Diffusion and Relaxation Probed by Mobile NMR

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RWTH

Diffusion Fundamentals IV, RPI, Troy, N.Y., 21.-24. August 2011

Diffusion Fundamentals IV

The Menue

Preface

Introduction

Magnets and applications

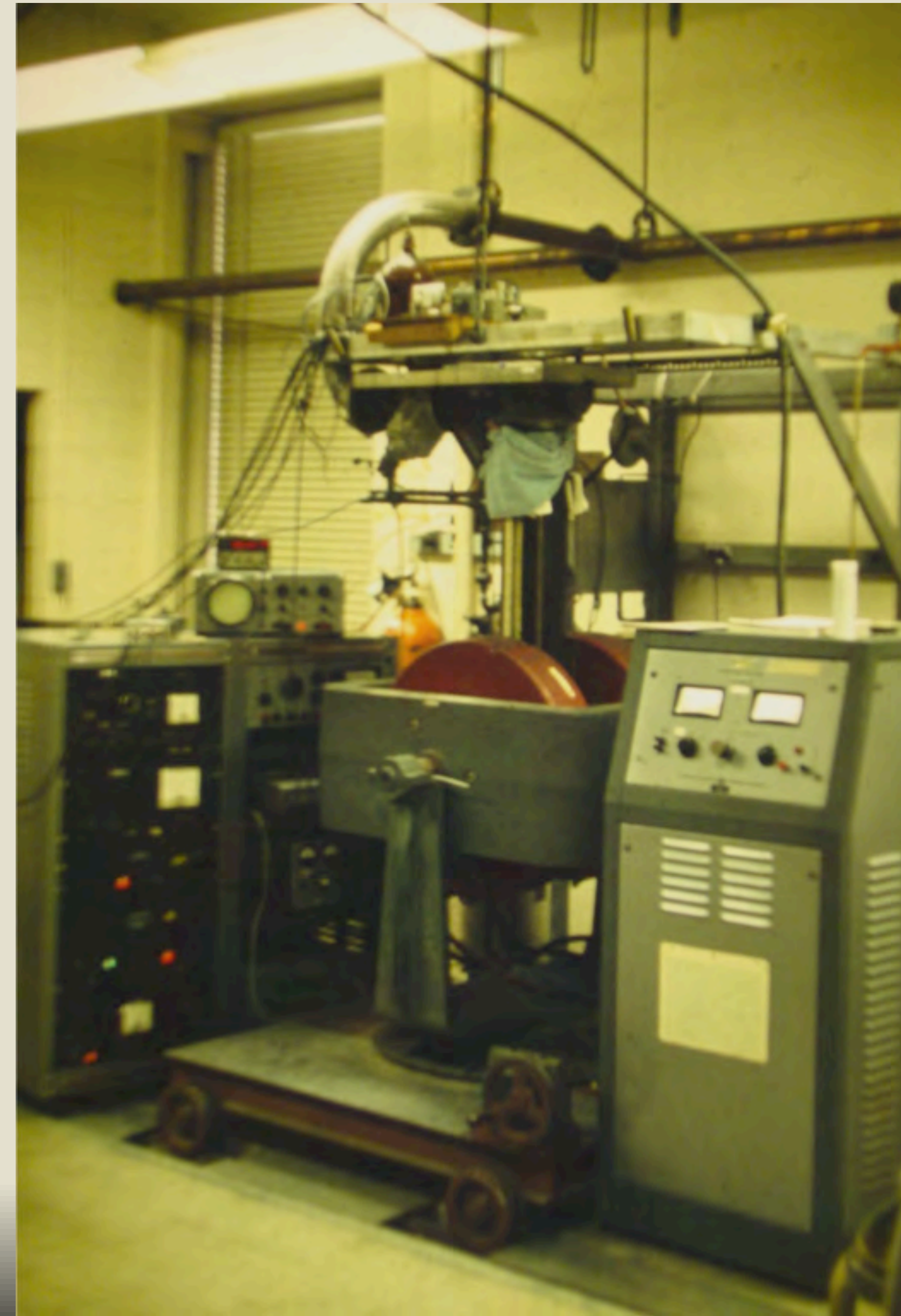
Summary

MS Thesis

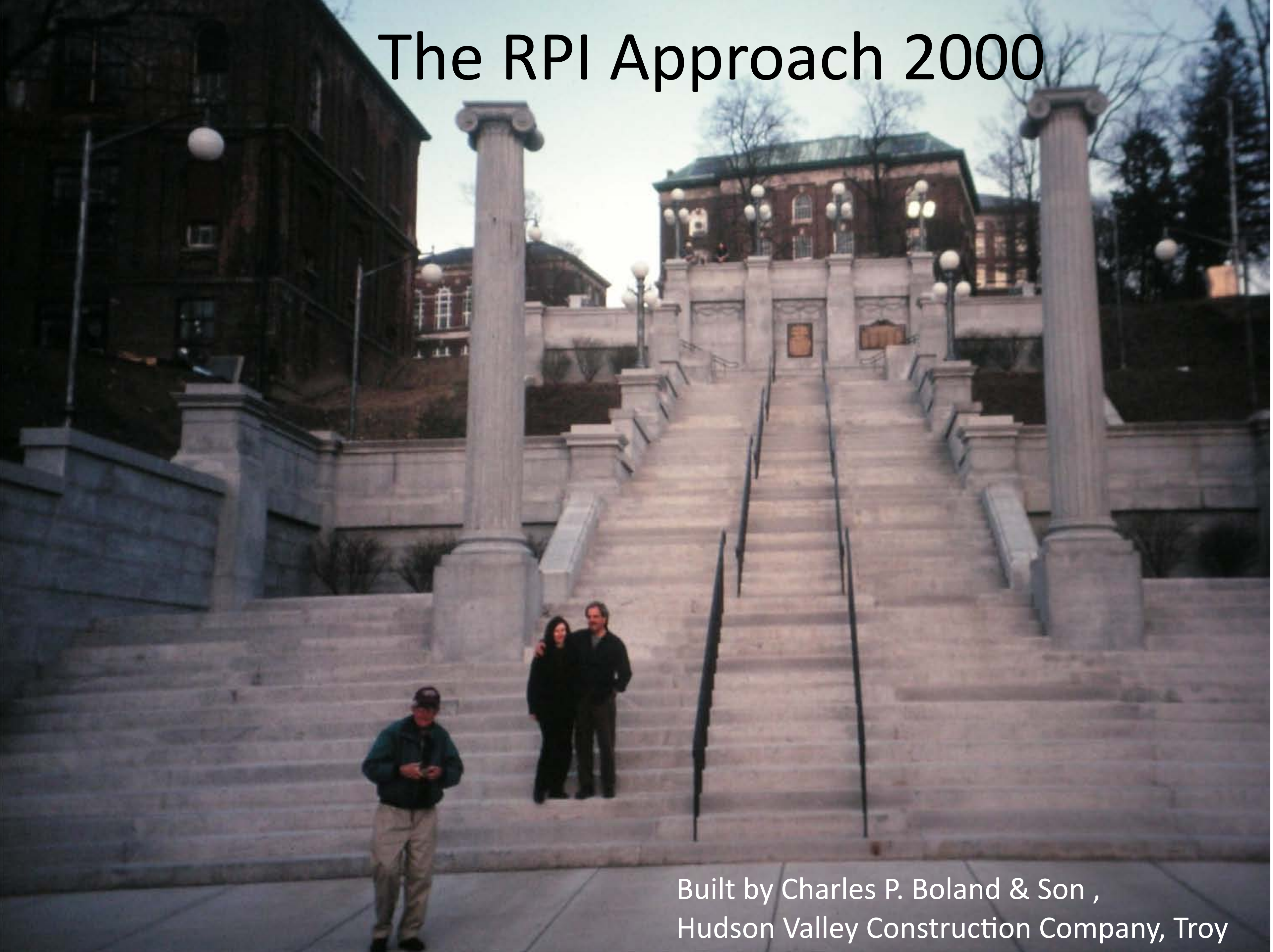
P. A. Casabella

Gerhard Salinger

NMR Investigation of Al^{27} in Rogers and Williamson Glass, RPI, February, 1976



The RPI Approach 2000



Built by Charles P. Boland & Son ,
Hudson Valley Construction Company, Troy


ROLL OF HONOR
IN MEMORY OF RENSSELAER MEN WHO GAVE THEIR LIVES
IN THE ARMED FORCES SERVING OUR COUNTRY
DURING THE SECOND WORLD WAR 1941-1945
MAURICE P. ALGER, JR.
ARTHUR F. AMADON, JR.
ELLSWORTH B. ATWOOD
JOHN J. AVIZA
ALBERT K. BACK
LEONARD F. BARRY
ROBERT J. BARTLEY, JR.
HILAND G. BATCHELLER, JR.
LESTER R. BESSELL, JR.
HOWARD J. BLIND
HARRY A. BOLLES
JAMES D. BONNYMAN
WILLIAM E. BOULEY, JR.
GEORGE W. BRADLEY
H. GUYON BRIGHTLY
ROBERT P. BROWN
WALTER BROWN, JR.
RICHARD M. BUCK, JR.
JAMES E. BUCKLEY
EDWARD R. BUDZ
ROBERT CAMPBELL, JR.
FRANK W. CAPEK
JOHN L. CHILDS
JAMES G. CHRESSANTHIS
JACK S. COLLINS
JAMES F. CONWAY
JOHN V. CROTTY
JEROME F. CURRAN
HUGH W. CURTIS
STEPHEN H. CURTIS, JR.
PHILIP S. DAVISON, JR.
FREDERICK S. DeBENEDETTO
W. WILLIAM DEBENHAM
DAVID O. DEVLIN
HOWARD H. DISBROW
PAUL A. DOCKLER
GORDON L. DOCKSTADER
FRANK A. DOLE, JR.
WILLIAM D. DUCHARME
EDWARD H. ENNERS, III
CHARLES W. ERICHSEN
J. DONALD FINDLAY
F. GURNEY FINE, JR.
ROBERT S. FINK
GEORGE S. FITCH
RALPH N. FOUNTAIN
GERALD A. FRANKENSTEIN
AUGUST GEIB, JR.
DONALD P. GILBERT
ROBERT C. GISE
HENRY D. HUDSON
ERNEST KERTSCHER, JR.
NORMAN H. KIES, JR.
