Characterisation of mesopores - Positronium lifetime measurement as a porosimetry technique

S. Thränert, D. Enke, R. Krause-Rehberg

SIG. ACADEMIÆ FRIDERICIANÆ HALLENS.

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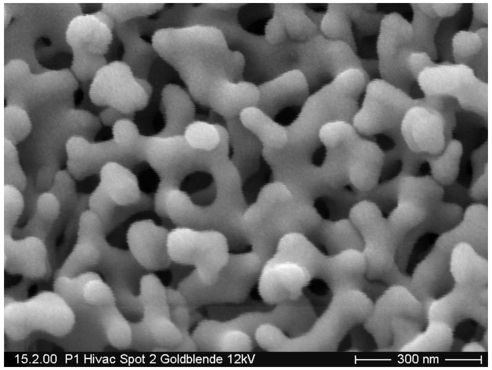
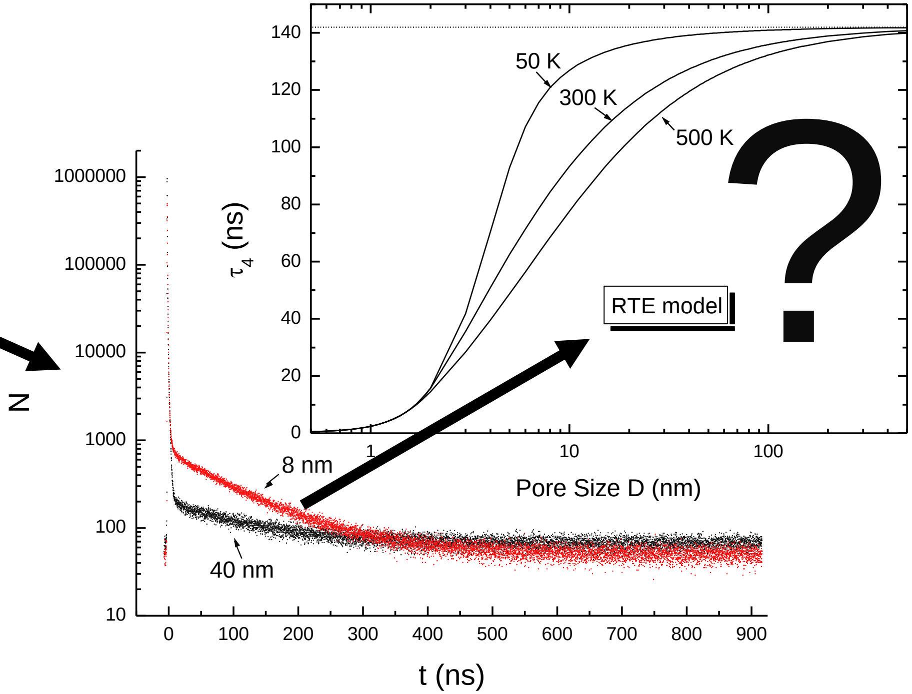
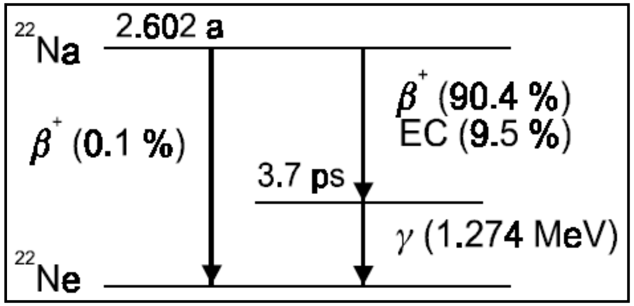
Characterising mesopores

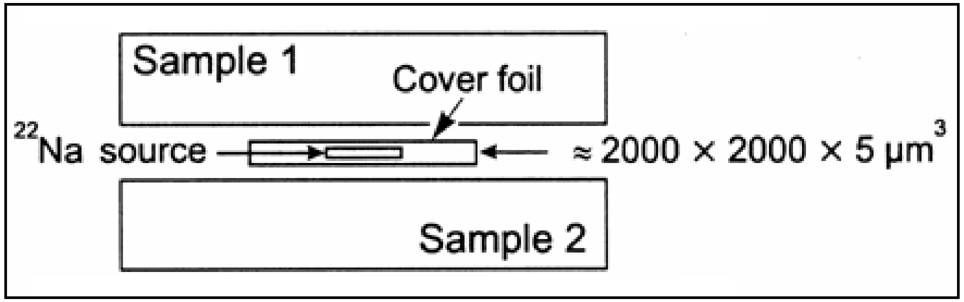
- Principles of PALS
  - Lifetime Measurement
  - Positronium
- Porous glass - CPG
  - Synthesis
  - Properties
- Models – the state of the art
  - Tao Eldrup
  - Tokyo
  - RTE
- Experimental results
  - Relation to RTE
- Summary

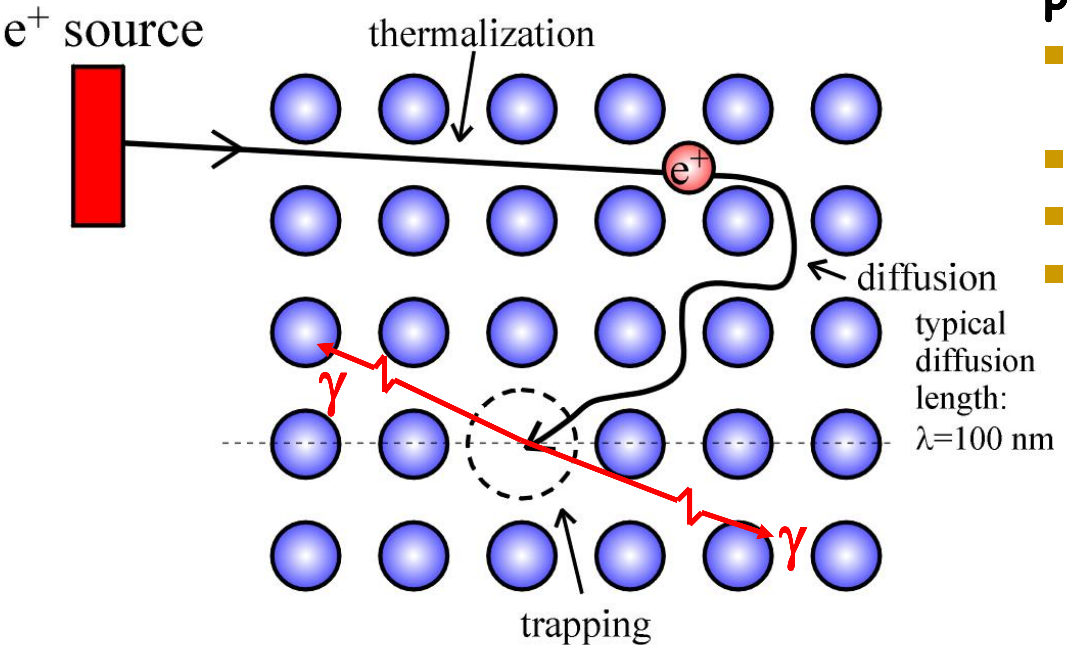




Principles of PALS







positrons:

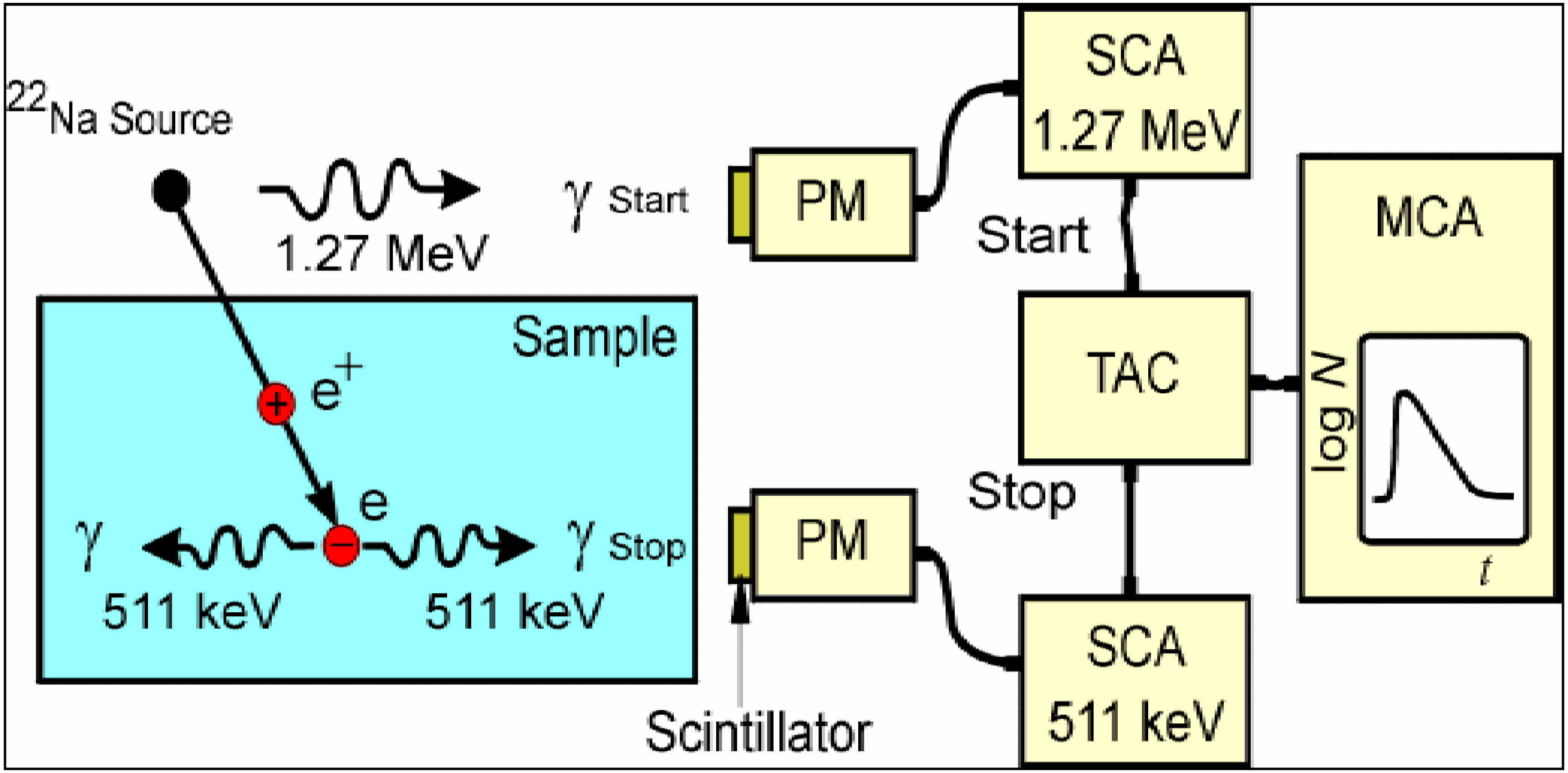
- thermalize (reach thermal energies)
- diffuse
- being trapped
- and annihilate

When trapped in vacancies:

- Lifetime increases

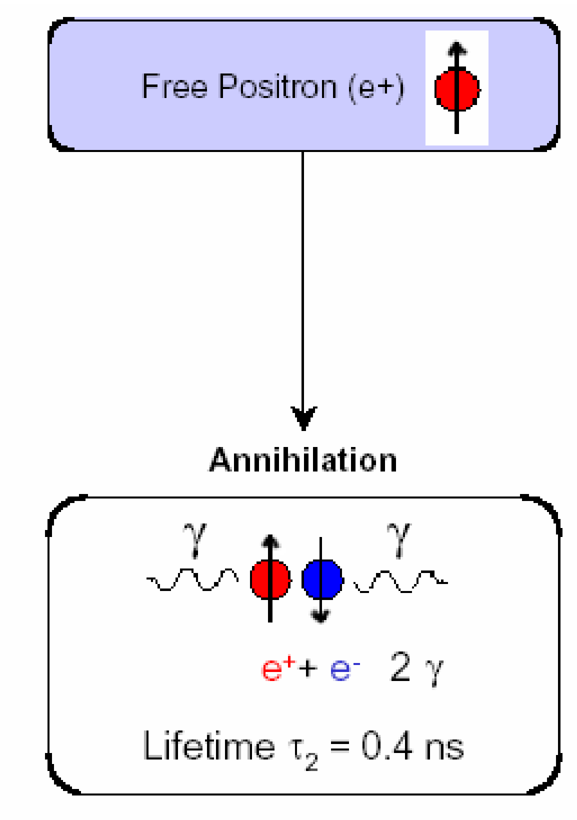
  due to smaller electron density in open volume

