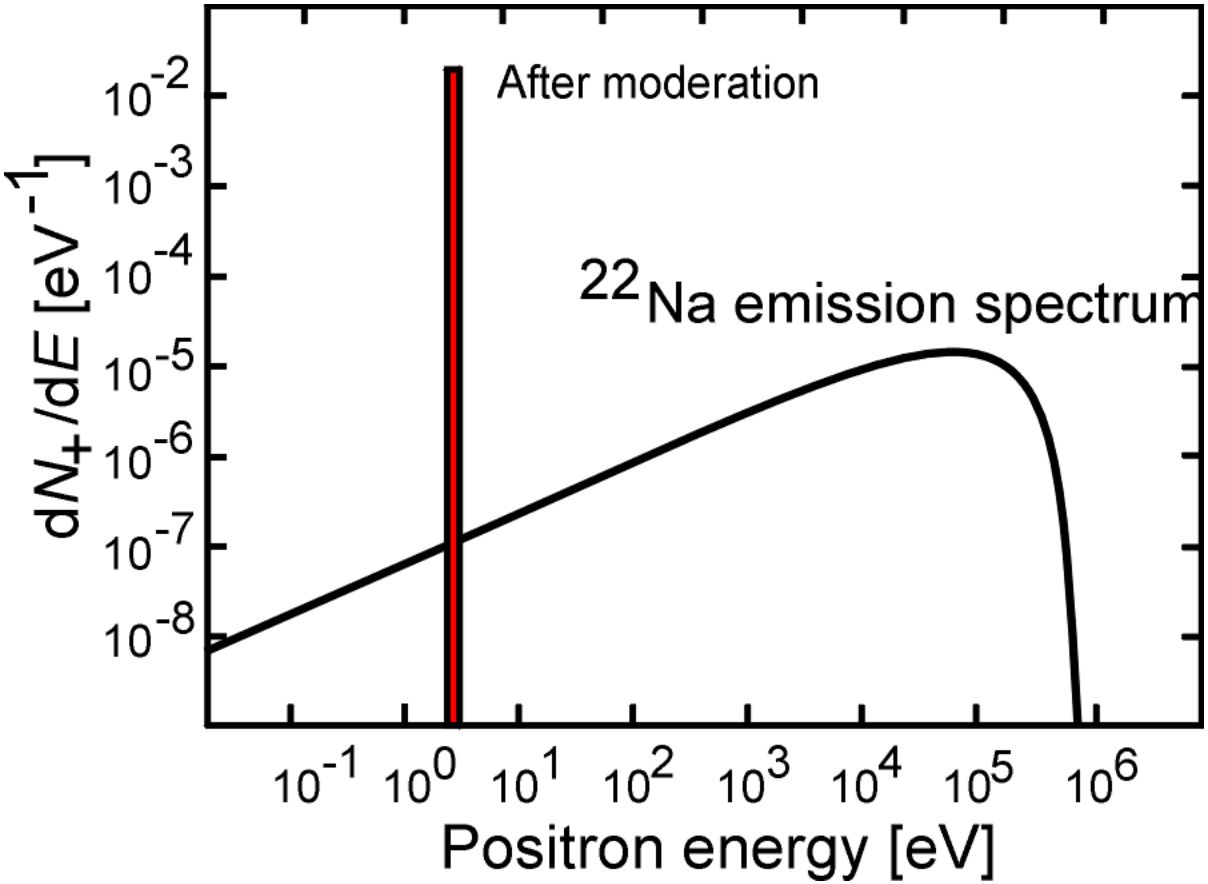




conventional data analysis

data analysis by MELT



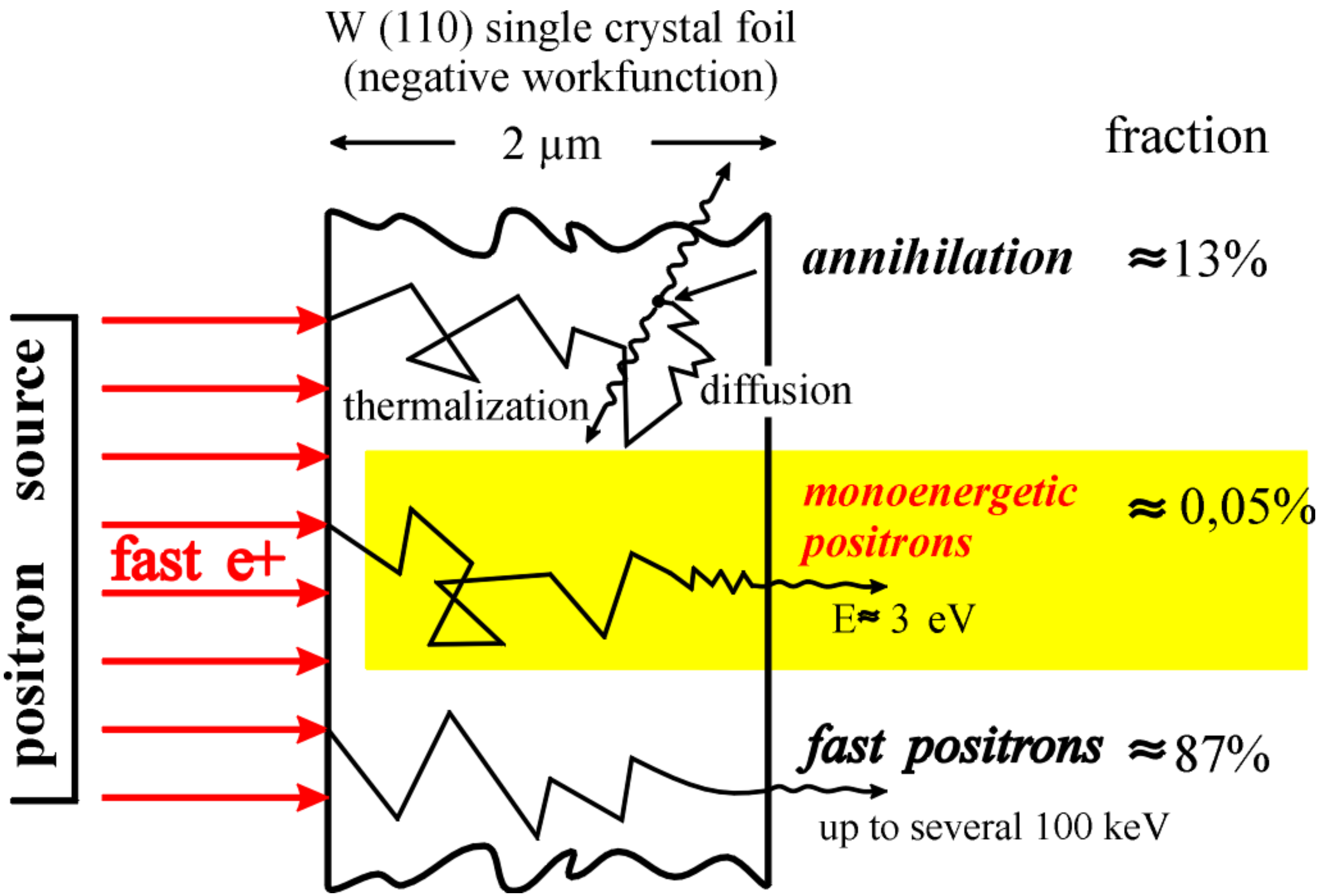
# The Slow-Positron Beam Technique




- broad positron emission spectrum from beta sources
- deep implantation into solids
- no use for study of defects in thin layers
- moderation necessary