ELMER KUPSENEL
C. WILLIAM LAW
ROY F. LAYER
WILLIAM M. LICKEL
ISAAC M. LOBELL
JOHN McBRIDE, JR.
WILLIAM S. McHENRY, JR.
F. TYLER MORRISON, JR.
JOSEPH M. ROCHE
FRED B. SCHUBERT
WILLIAM V. SCRIBNER
FRANK K. SEIDEL, JR.
H. OAKLEY SHARP, JR.
JOHN L. SHARP
ROBERT L. SHAW
DAVID H. SHERWOOD
DONALD R. SHERWOOD
GILBERT C. SINGER
THOMAS H. STANLEY
PAUL G. STYGER
CHARLES A. TEDESCHI
JOHN E. THELEN
CARL M. THOMAJAN
ROGER S. THOMAS
LEONARD H. THORNTON
TORAEF TOBIASEN
ROBERT V. TURCHETTO
RICHARD M. VAN GALDER
IGOR V. VASSILIEFF
RICHARD G. VILLOCHI
JAMES M. WALLACE
WILLIAM A. WALSH
WILLIAM J. WALSH
DONALD M. WILKIE
JOHN H. WINSCHUH
JOHN A. ZIMMERMANN

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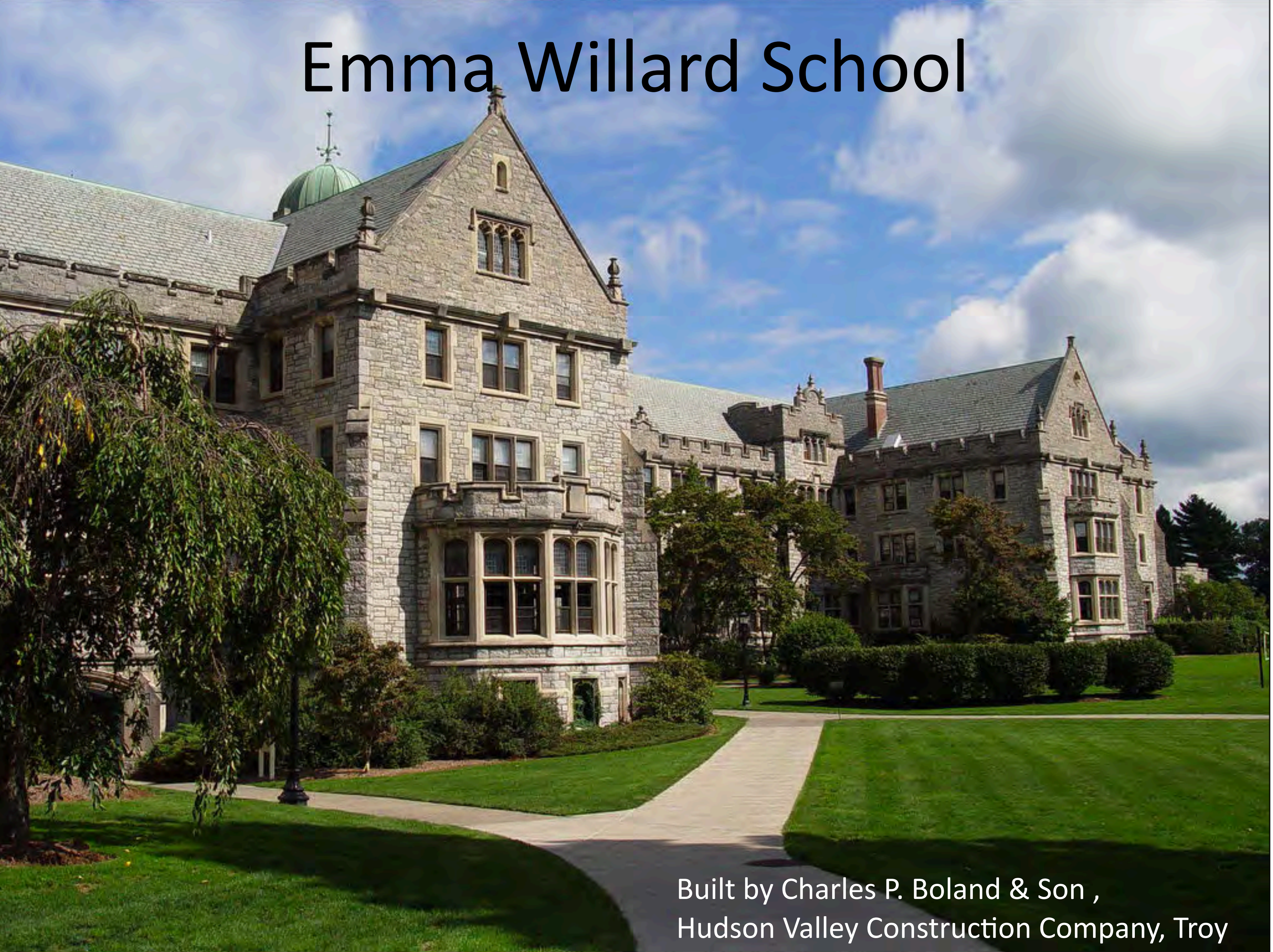
Emma Willard School



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McCarthy Building

The **McCarthy Building** is located on River Street on the west side of Monument Square in Troy, New York, United States. It was built in 1904, and remains in use as a commercial building. In 1970 it was added to the National Register of Historic Places in 1970, along with the nearby Cannon Building. Since 1986 it has also been a contributing property to the Central Troy Historic District.

Charles P. Boland,
Hudson Valley Construction Company, Troy

Proctor's Theatre

Troy

Schenectady

Troy: It cost $325,000[3] to construct, and when it opened in 1914 it became the largest theater in the state and was praised as "a structure ranking foremost in American theatrical circles".

Stairs of the NY State Capitol

Built by Charles P. Boland & Son , Hudson Valley Construction Company, Troy

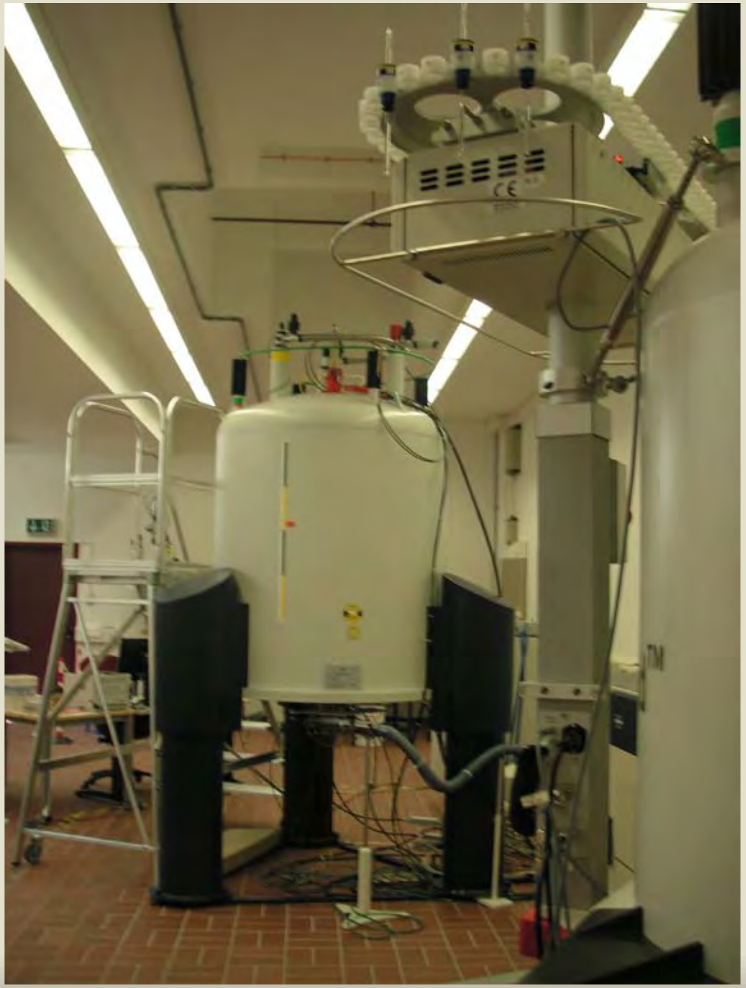
The D&H Building (SUNY administration)