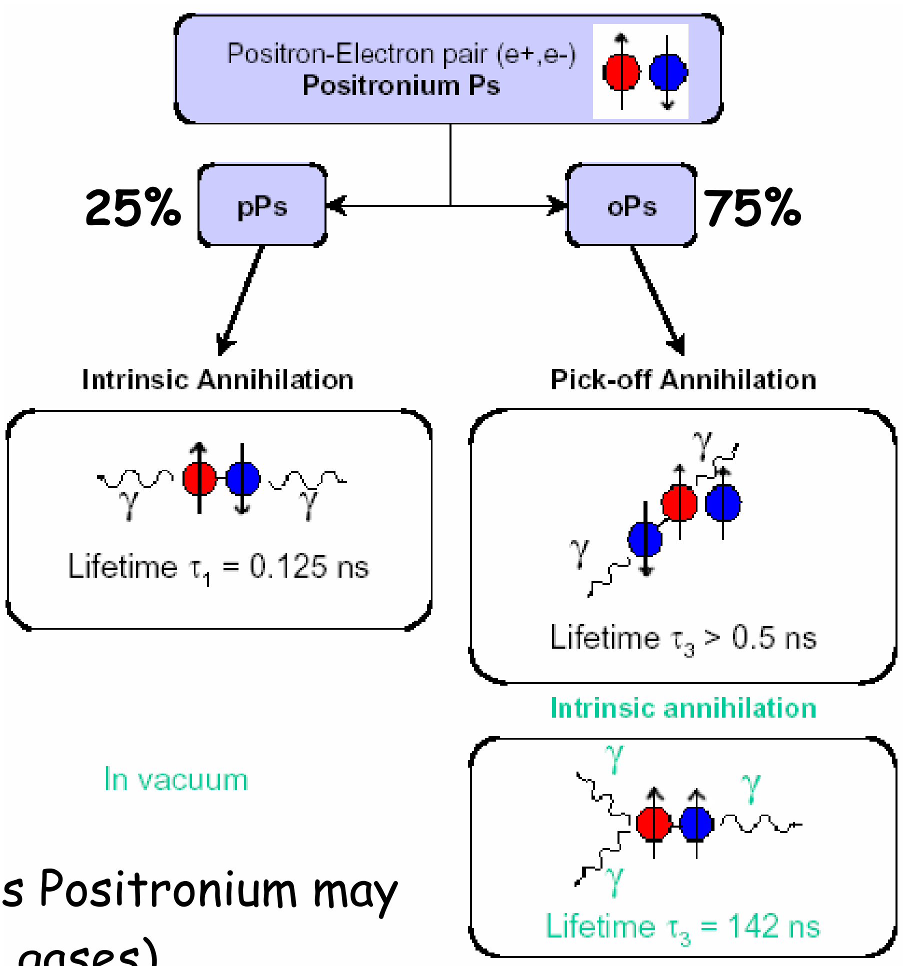
Principles of PALS



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

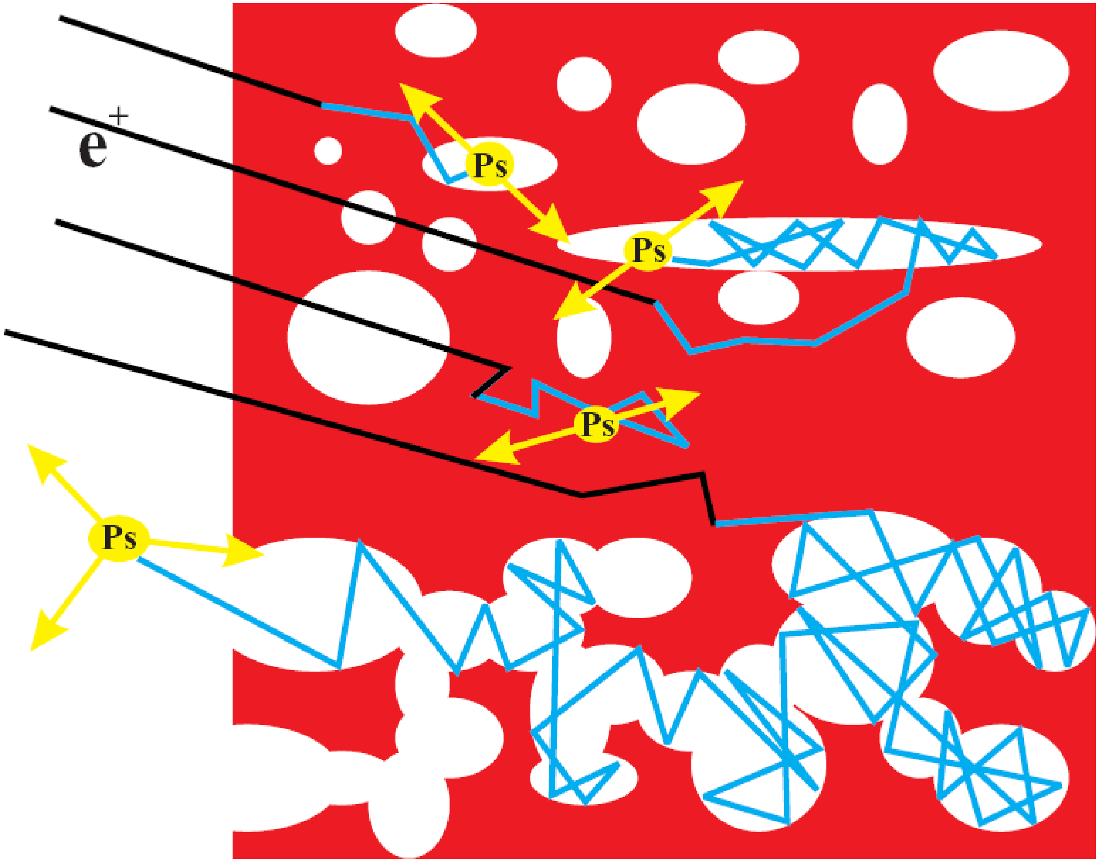
Principles of PALS: ortho-Positronium





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

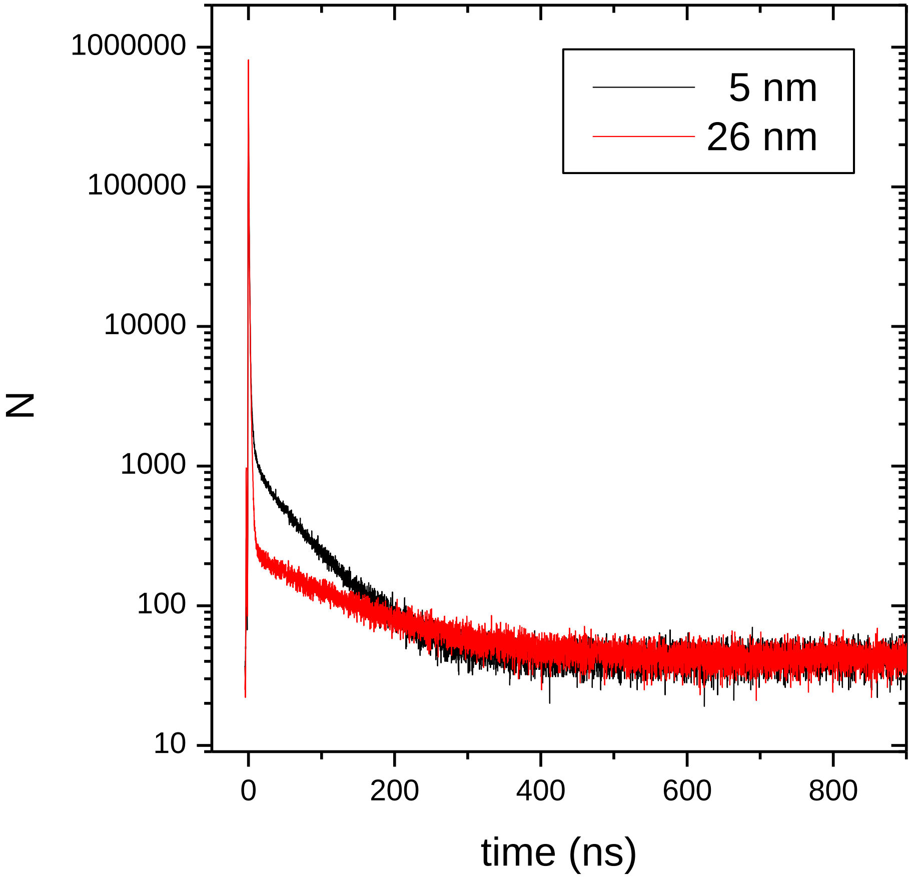
Principles of PALS: pick-off annihilation



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

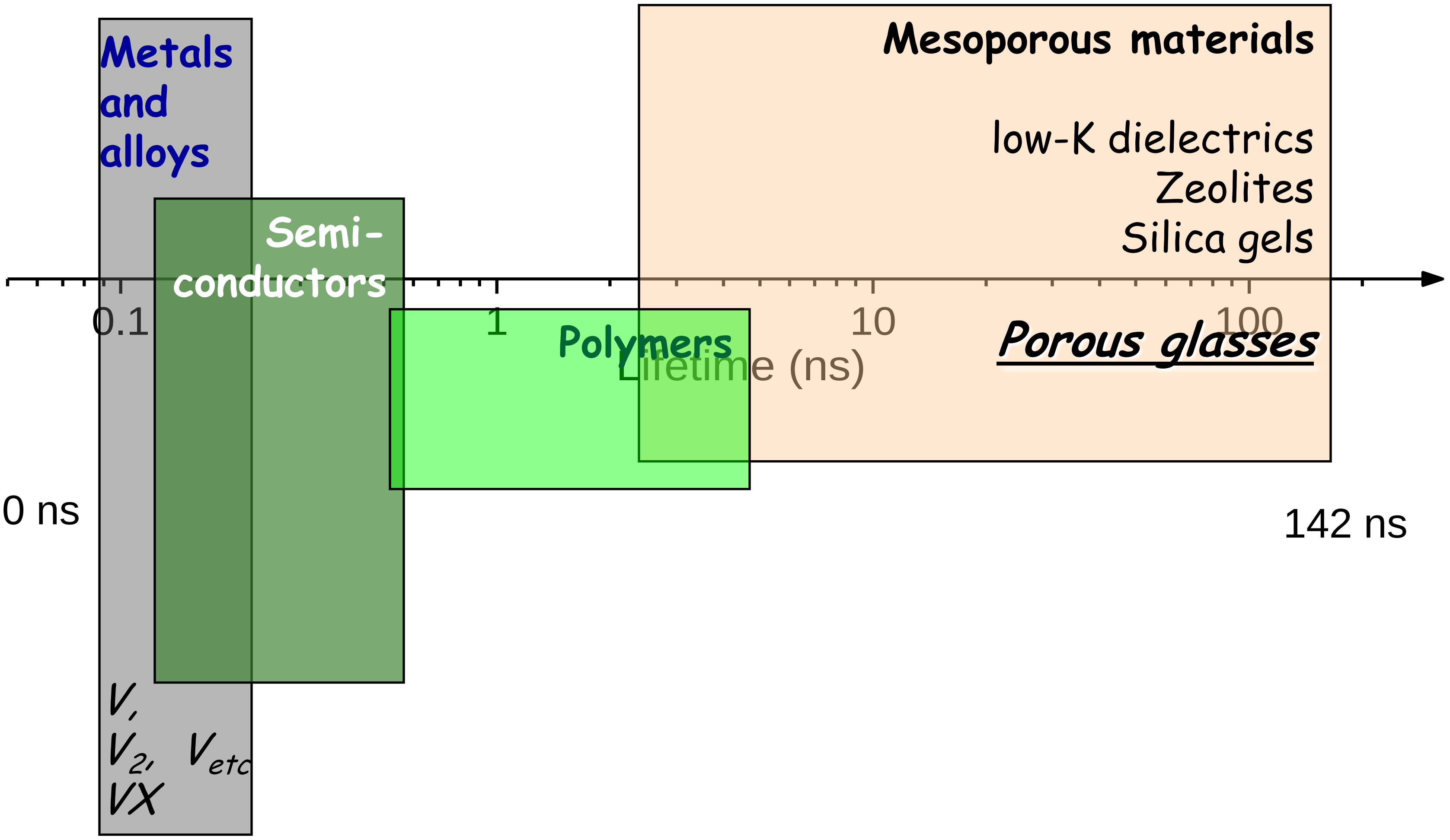


typical lifetime spectrum for porous glass:

- 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

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

Principles of PALS: typical lifetimes



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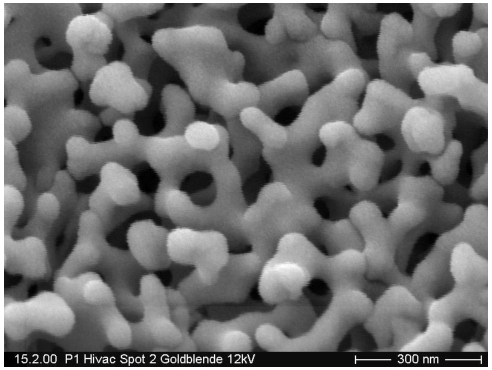
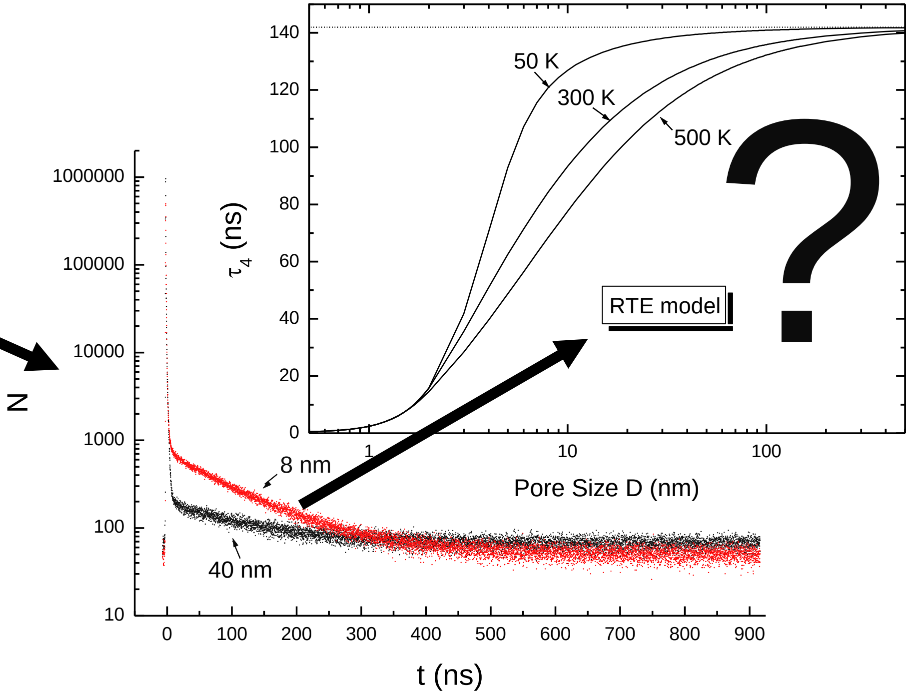
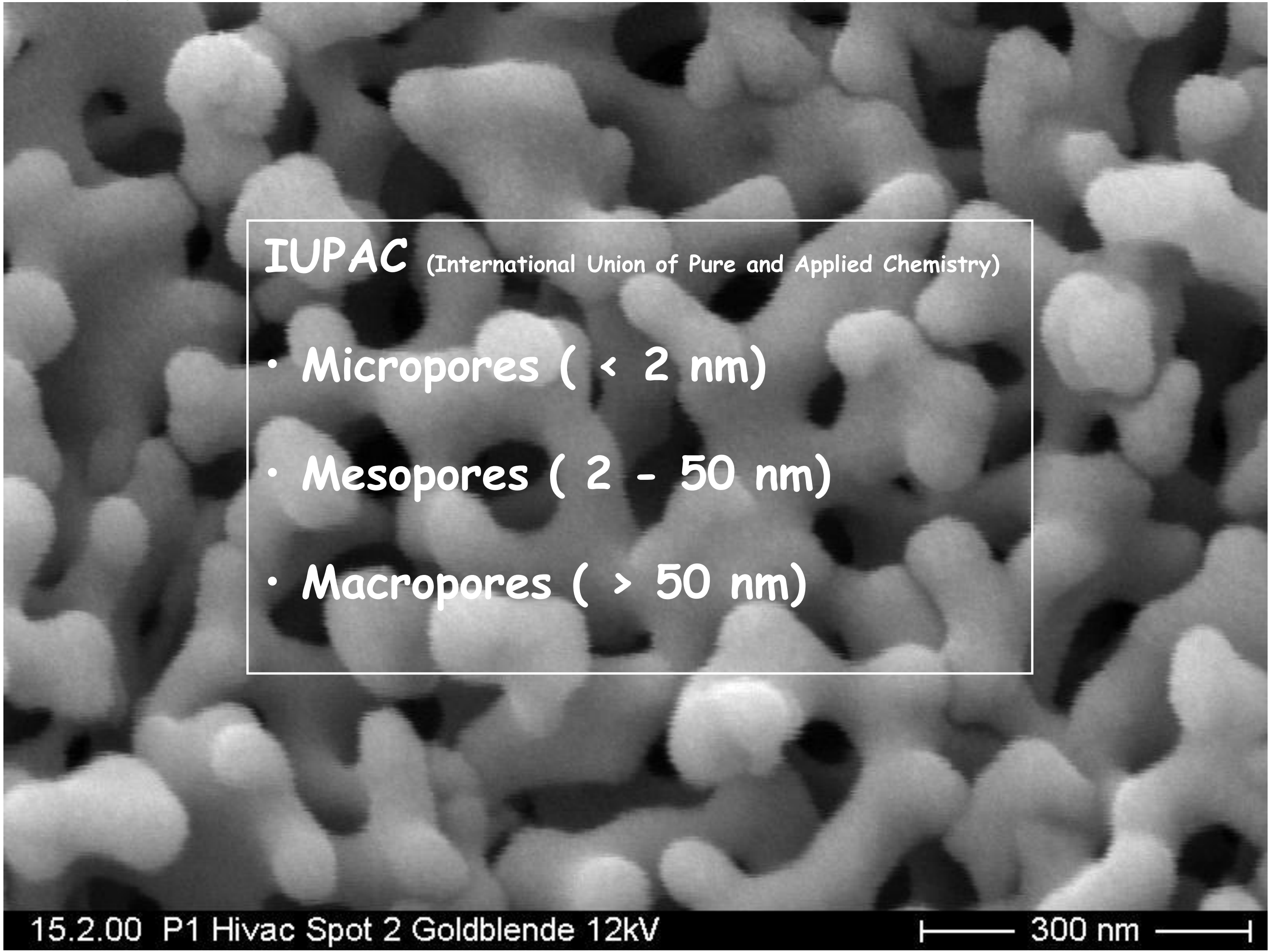




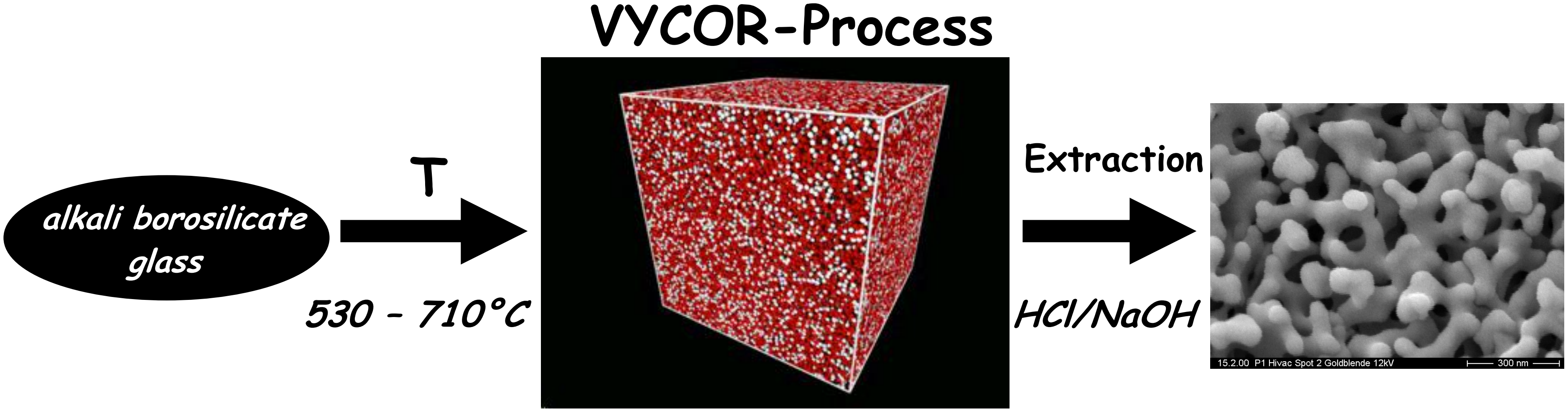
Mesopores - Controlled pore glasses



IUPAC (International Union of Pure and Applied Chemistry)

- Micropores (< 2 nm)
- Mesopores (2 - 50 nm)
- Macropores (> 50 nm)

Controlled pore glasses - CPG

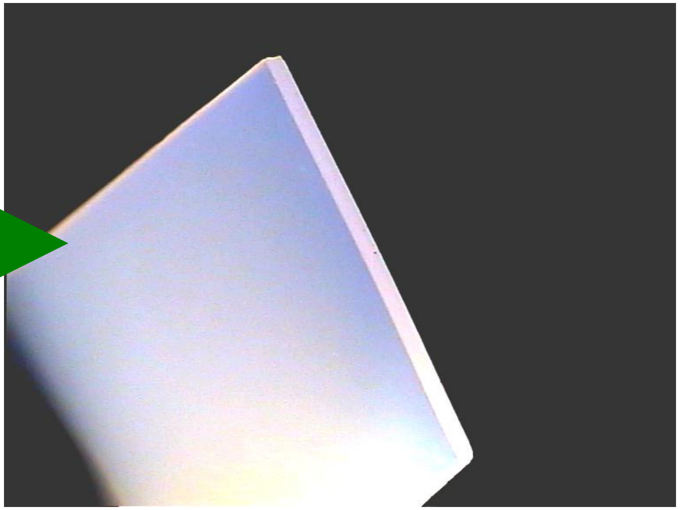


d_P 1 to 110 nm

- 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:

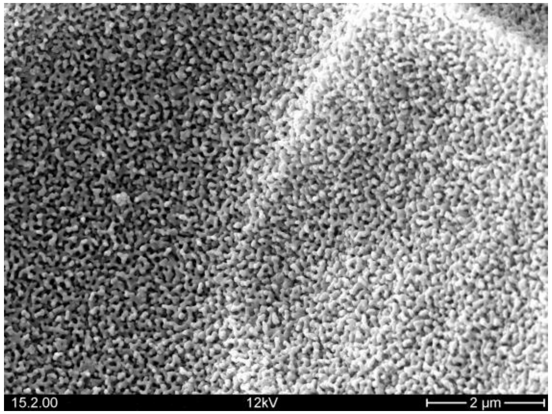
- 100 µm

porous membranes:

- 20 x 20 x 0.2 mm

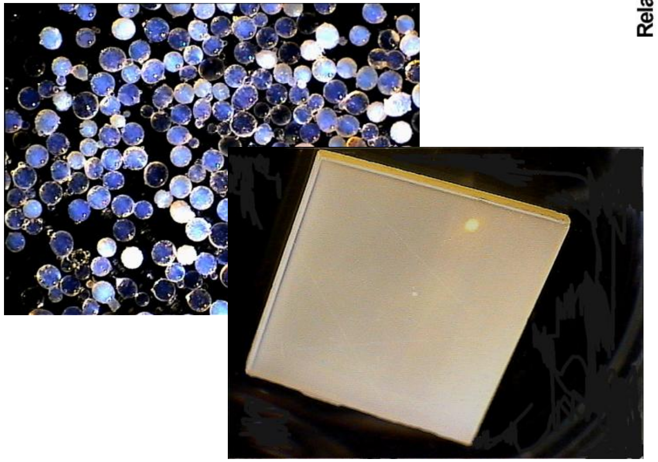
DE-Patent 19848377 A1

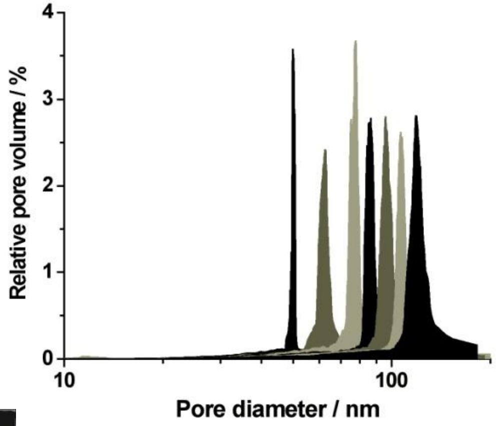
Controlled pore glasses - CPG



- **homogenous microstructure**
- **small pore size distribution**

- **different geometries possible**





- **pore size arbitrary**

D. Enke, F. Janowski, W. Schwieger, *Microporous and Mesoporous Materials* **2003**, *60*, 19-30.

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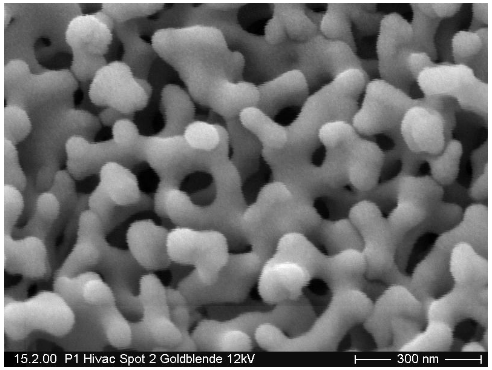
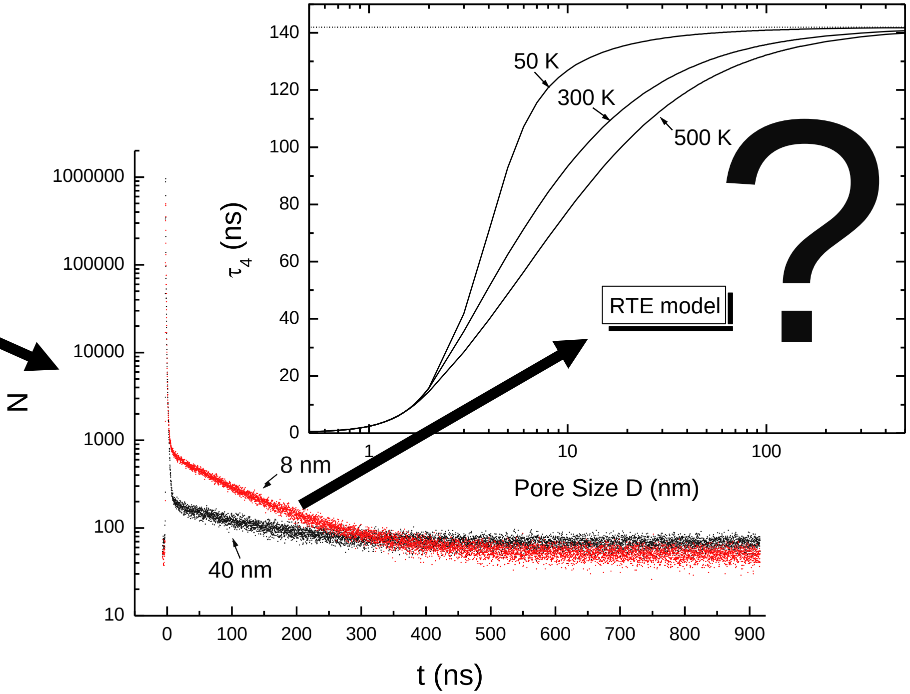
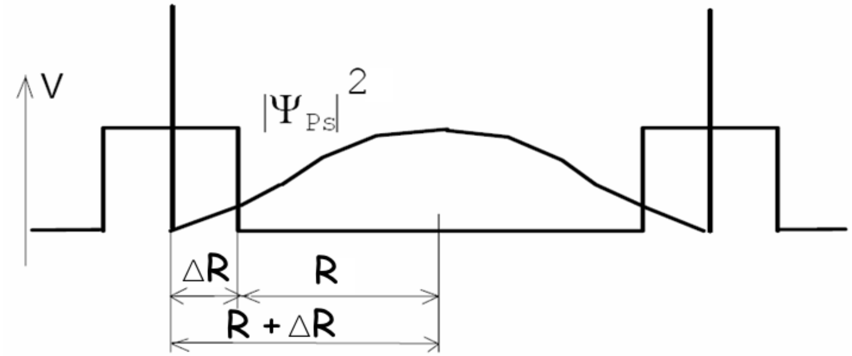




The TE model



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

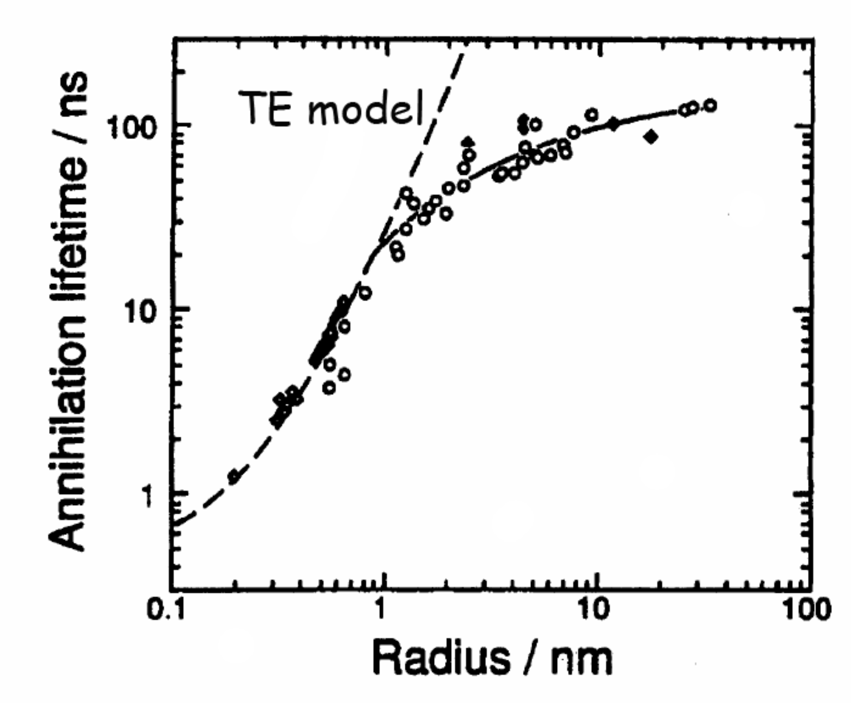
$$\lambda_{TE}(R) = \lambda_A\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]$$

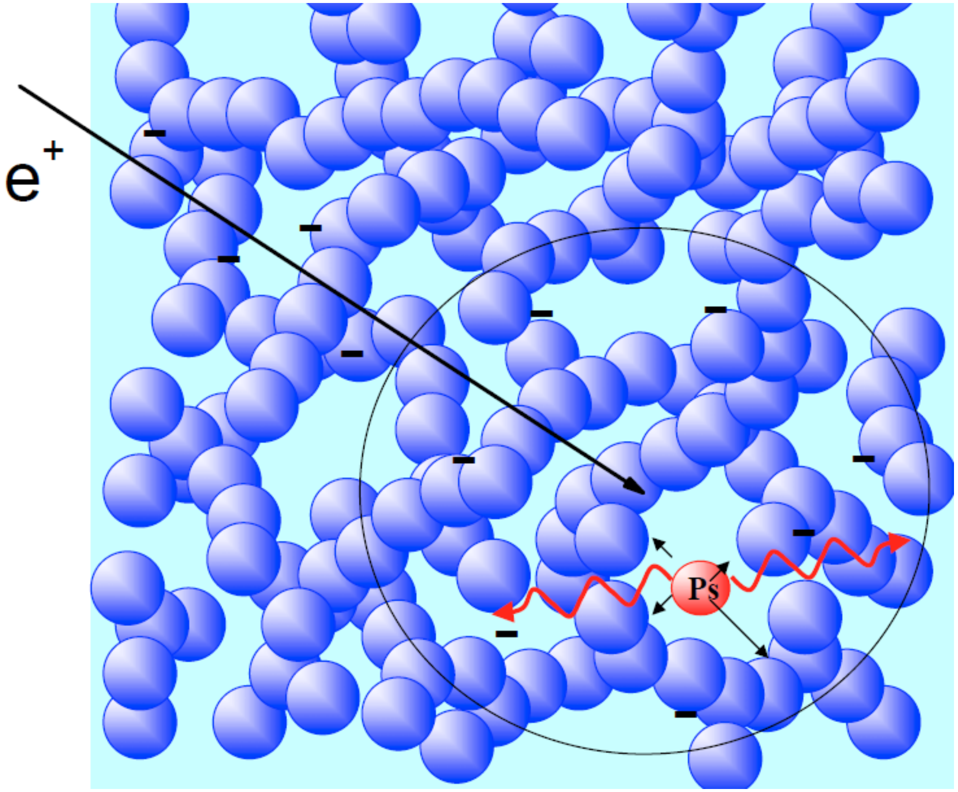
- ΔR= 0.166 nm determined by Eldrup and Jean
- Pore size > 1 nm -> $\lambda_{3\gamma}$ can not be neglected, temperature dependence of o-Ps lifetime (excited states)

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

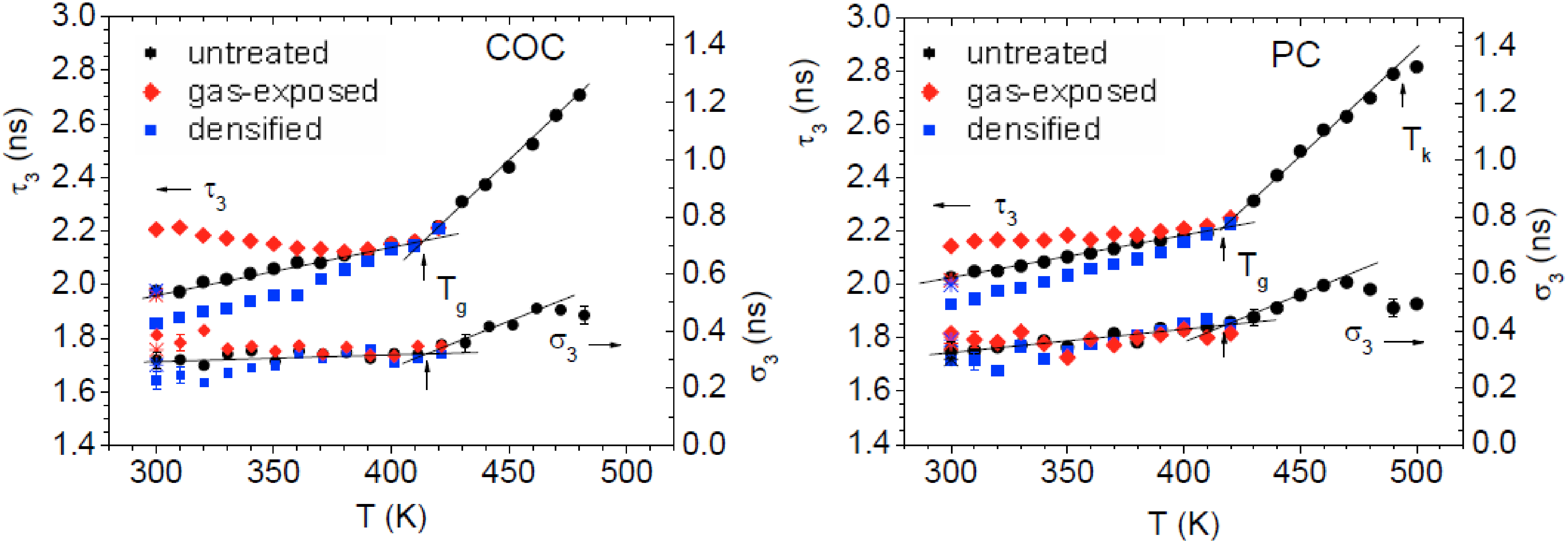
- TE model valid for r > 2nm
- very successful for open-volume characterization in polymers