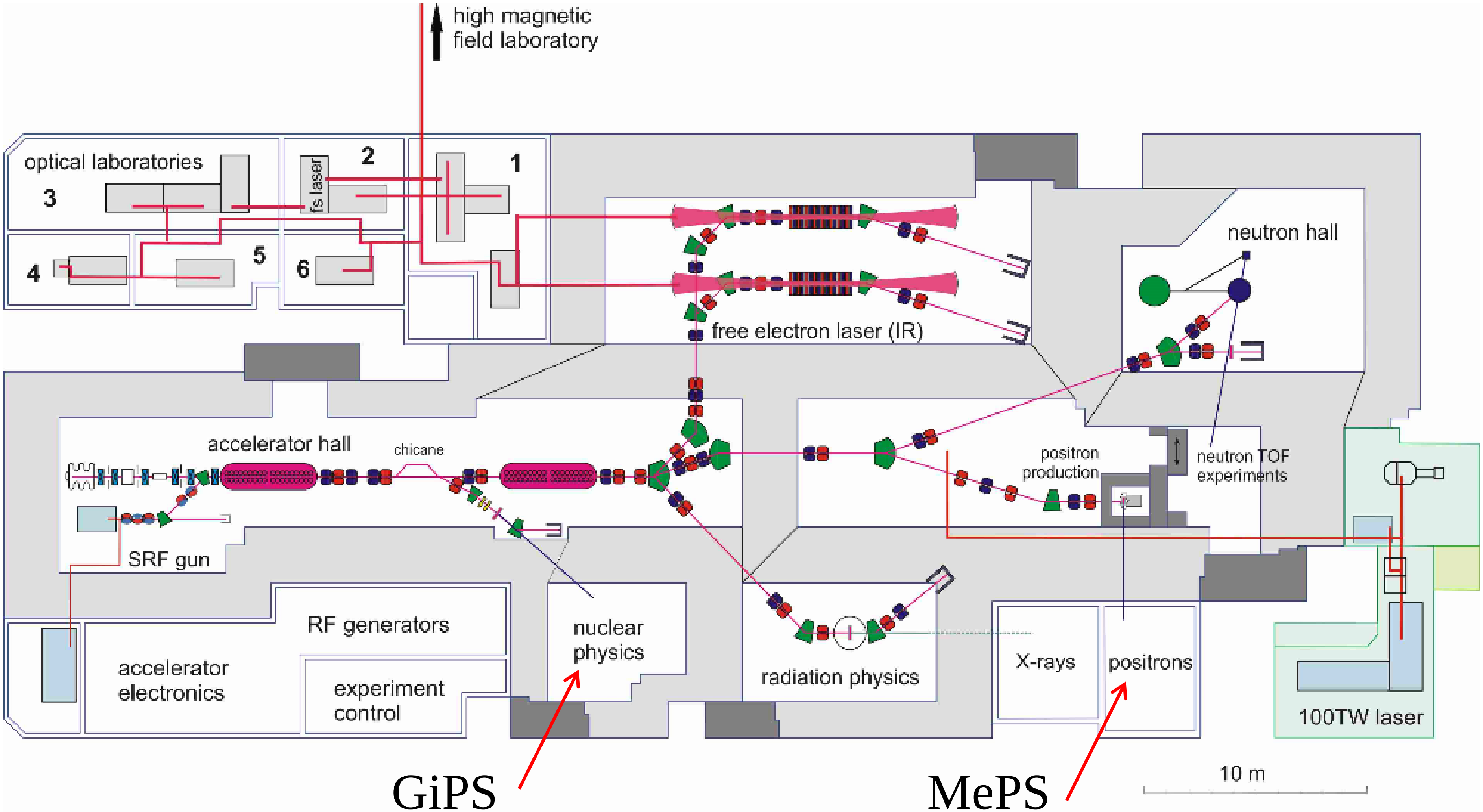
Mean implantation depth of un-moderated positrons (1/e): Si: 50µm