Built by Charles P. Boland & Son ,
Hudson Valley Construction Company, Troy

Conventional NMR Magnets

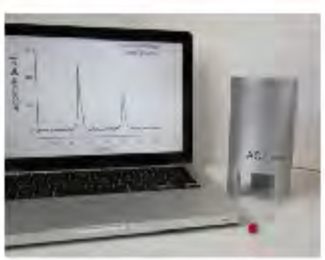
The object is enclosed by the magnet

Electromagnet from Königsberg / Jena



High-field NMR at RWTH Aachen University

State-of-the-Art NMR Instrumentation

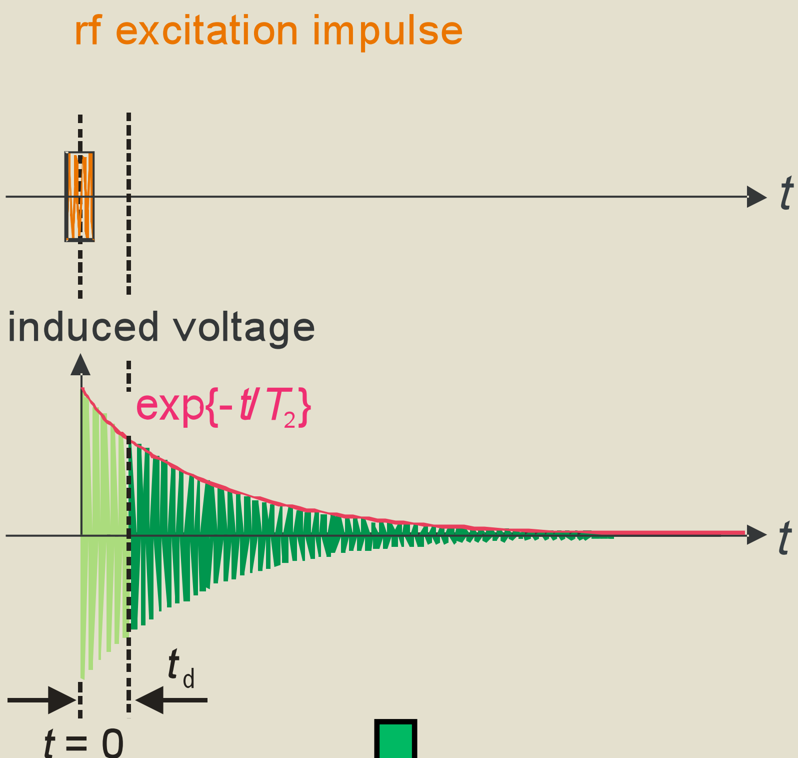
	Small-scale NMR		Large-scale NMR	Nobel prizes
	Closed magnets	Open magnets: NMR-MOUSE		
Relaxometry				1952 Nobel prize in Physics: Edward Purcell, Felix Bloch ... for measuring NMR ...
Tomography				2003 Nobel prize in medicine: Paul Lauterbur, PeterMansfield ... discovery of NMR tomography...
Spectroscopy				1991 Nobel prize in Chemistry: Richard Ernst ... high-resolution NMR spectroscopy... 2002 Nobel prize in Chemistry: Kurt Wüthrich ... NMR of biological macromolecules...

B. Blümich, F. Casanova, S. Appelt, *NMR at low magnetic fields*, **Chem. Phys. Lett. 477** (2009) 231-240

Basic NMR Methods

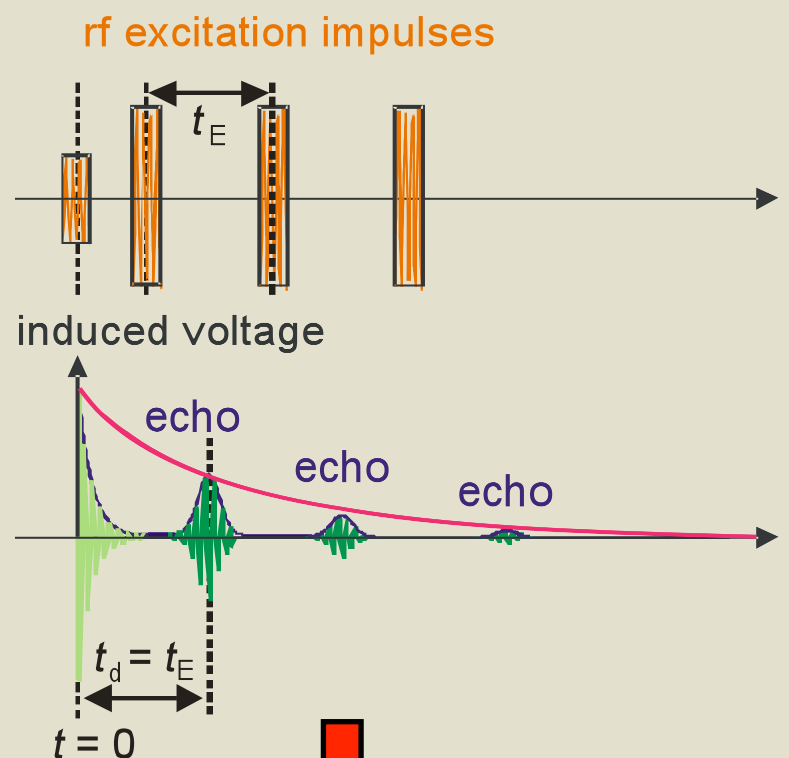
pulsed excitation

homogeneous magnetic field



Fourier transformation

inhomogeneous magnetic field



Laplace transformation

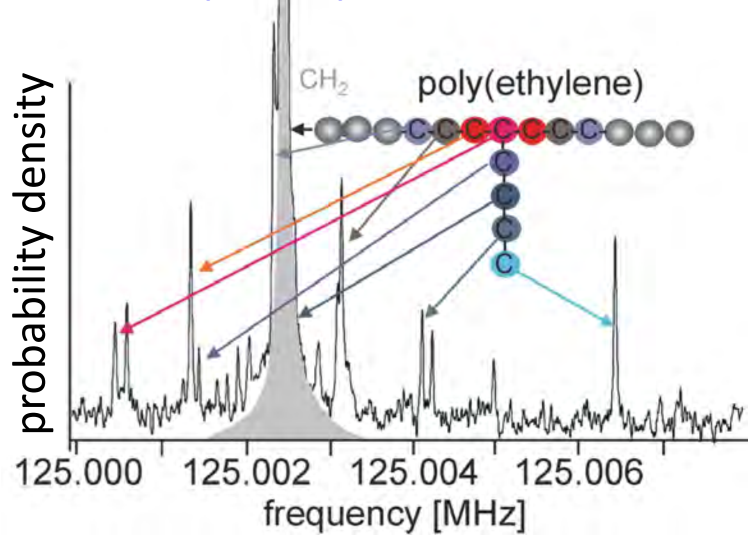
frequency distributions: spectrum, image