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



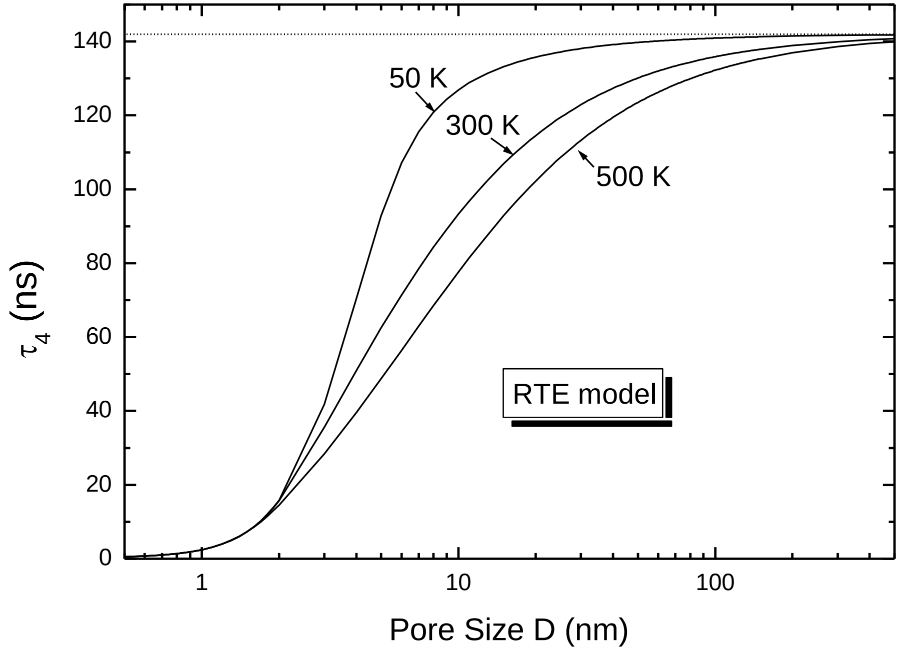
The mean, τ_3, and the mean dispersion, σ_3, of *o*-Ps lifetimes as a function of temperature *T* for densified at 200 MPa (blue), gas-exposed (read) and untreated (black) COC and PC.

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

Model for R > 1 nm – RTE

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

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



- Boltzmann statistics ascribes explicit temperature dependence to the lifetime
- Rectangular geometry -> prevention of complicated Bessel functions
- δ= 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.

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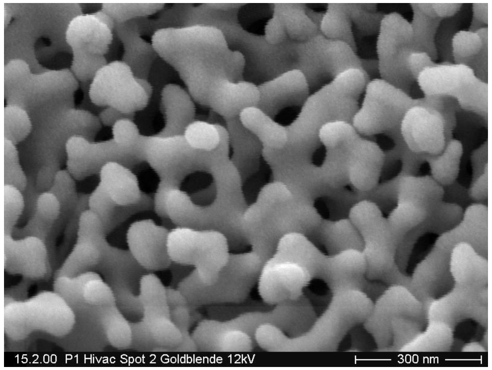
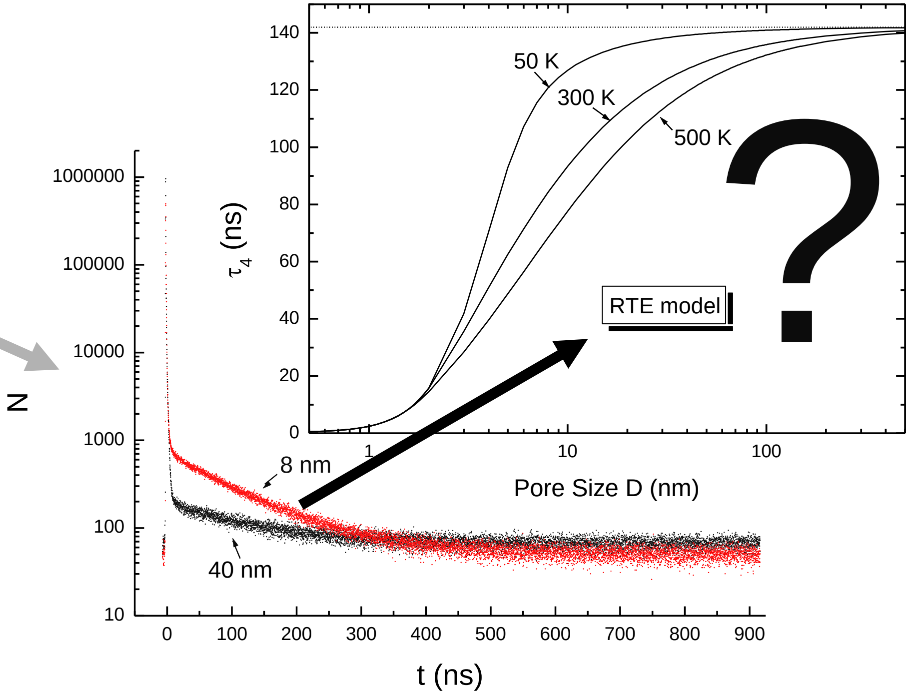


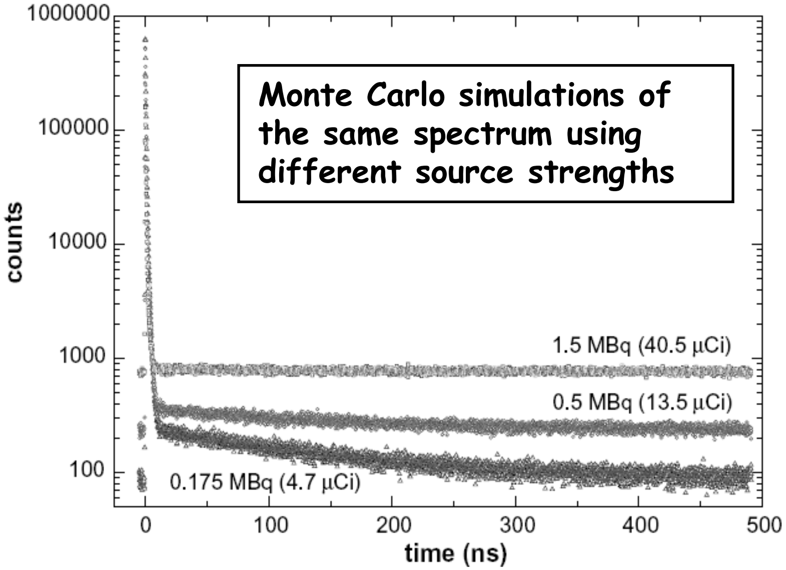


The experiments

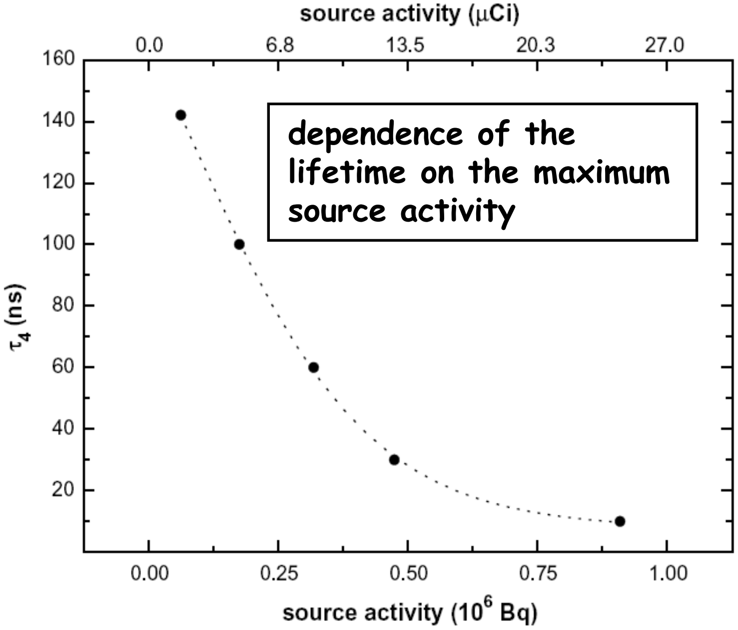
- Important: weak source required to obtain o-Ps lifetime properly (long lifetime component disturbed by chance coincidences)

- When expecting a lifetime of e.g. 120 ns -> max. source strength of 3 µCi recommended

- At first measurements at
  T = 300 K on different pore sizes



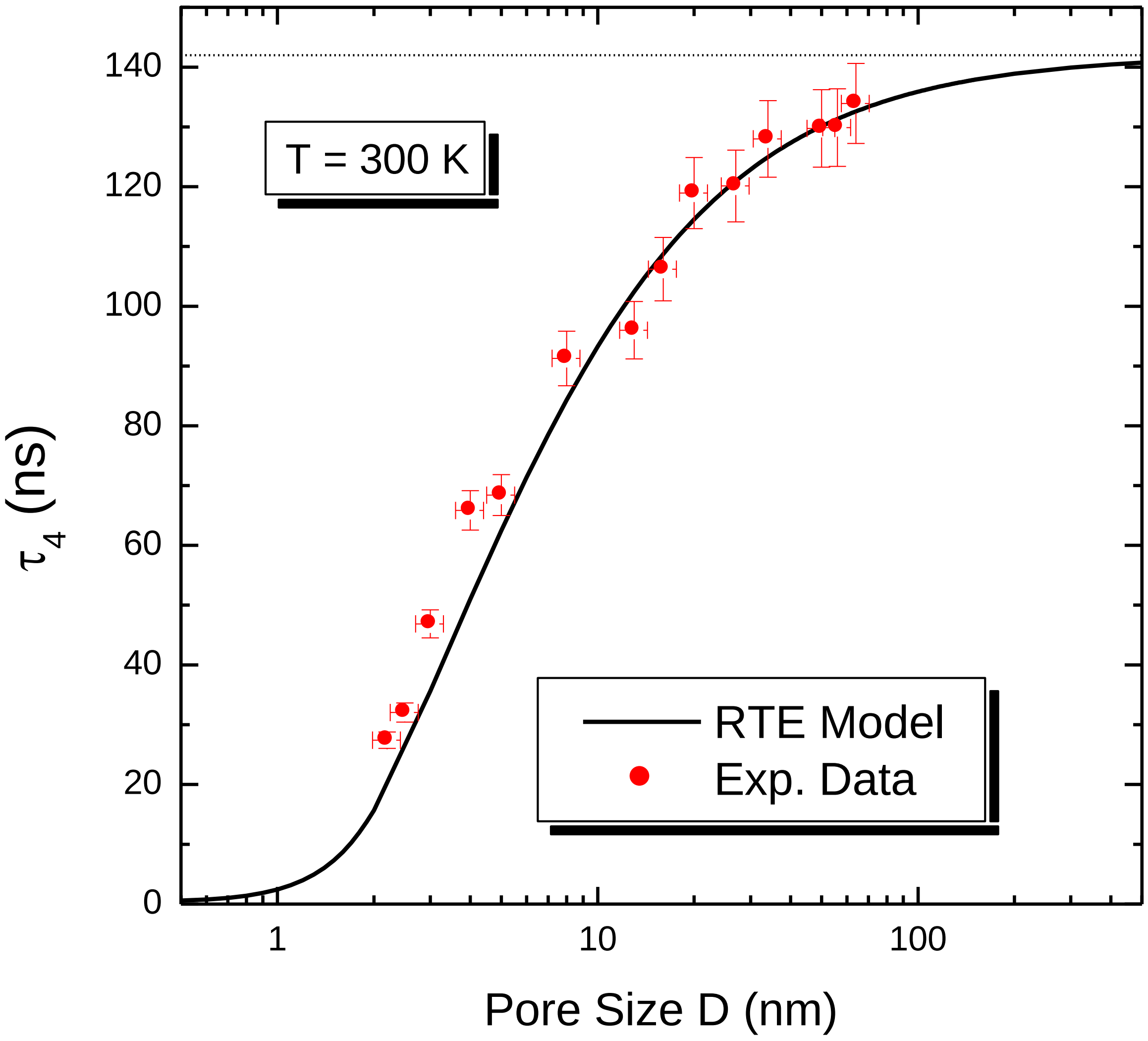
Monte Carlo simulations of the same spectrum using different source strengths