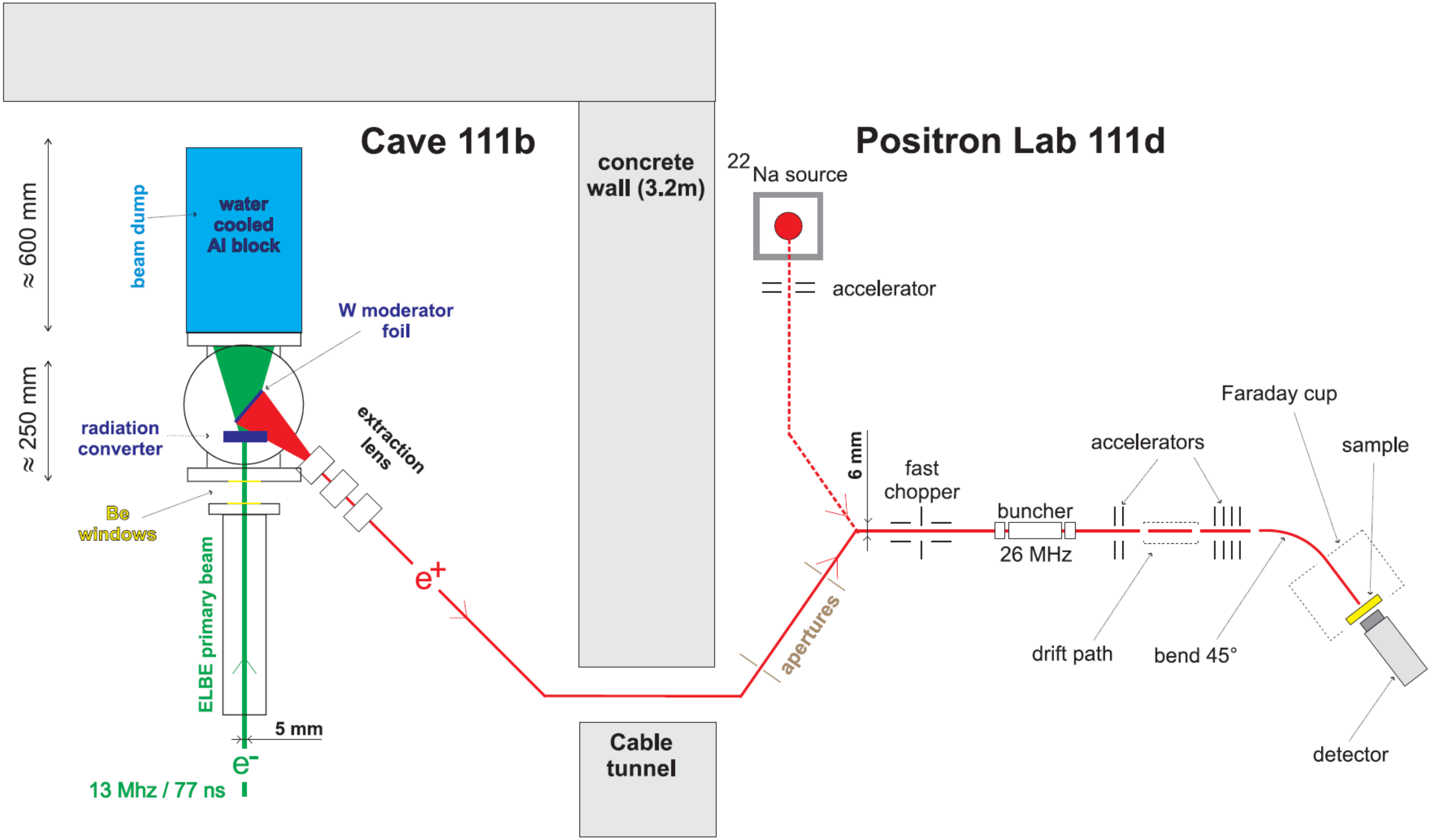
# Moderation of Positrons

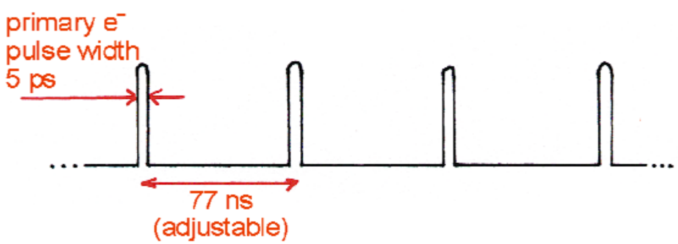