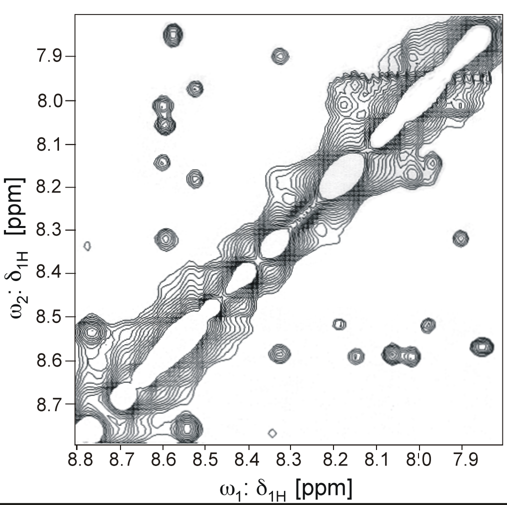
relaxation-time distributions

Fourier and Laplace NMR

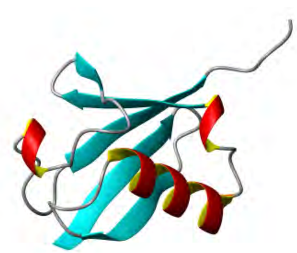
Fourier NMR: Spectroscopy, Imaging

Frequency Distribution



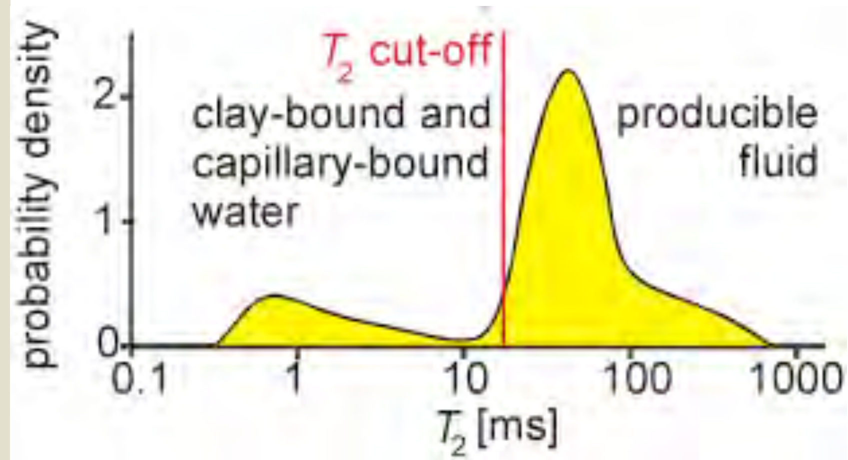


chemical structure and conformation

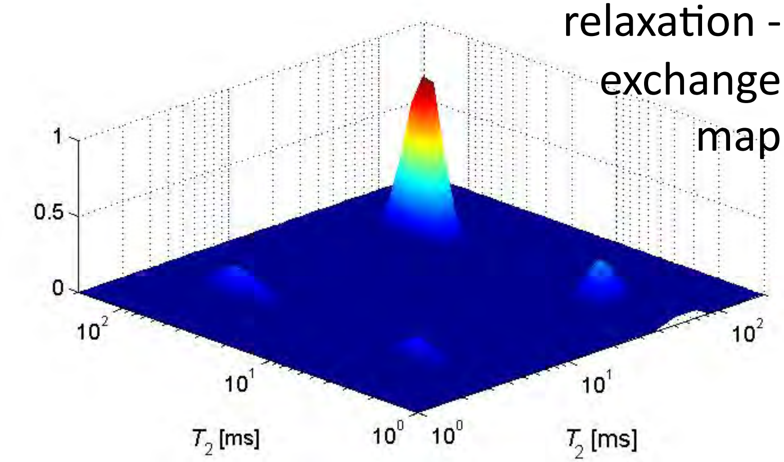


Laplace NMR: Material Properties

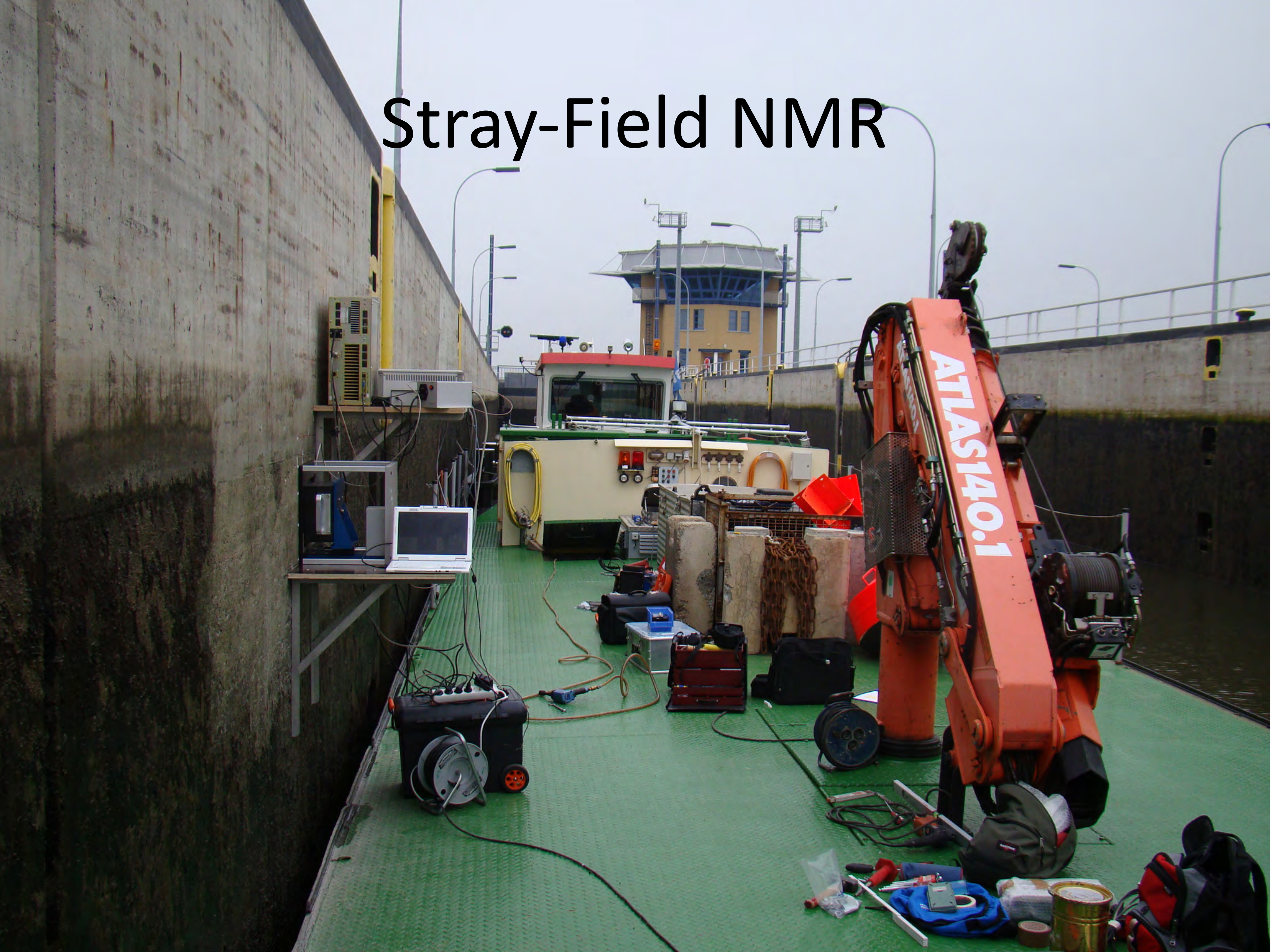
Relaxation-Time Distribution



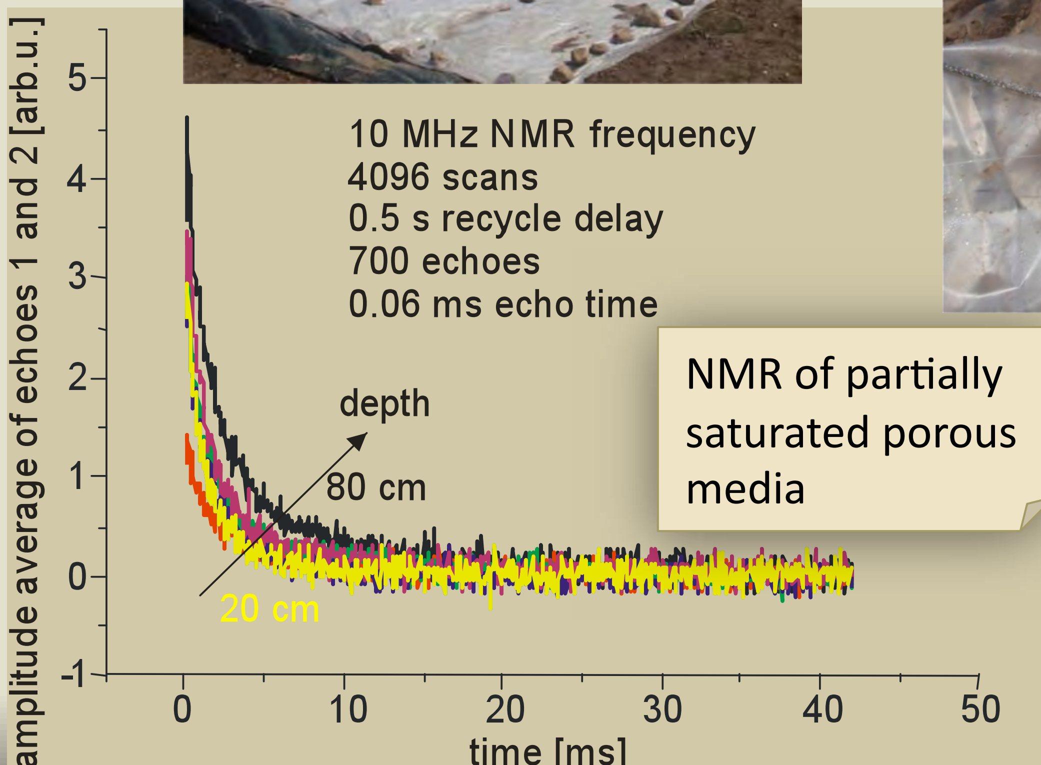
relaxation - exchange map

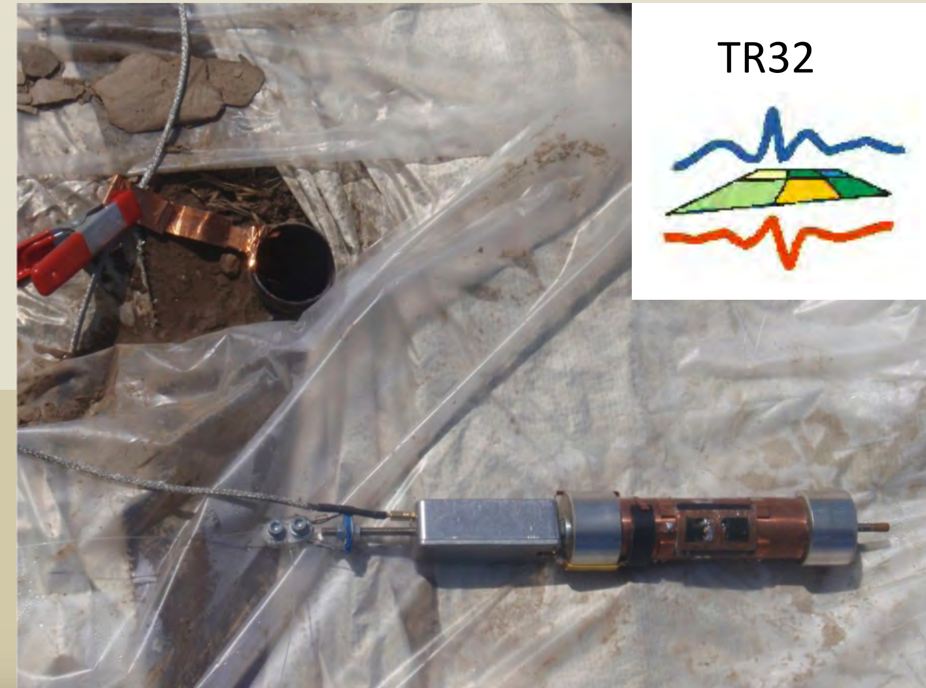


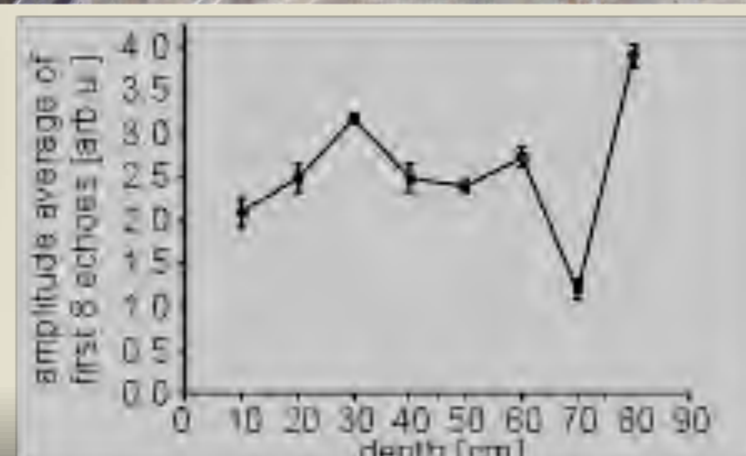
Stray-Field NMR



Slim-Line Tool for Soil Moisture Logging



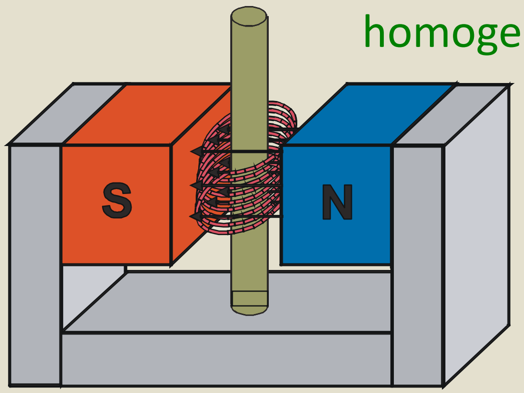