dependence of the lifetime on the maximum source activity

S. Thraenert, E.M. Hassan, R. Krause-Rehberg, *Nucl. Instrum. and Meth. B* **2006**, *Vol. 248 No. 2,* 336.

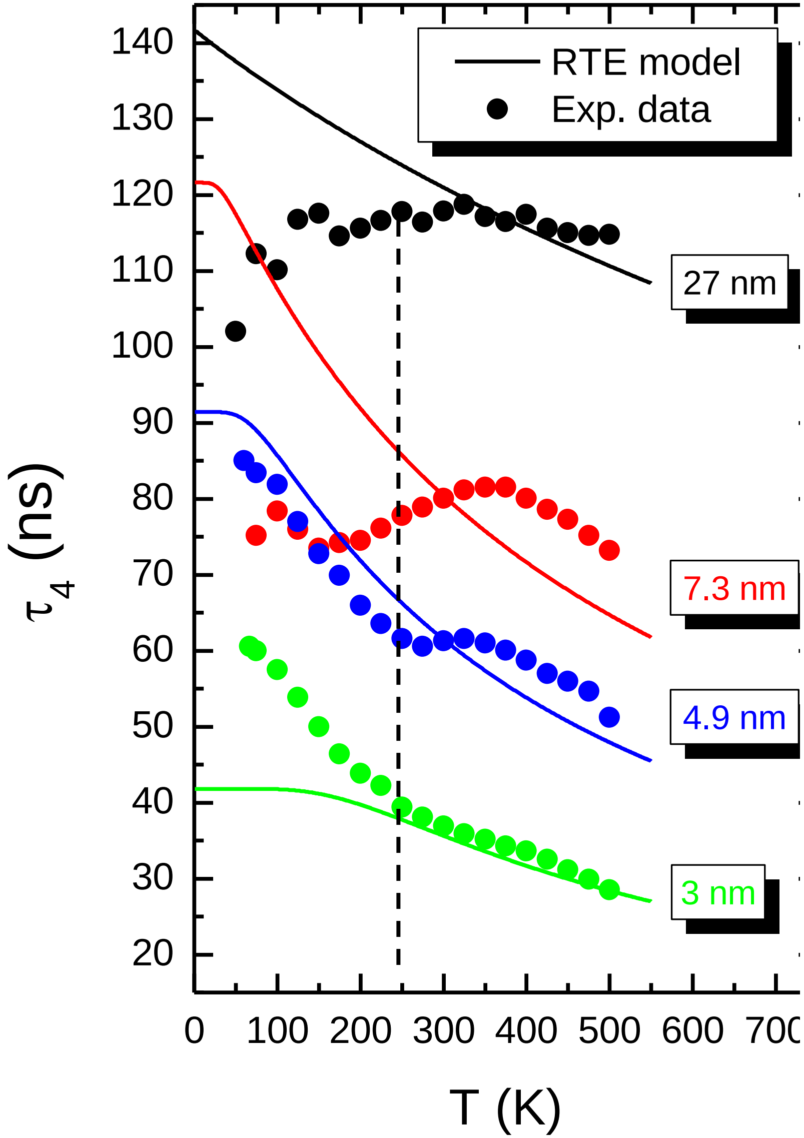
The experiments at T = 300 K



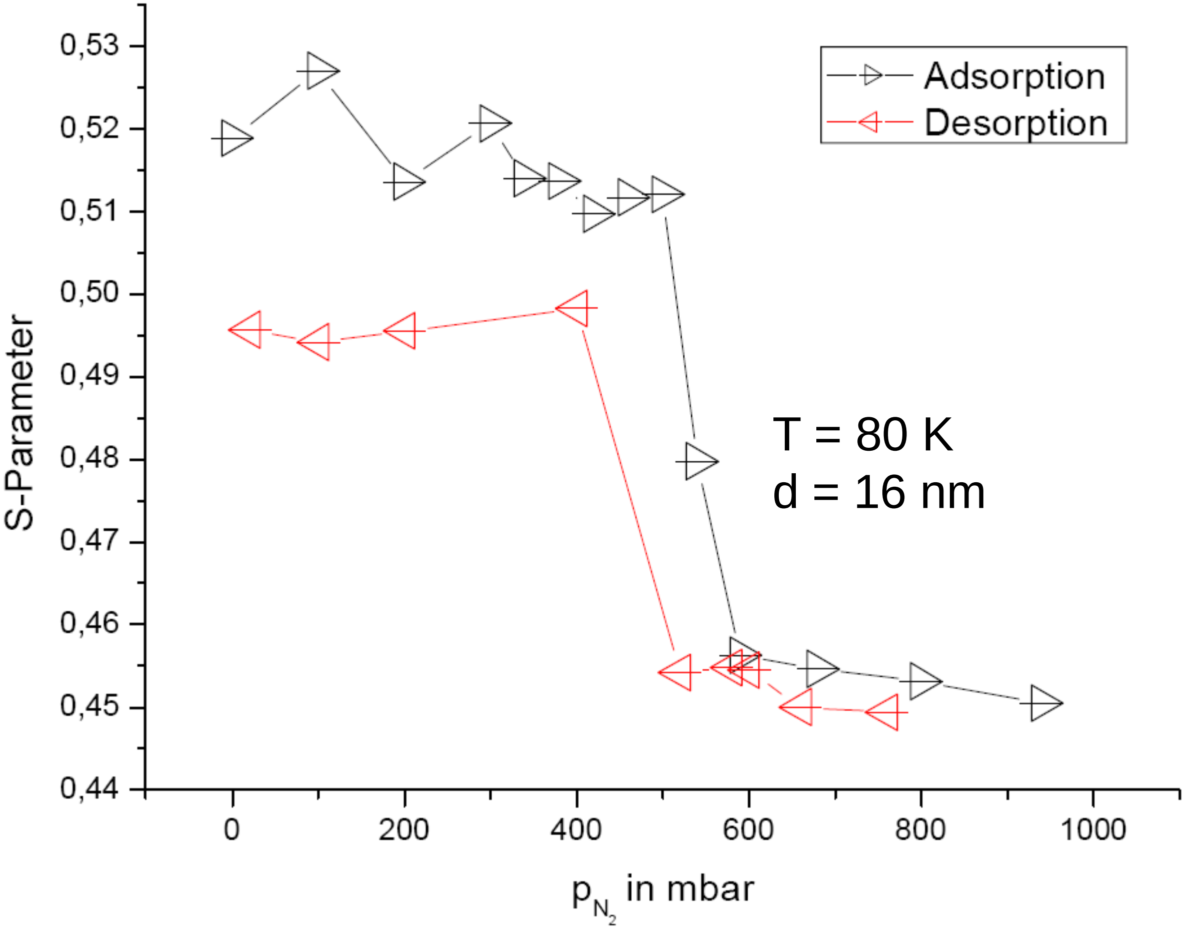
- we measured porous glass in a broad pore size range
- pore size obtained by N_2-adsorption method
- for T=300 K general agreement to the RTE model
- calibration curve for the correlation of o-Ps lifetime and pore size

The T-dependence

- although we found good agreement for T = 300 K
- temperature behavior cannot be explained very well at low temperatures
- model too simple



Cryo-condensation in nano-pores

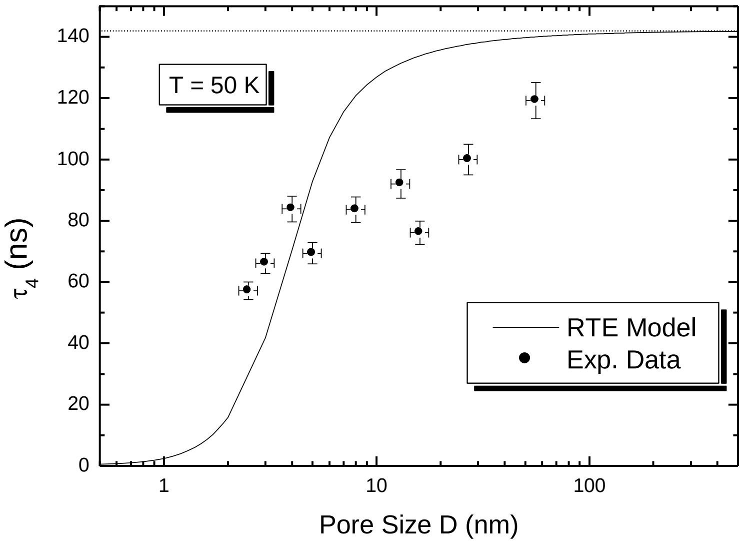


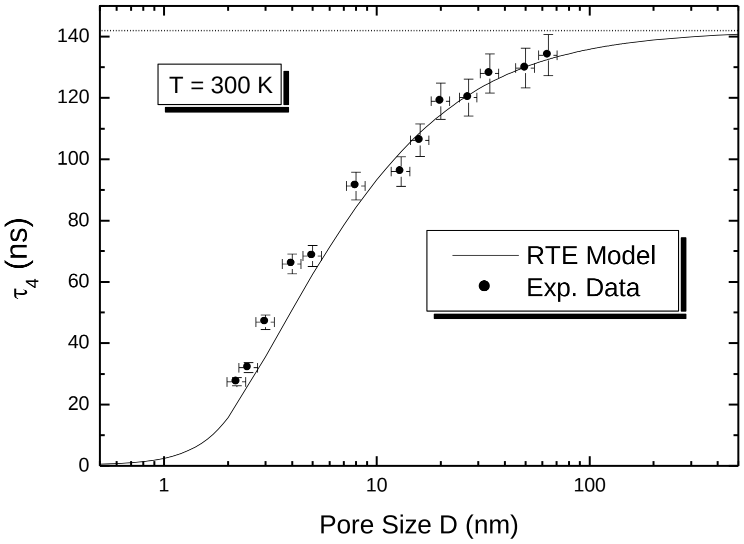
- S-parameter behaves similar like intensity of o-Ps lifetime component
- cryo-condensation can be observed as filling of pores
- phase transition can be studied in a nano-volume as function of size, gas, T and p