moderation efficiency: $\approx 10^{-4}$

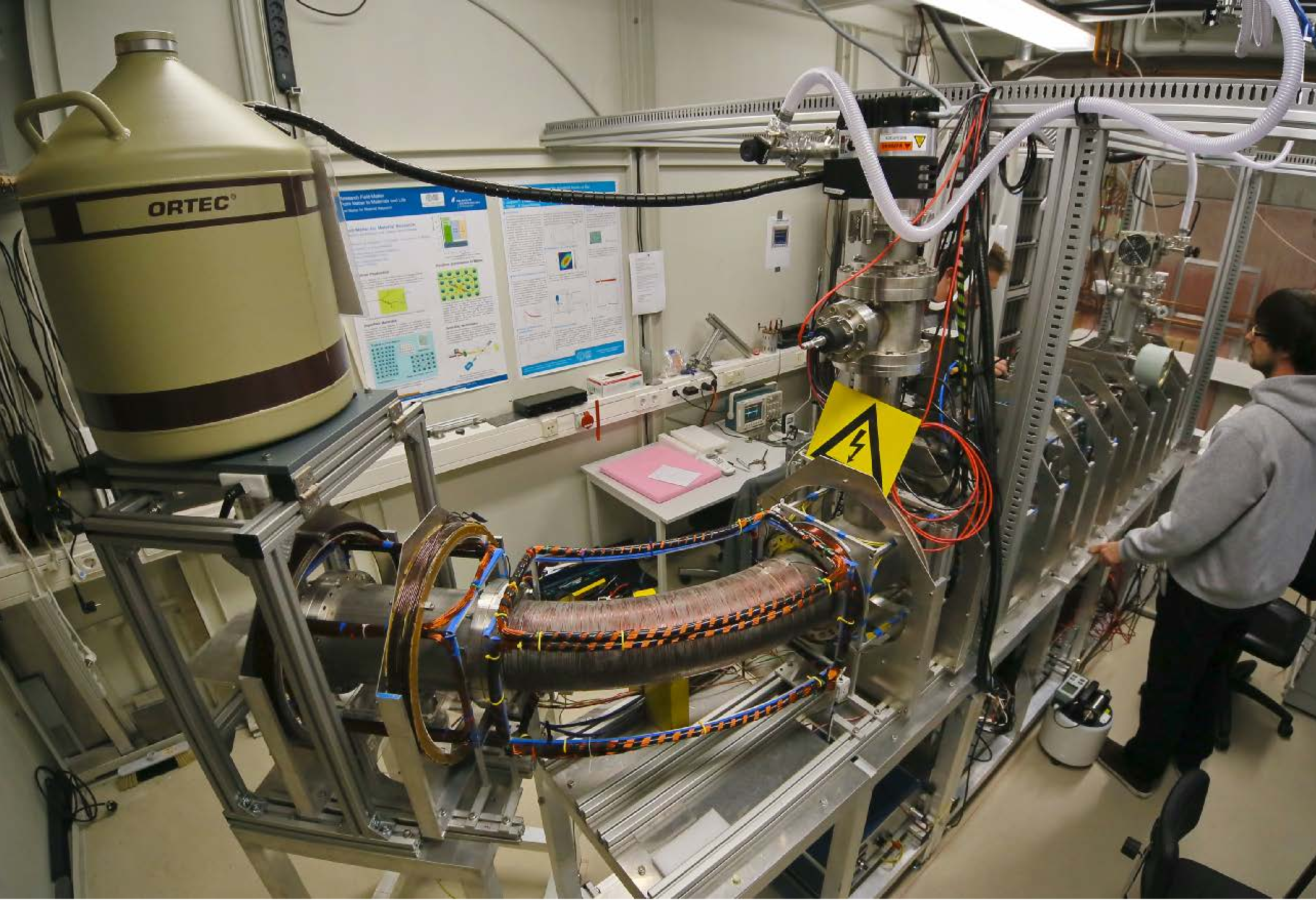
# HZDR Dresden-Rossendorf: Ground map of the ELBE hall