B. Blümich, F. Casanova, M. Dabrowski, E. Danieli, L. Evertz, A. Haber, M. Van Landeghem, S. Haber-Pohlmeier, A. Olaru, J. Perlo, O. Sucre, *Small-scale instrumentation for nuclear magnetic resonance of porous media*, **New J. Phys 13 (2011)** 015003

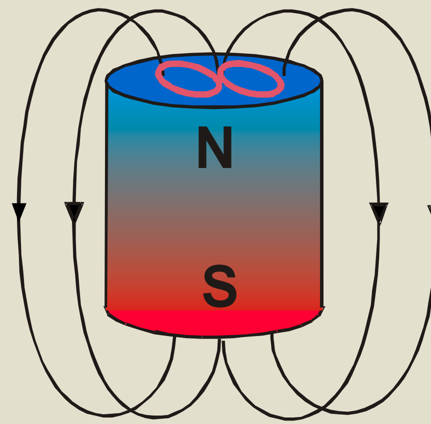
Magnets

homogeneous $\boldsymbol{B}_0$



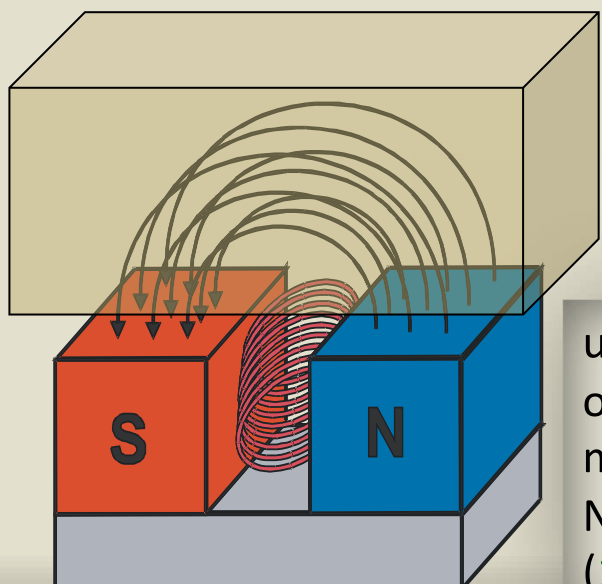
conventional NMR (1945): object inside magnet

inhomogeneous $\boldsymbol{B}_0$



the most simple NMR-MOUSE (2002)

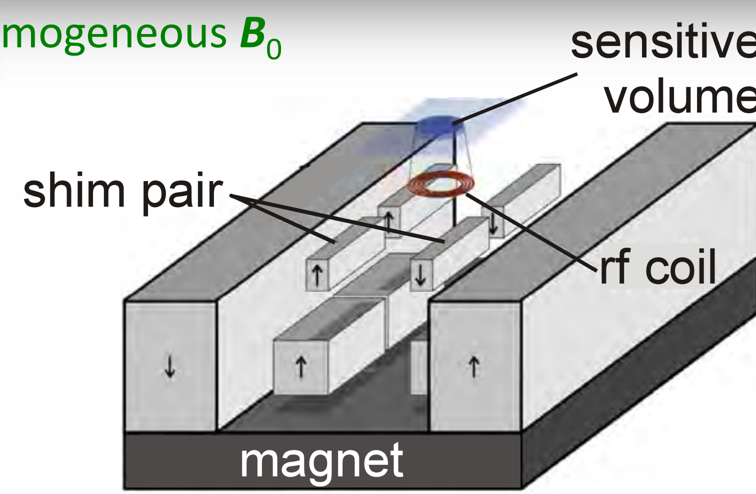
inhomogeneous $\boldsymbol{B}_0$



well logging, inside-out NMR (1980)

unilateral NMR: object outside magnet; NMR-MOUSE (1995)