Summary

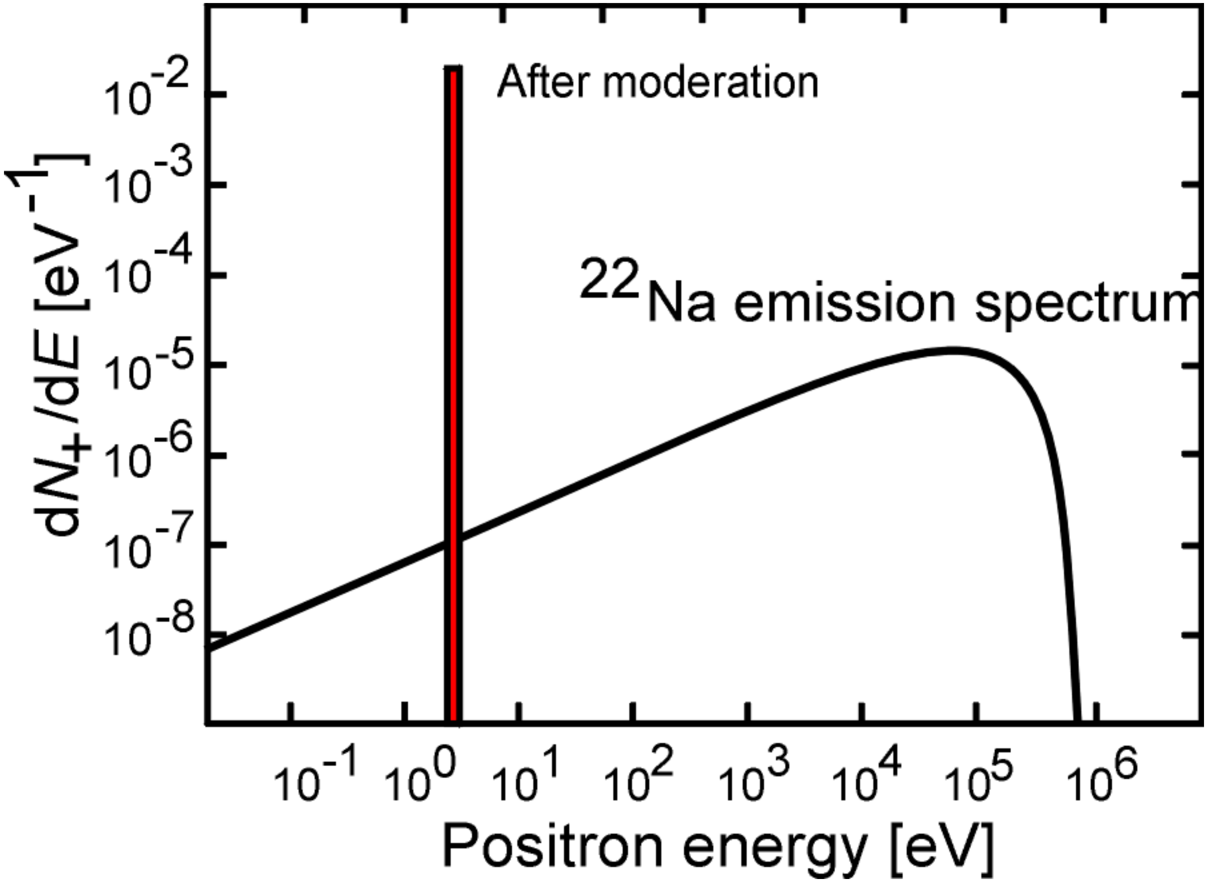
- for T = 300 K general agreement to the RTE model -> at room temperature, PALS is a useful porosimetry tool!
- for T > 300 K still acceptable agreement to the RTE model.
- for low temperatures the measurements show disagreement to the RTE model

- Advantages:
  - very sensitive method for small pores (1 nm to 10 nm)
  - also encapsulated pores can be measured
  - non destructive





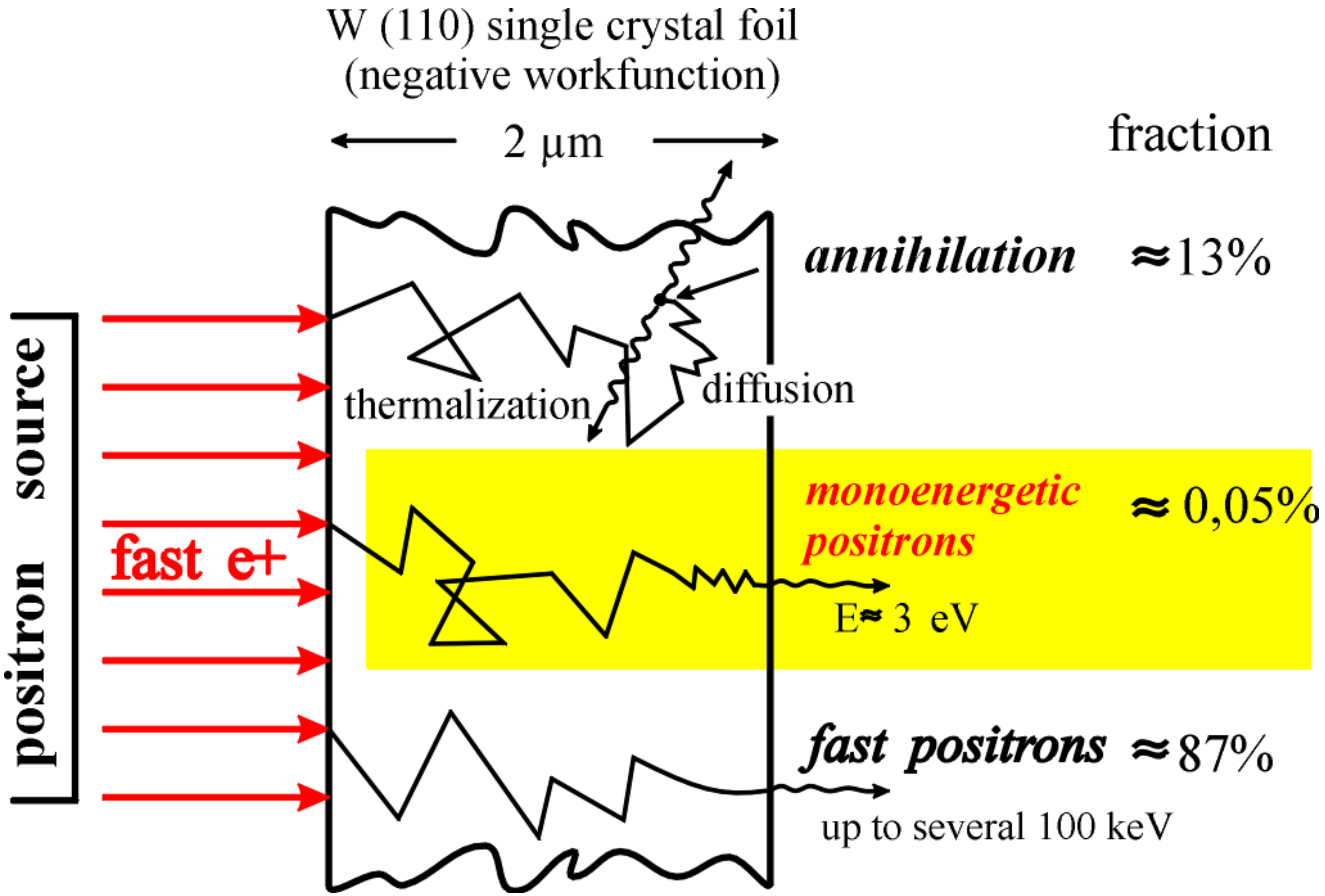
The Slow-Positron Beam Technique



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

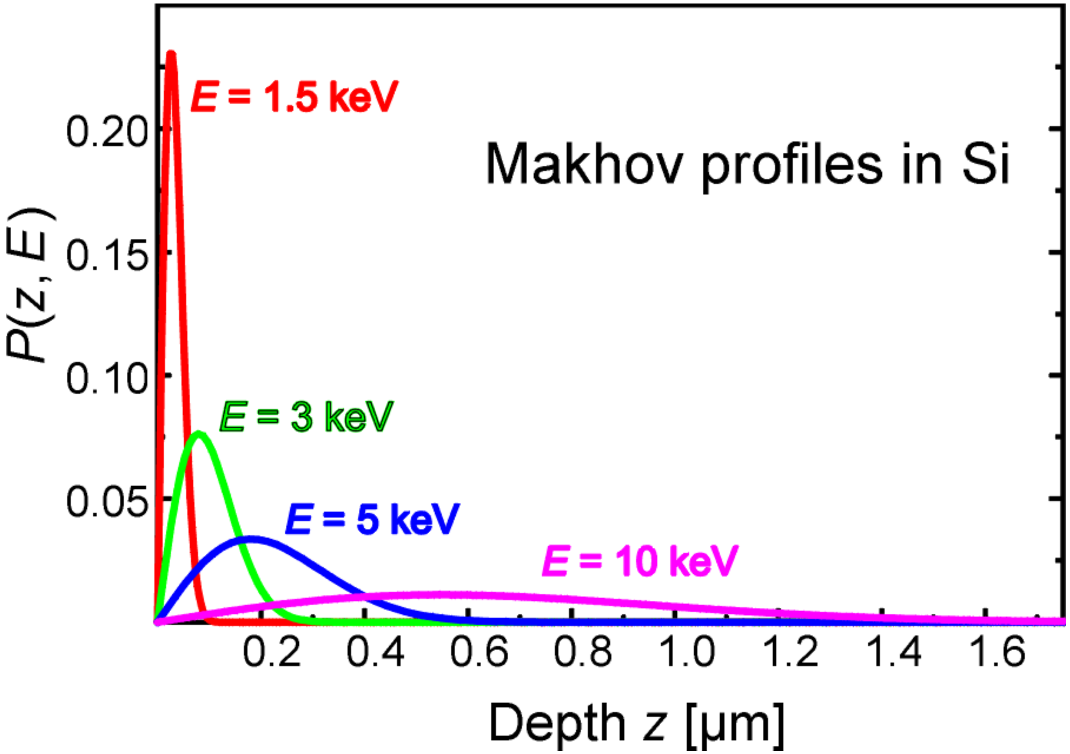
Mean implantation depth of un-moderated positrons (1/e): Si: 50µm

Moderation of Positrons



moderation efficiency: ≈10^{-4}

Implantation Profiles of monoenergetic Positrons



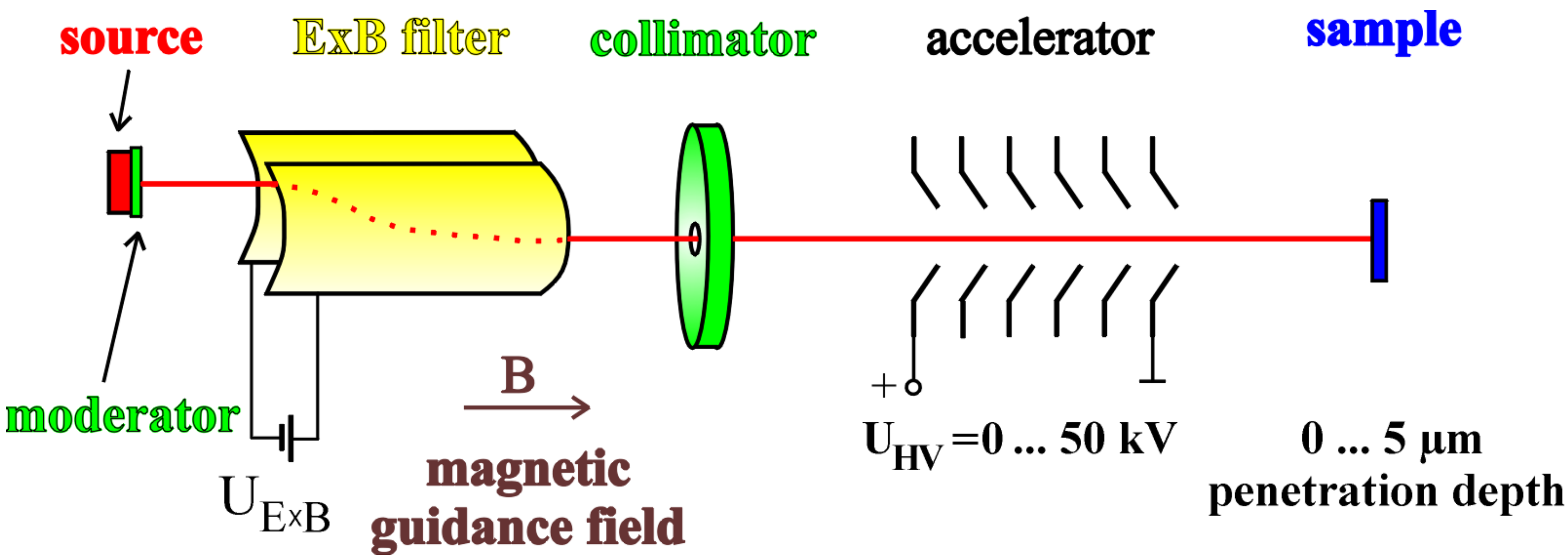
- depth resolution is function of implantation depth
- exact implantation profiles are obtained by Monte-Carlo simulations