Cave 111b
Positron Lab 111d
concrete wall (3.2m)
≈ 600 mm
≈ 250 mm
beam dump
water cooled Al block
W moderator foil
radiation converter
extraction lens
Be windows
ELBE primary beam
5 mm
e-
13 Mhz / 77 ns
e+
Cable tunnel
22Na source
accelerator
apertures
6 mm
fast chopper
buncher
26 MHz
accelerators
drift path
bend 45°
Faraday cup
sample
detector


primary e-
pulse width
5 ps
77 ns
(adjustable)

# MePS scheme



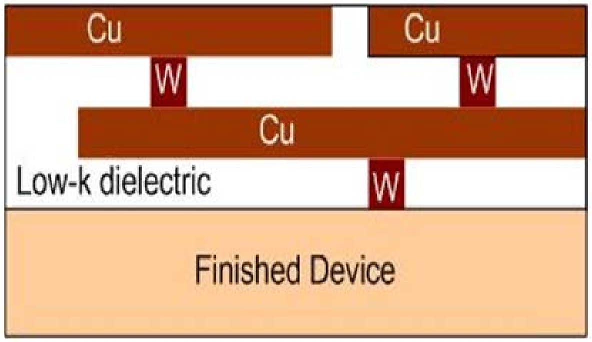

**MePS system @ ELBE, 26. November 2013**

# Low-K dielectric layers

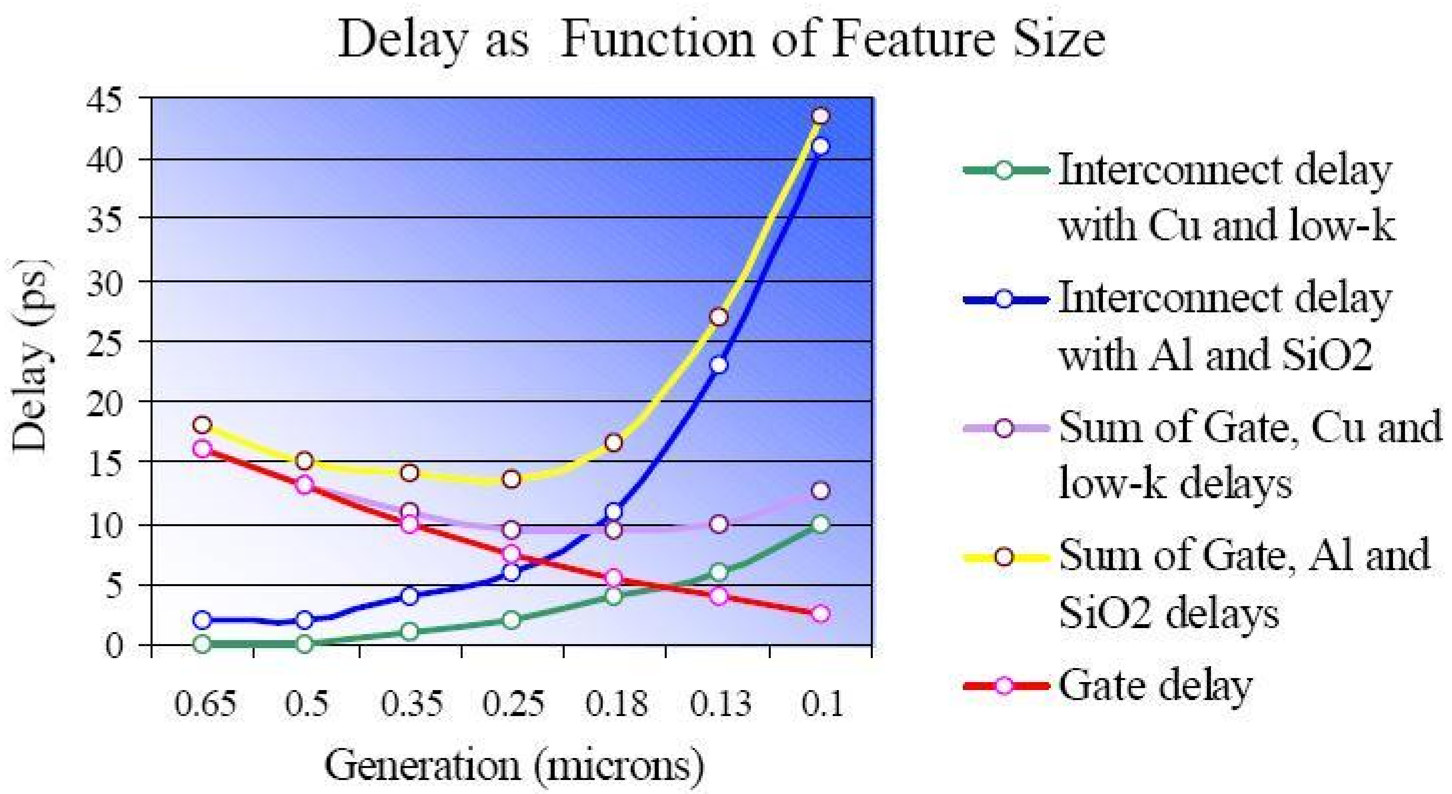