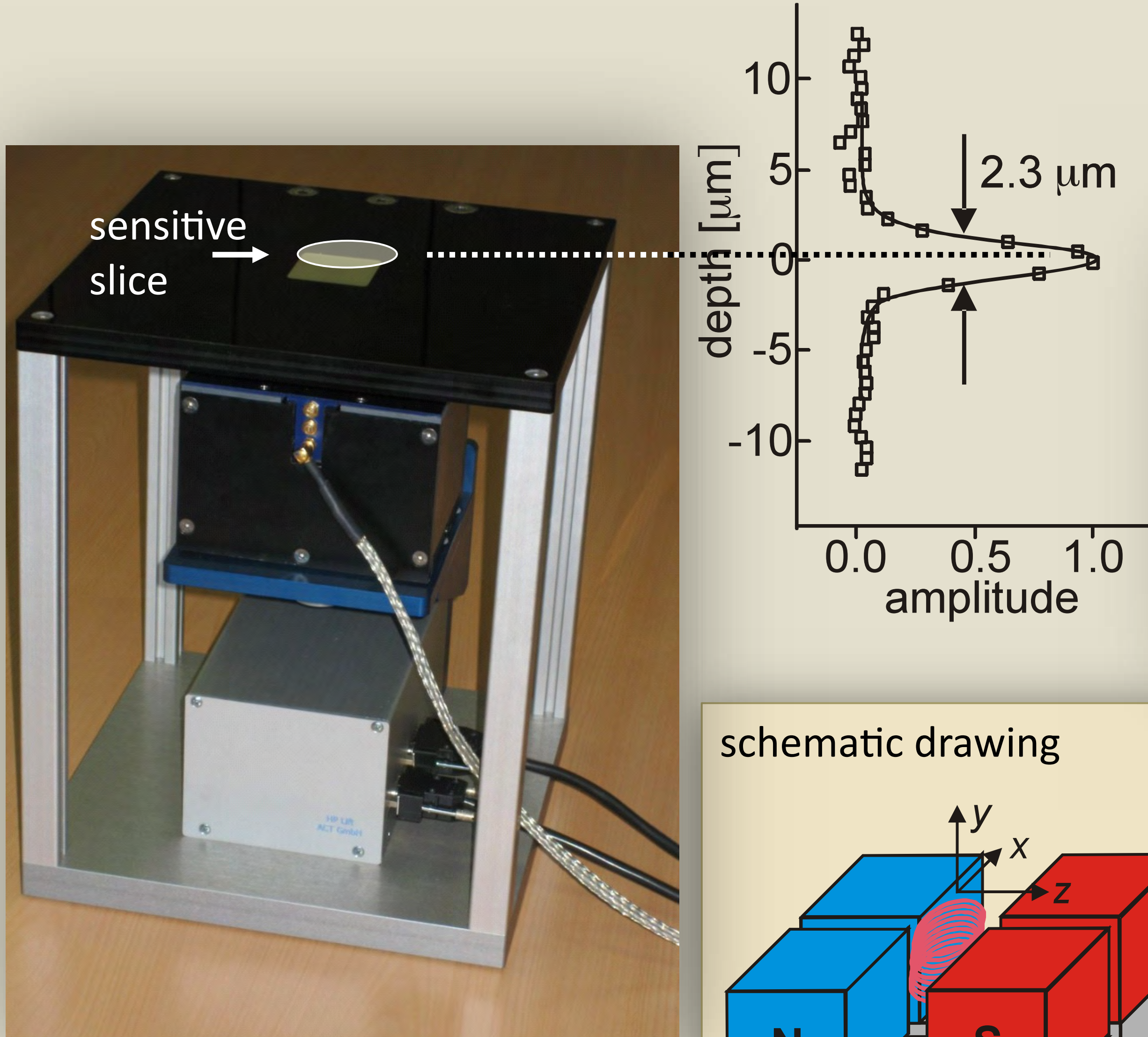
homogeneous $\boldsymbol{B}_0$

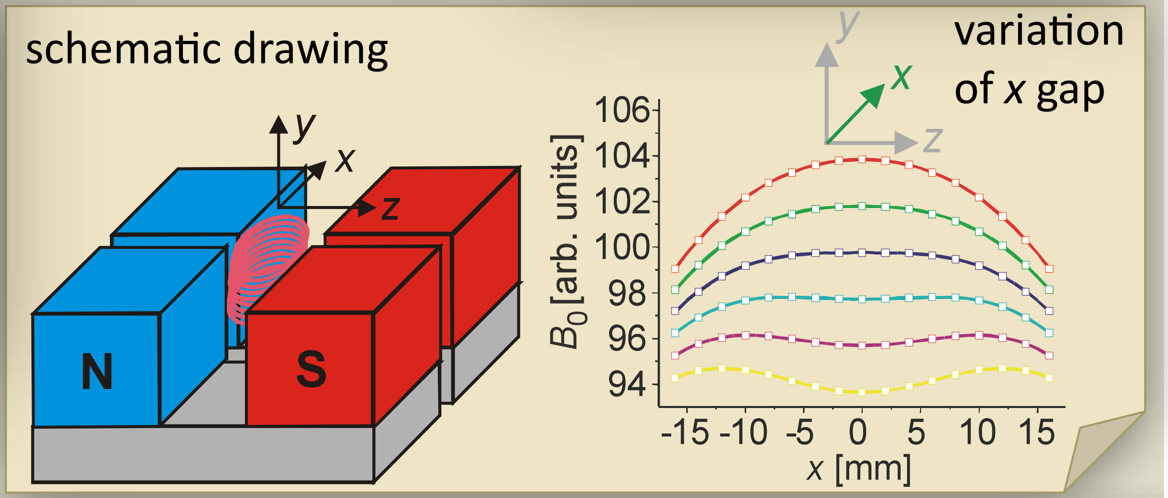


the most sophisticated NMR-MOUSE (2007): shimming the stray field

B. Blümich, F. Casanova, J. Perlo, *Mobile single-sided NMR*, **Progess Nucl. Magn. Reson. Spectrosc. 52** (2008) 197–269

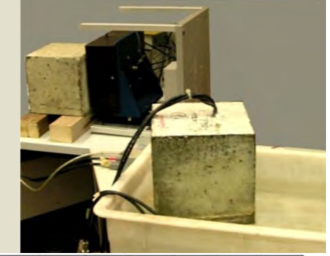
The Profile NMR-MOUSE®

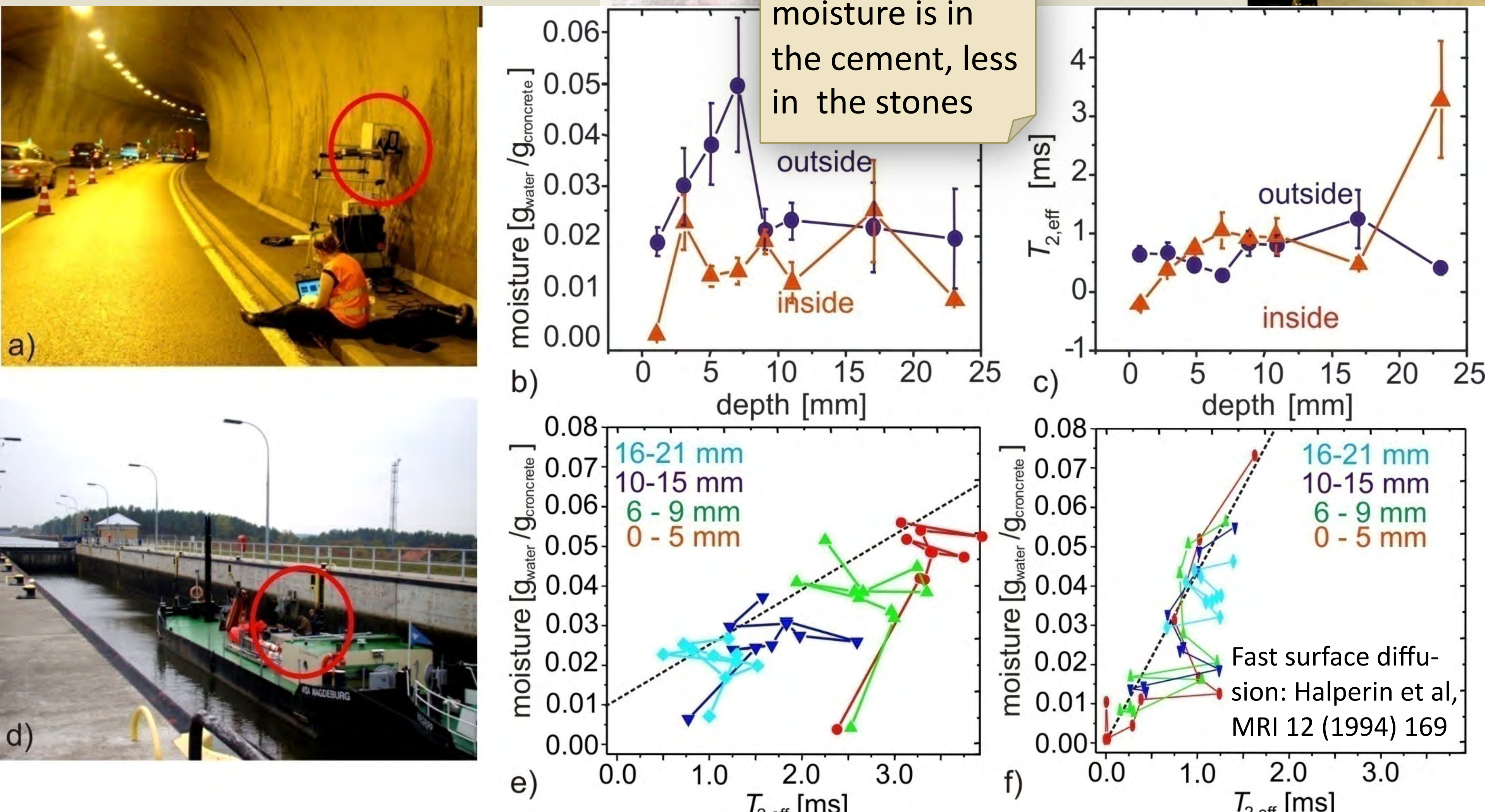




J. Perlo, F. Casanova, B. Blümich, *Profiles with microscopic resolution by single-sided NMR,* **J. Magn. Reson. 176** (2005) 64–70; B. Blümich, F. Casanova, J. Perlo, F. Presciutti, C. Anselmi, B. Doherty, *Noninvasive Testing of Art and Cultural Heritage by Mobile NMR,* **Acc. Chem. Res. 6 (2010)** 761 – 770

Moisture Content in Grey Concrete





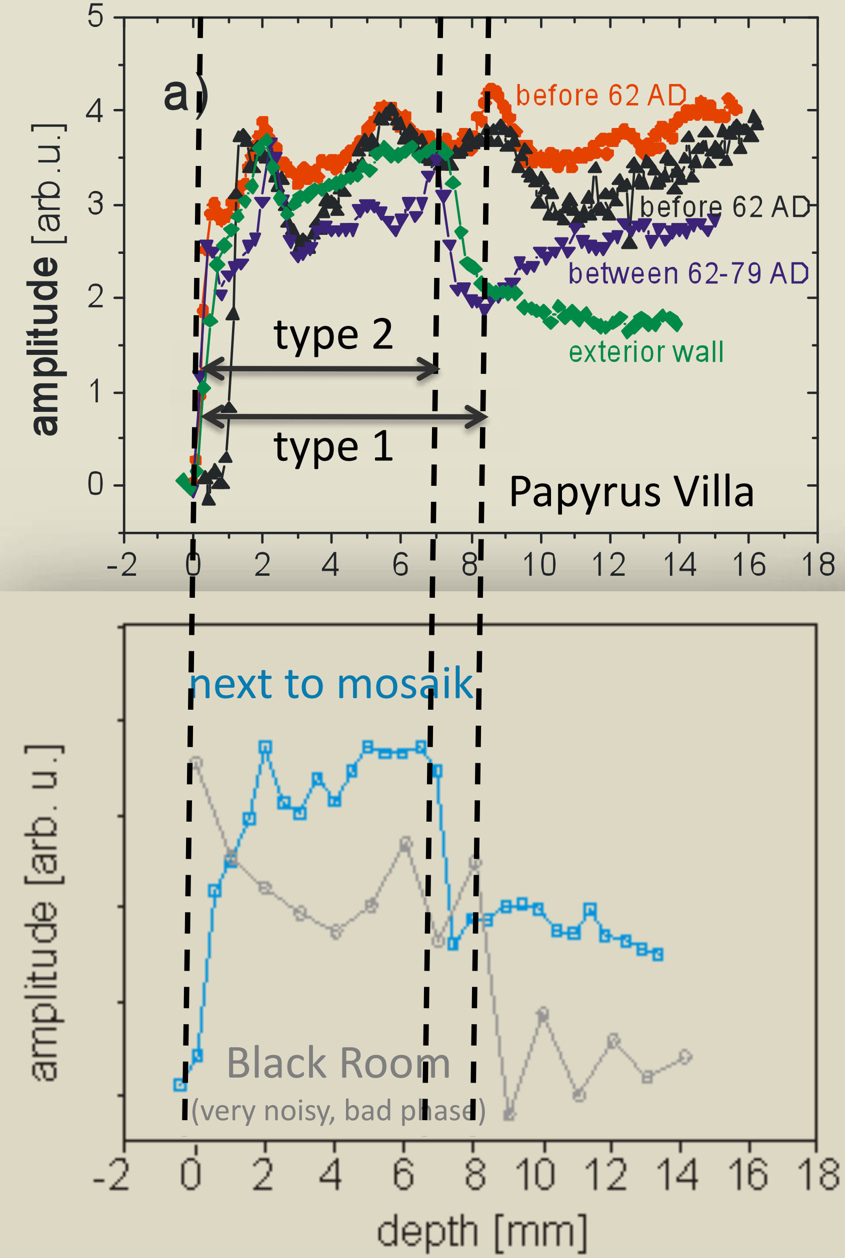
B. Blümich, F. Casanova, M. Dabrowski, E. Danieli, L. Evertz, A. Haber, M. Van Landeghem, S. Haber-Pohlmeier, A. Olaru, J. Perlo, O. Sucre, *Small-Scale Instrumentation for NMR of Porous Media*, special issue on Physics of Magnetic Resonance of Porous Media, **New Journal of Physics 13** (2011) 015003 1-15