$$P(z,E)=\frac{mz^{m-1}}{z_0^m}\exp\left[-\left(\frac{z}{z_0}\right)^m\right]$$

$z = f(E,\rho)$ $z_0 = \text{const.}$ $m = 2$

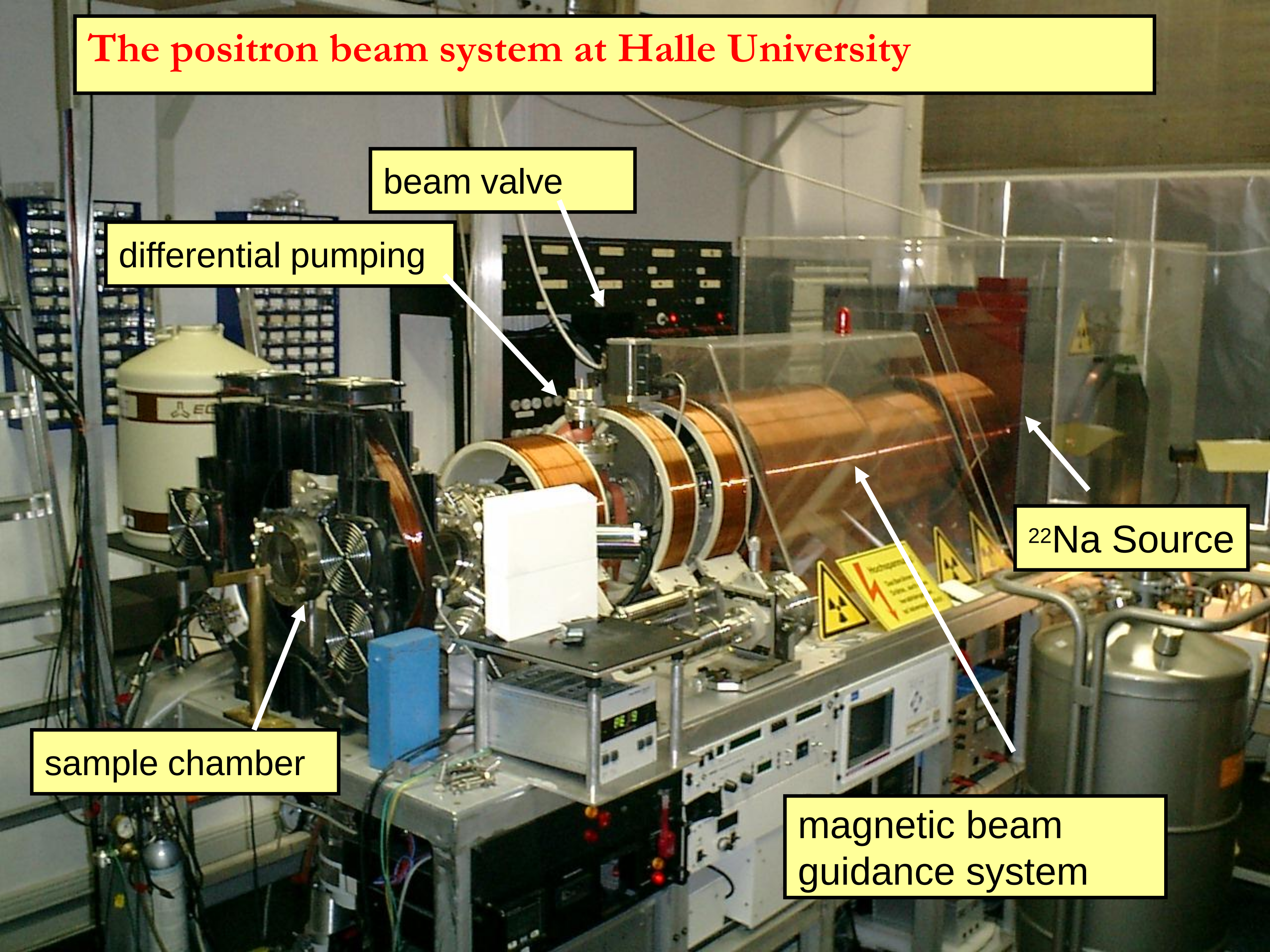
(Makhov, 1961)

The Positron Beam System at Halle University



- spot diameter: 5mm
- time per single Doppler measurement: 20 min
- time per depth scan: 8 hours

The positron beam system at Halle University



beam valve

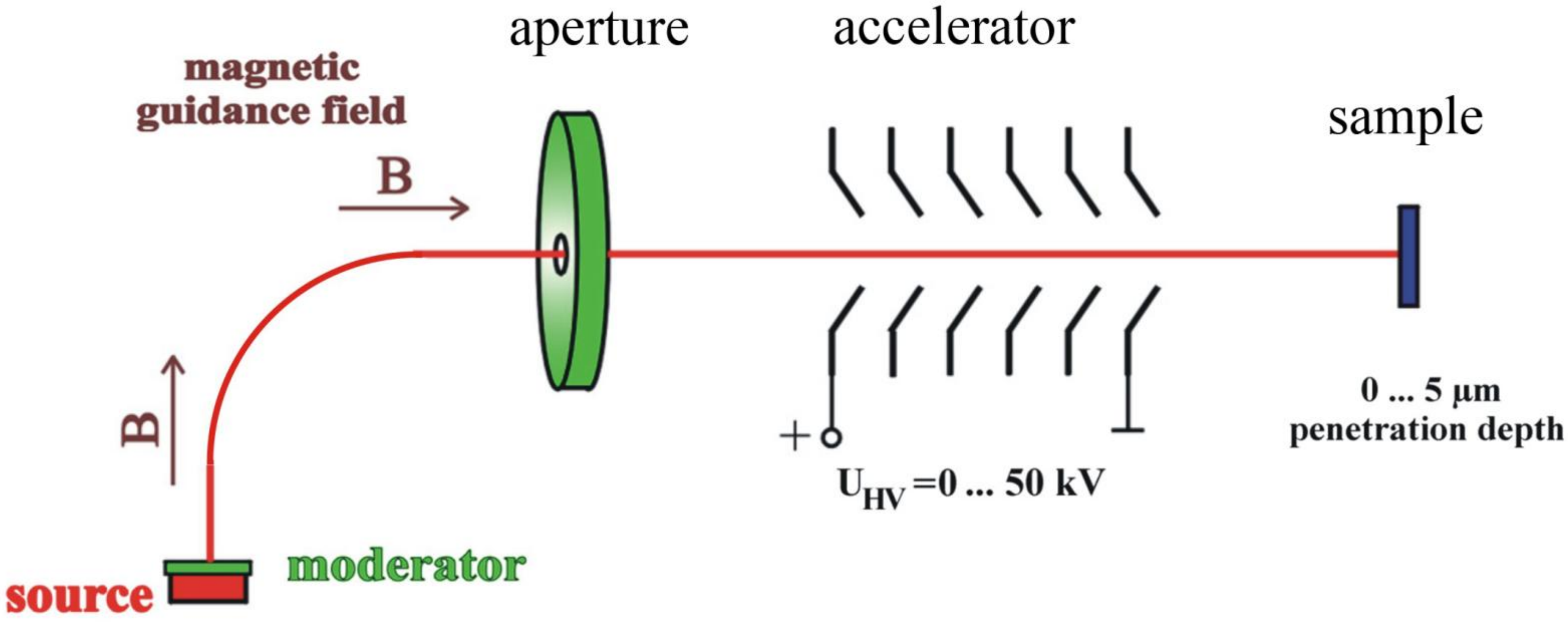
differential pumping

^{22}Na Source

sample chamber

magnetic beam guidance system

Positron Beam System at Halle University – new setup



- Energy selection now done by a bended tube: slow positrons follow the longitudinal magnetic field
- radiation screening at the floor easier

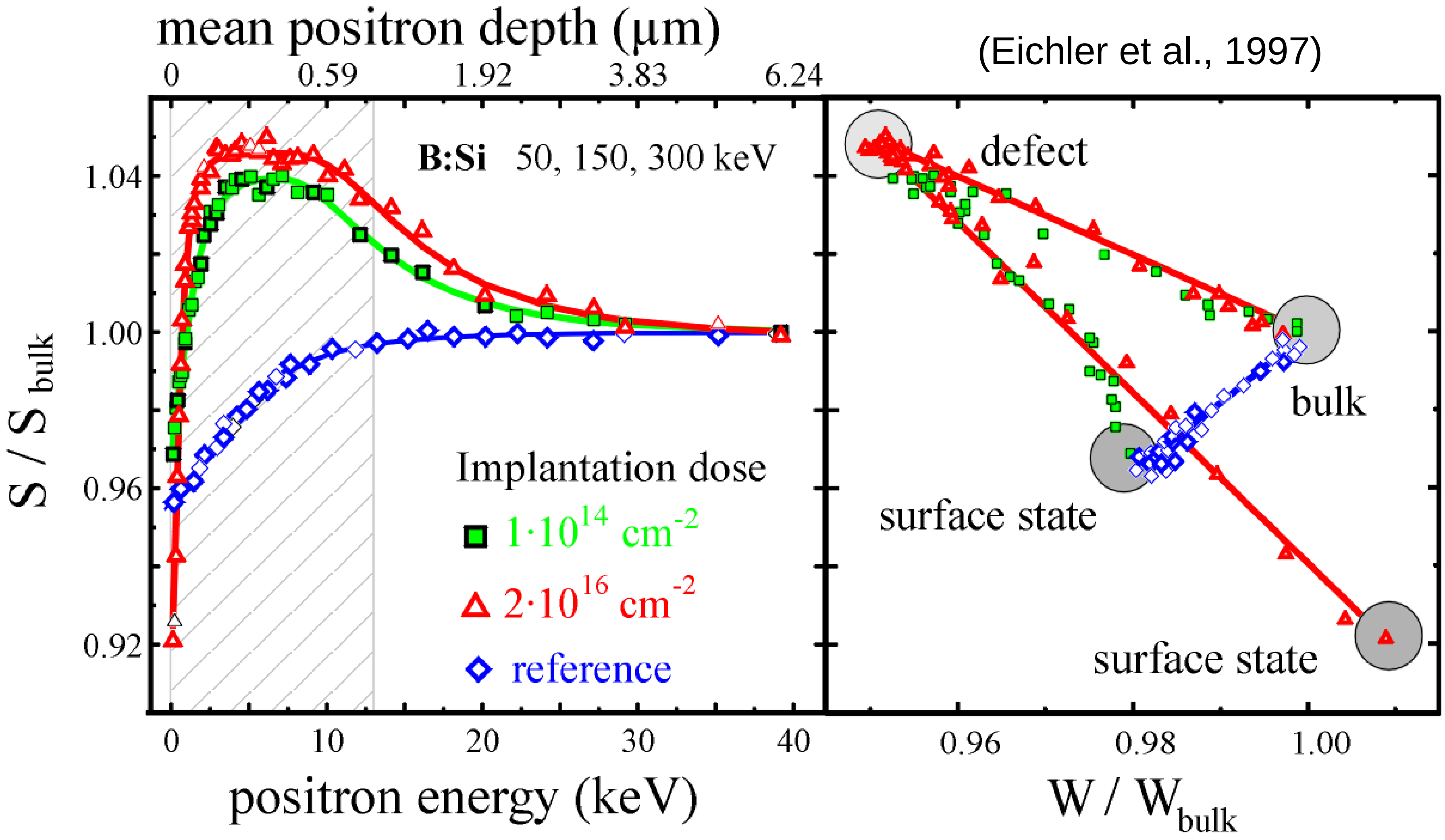
Earth magnetic field must be compensated

- Earth field of 50 μT (0.5 G) at a length of 3m and 2 keV beam energy: 25 mm deviation! But most beams are slower…
- Must be compensated
- Compensation necessary only in the two perpendicular directions to the beam
- We used thin Al profile and 10 turns of wire and a few amps

Defects in Si induced by Ion Implantation

- ion implantation is most important doping technique in planar technology
- main problem: generation of defects ⇒ positron beam measurements

(Eichler et al., 1997)



- Thanks for your patience!

- This talk as pdf?

- http://positron.physik.uni-halle.de