- modern ultra-large scale microprocessors suffers from long relaxation times
- information transport is limited by product R × C
- R has been decreased: Copper technology (instead of Al)
- C is relatively high when $SiO_2$ is used as isolation layer; $\varepsilon_r$=4

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

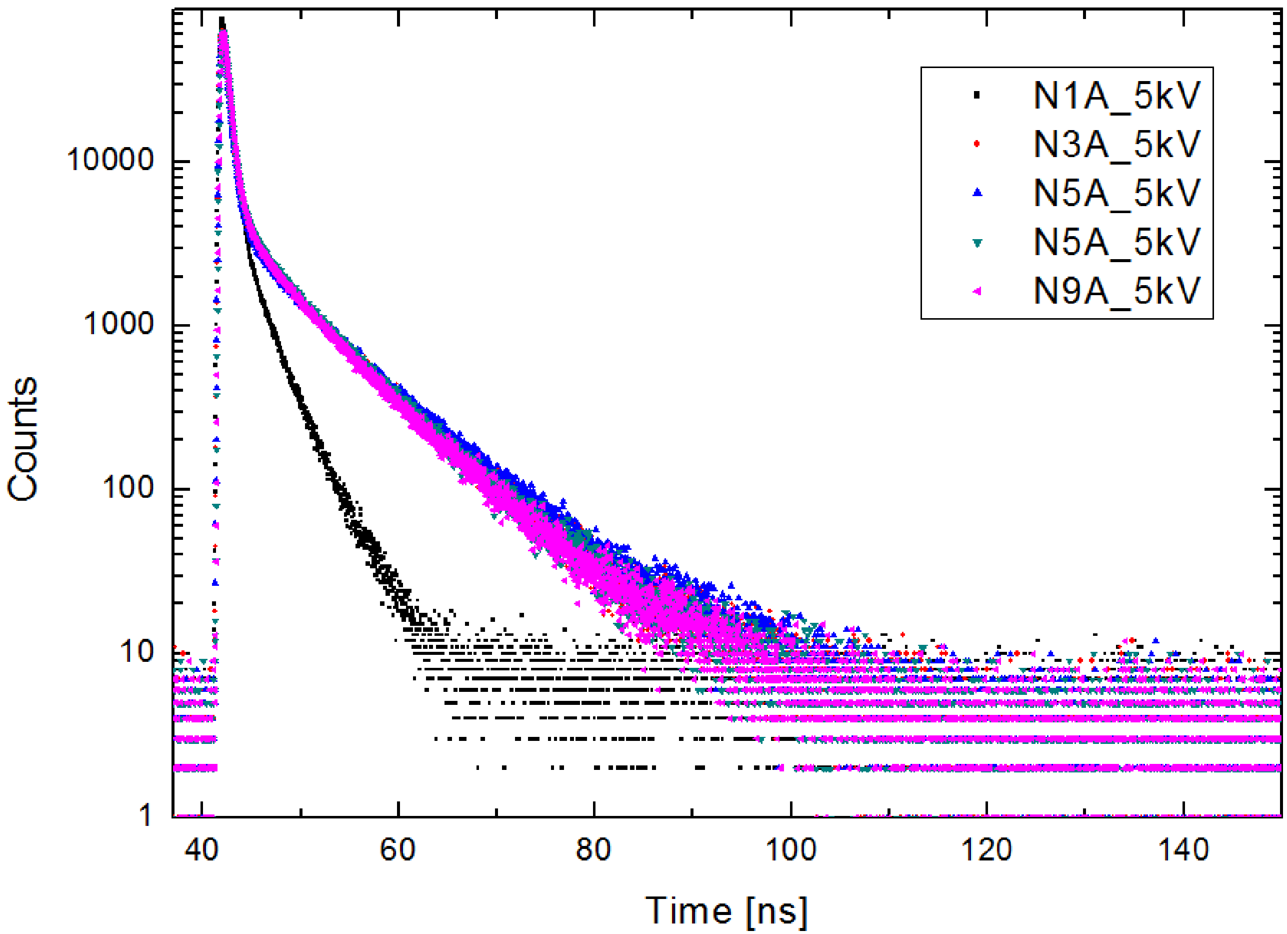
- low-k (small $\varepsilon_r$ = 2…2.5) layers may help
- these are layers with micropores with pore size of d≈1 nm with high porosity
- problem for characterization: closed porosity