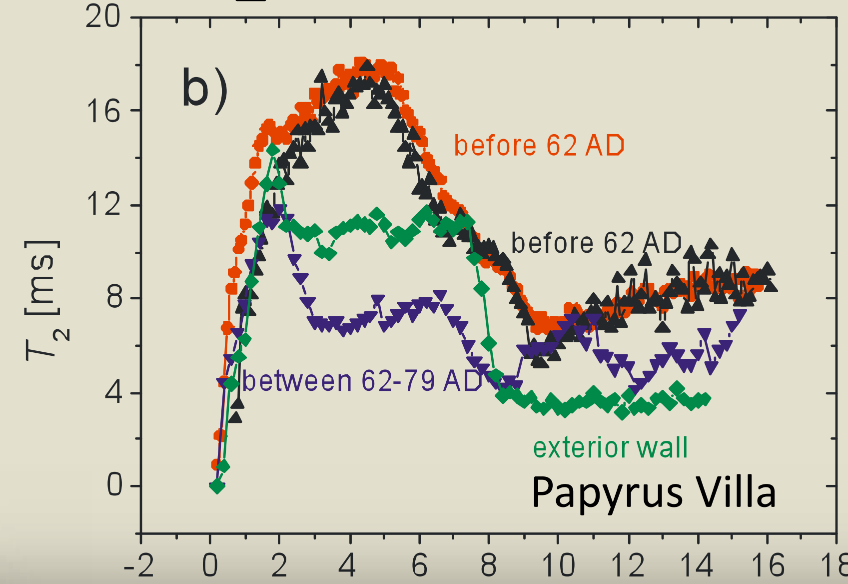
Papyrus Villa in Herculaneum

Earthquake: 62 AD
Eruption of Vesuvius: 79 AD



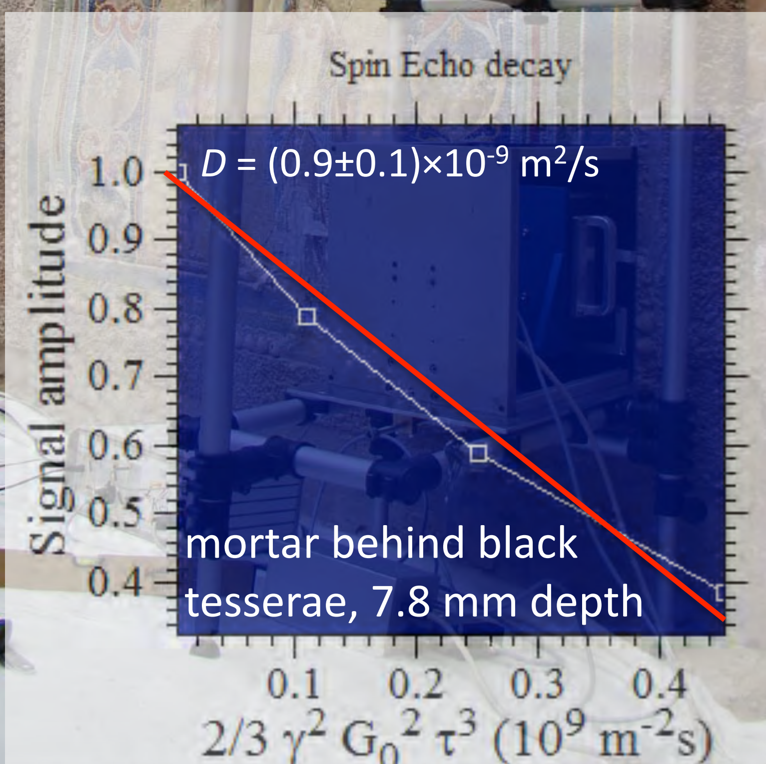

Amplitude and T_2 Profiles

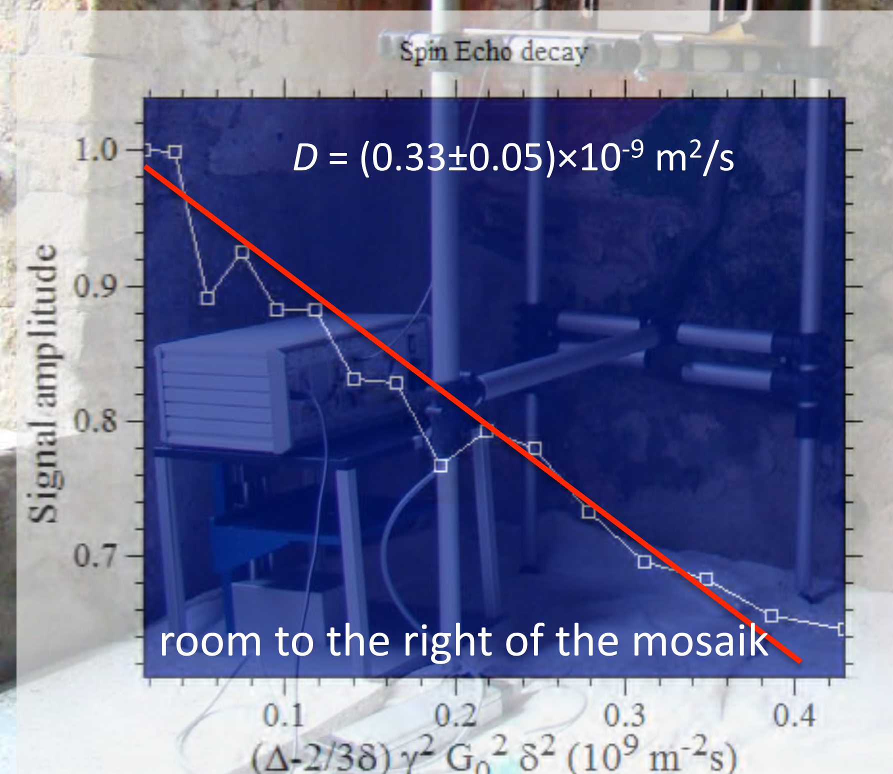




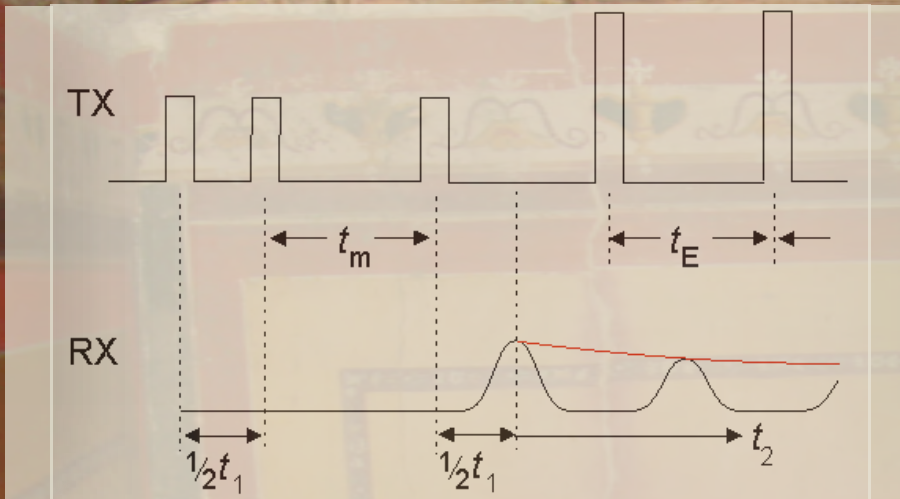
In Situ Measurement of Diffusion

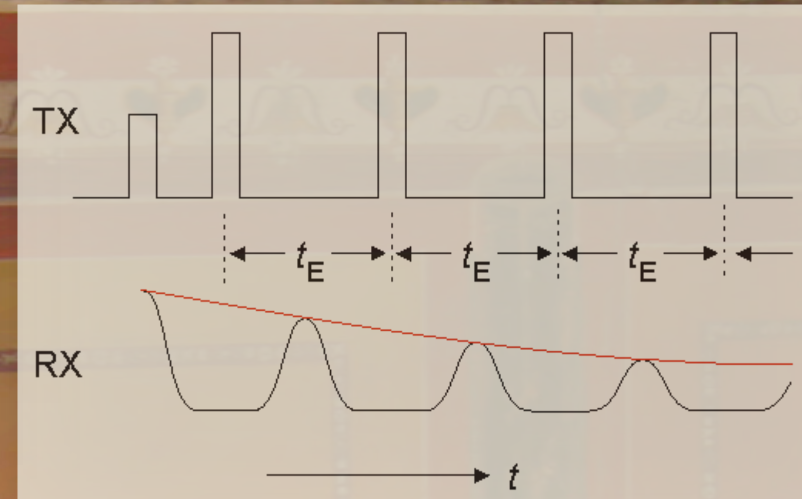
partial water saturation





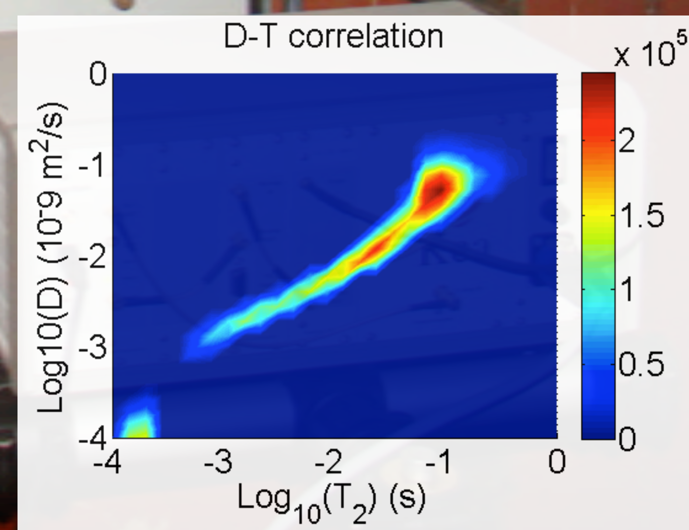
Correlation of Relaxation and Diffusion





$$s(t_1,t_2) = s(0)\exp\{-(\frac{1}{T_{2,\mathrm{bulk}}} + \rho_2\frac{S}{V})\,t_1 - \frac{D\,(\gamma G t_1)^2}{4}(t_m + \frac{1}{3}t_1)\}$$
$$\times \exp\{-(\frac{1}{T_{1,\mathrm{bulk}}} + \rho_1\frac{S}{V})t_m\}$$