# Low-K dielectric layers

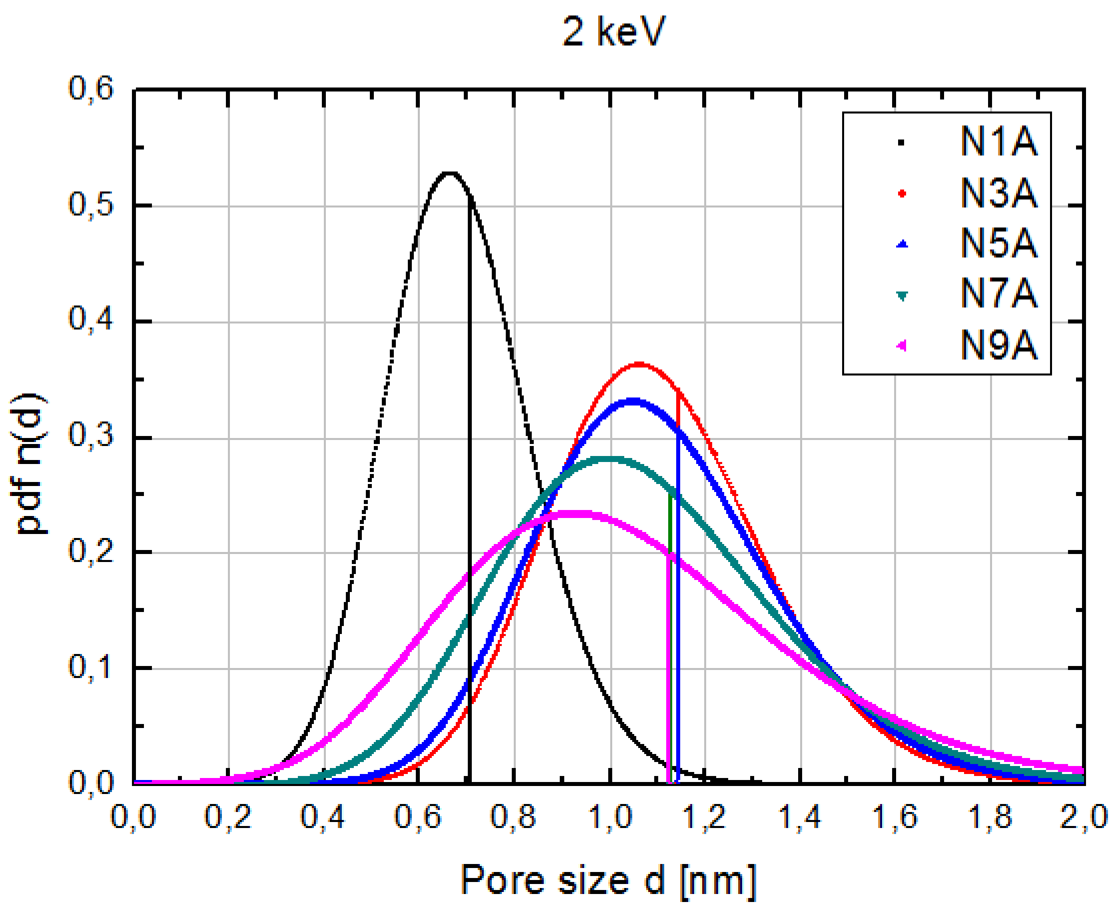


# Low-K dielectric layers



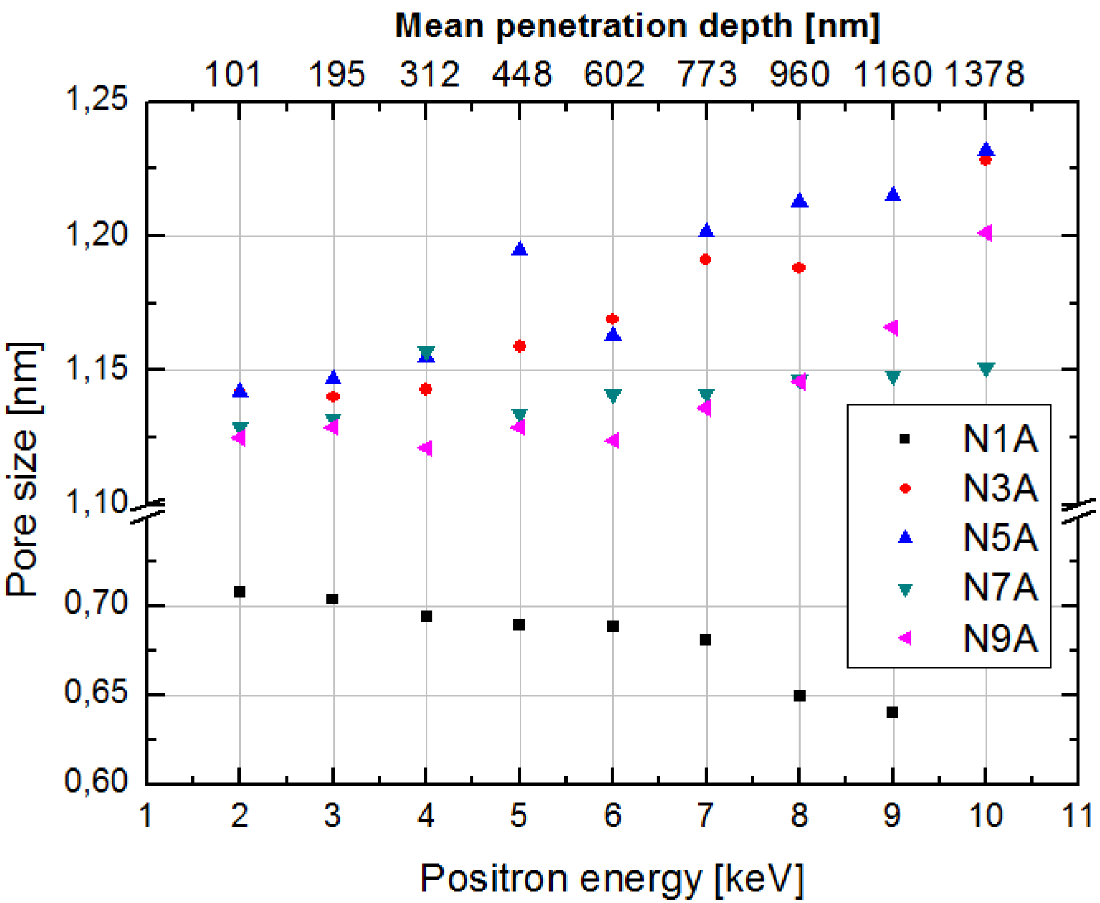

- Positrons are ideal tool for closed porosity in low-k layers
- Lifetime spectra of differently treated low-K layers
- Treatment:
  - untreated porous layer
  - plasma treatment for compactation
  - TiN cap layer

# Low-K dielectric layers




- dispersion of lifetime gives the size distribution of the pore system

# Low-K dielectric layers




- monoenergetic positrons can be used to depth scan the layer
- monoenergetic positrons are obtained by moderation

# Summary

- for T = 300 K general agreement to the RTE model -> at room temperature
- PALS is a useful porosimetry tool

- Advantages:
  - very sensitive method for small pores (0.3 to 10 nm)
  - upper sensitive limit ≈ 60 nm
  - non-destructive method
  - also for closed pore systems
  - applicable also for thin layers (50 … 2000 nm)

*"A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it."*

*Albert Einstein (American German 1879-1955)*

**Acknowledgement**
Stefan Thränert
Dirk Enke
Marco Jungmann
Maik Butterling
Steve Zieger
Thomas Cudrig
Mohamed Elsayed