$$\times \exp\{-(\frac{1}{T_{2,\mathrm{bulk}}} + \rho_2\frac{S}{V} + \frac{D\,(\gamma G t_E)^2}{12})t_2\}$$

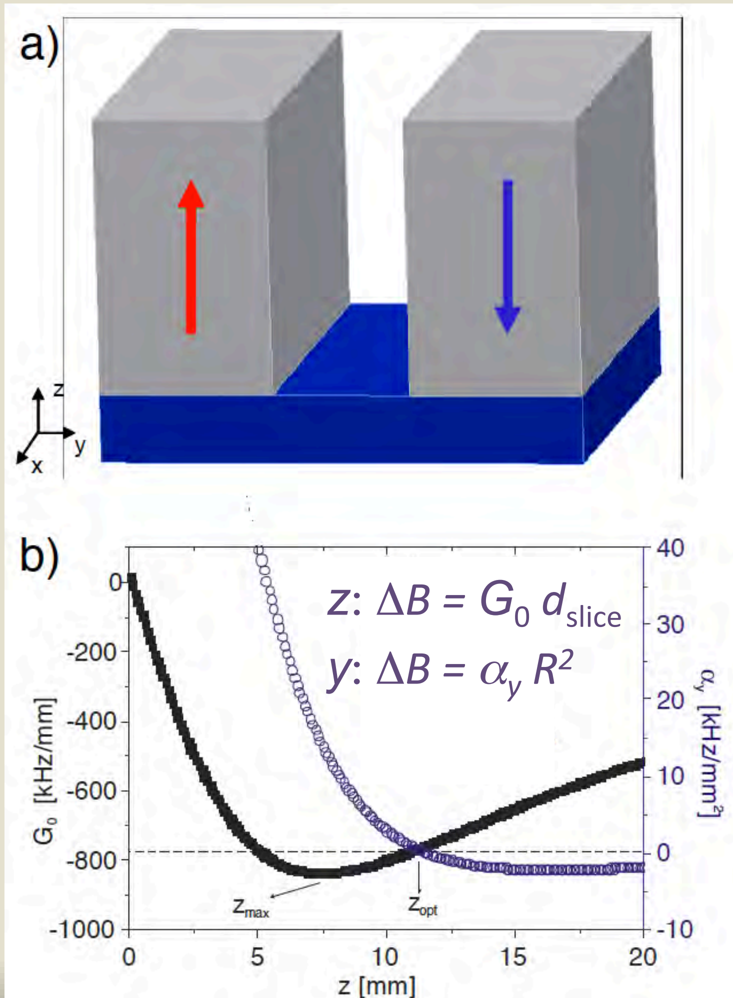
$$s(t) = s(0)\exp\{-(\underbrace{\frac{1}{T_{2,\mathrm{bulk}}} + \rho_2\frac{S}{V}}_{\propto\, t} + \underbrace{\frac{D\,(\gamma G t_E)^2}{12}}_{\propto\, t_E^2\, t})t\}$$



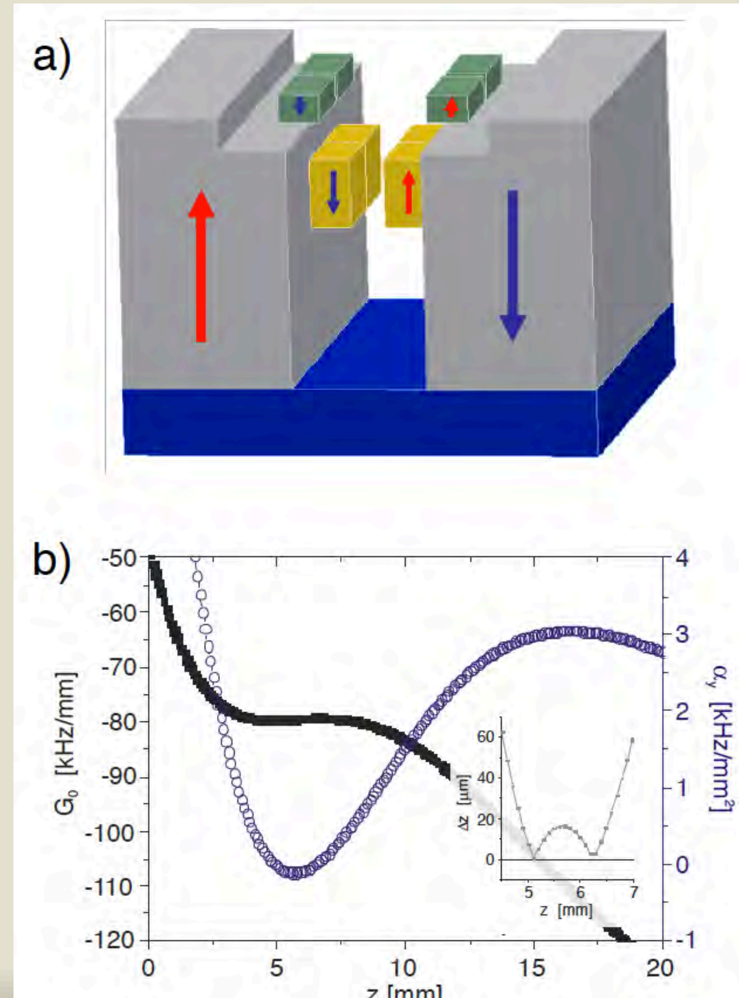
D.G. Rata, F. Casanova, J. Perlo, D.E. Demco, B. Blümich, Self-diffusion measurement by a mobile single-sided NMR sensor with improved magnetic field gradient, J. Magn. Reson. 180 (2006) 229 – 235

The Fourier NMR-MOUSE

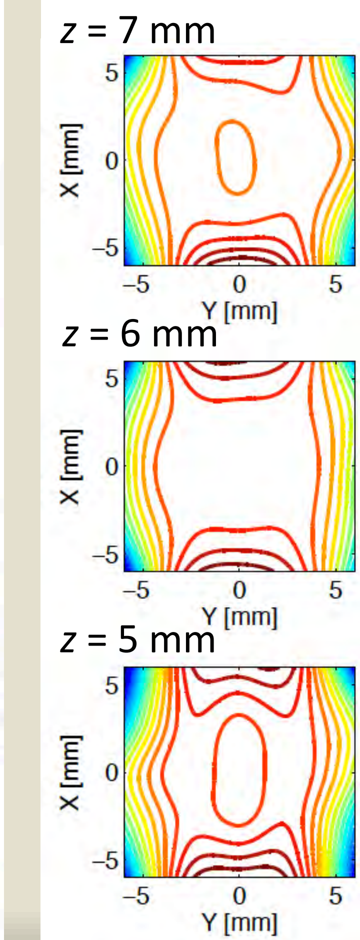
U-shaped NMR-MOUSE



Fourier NMR-MOUSE

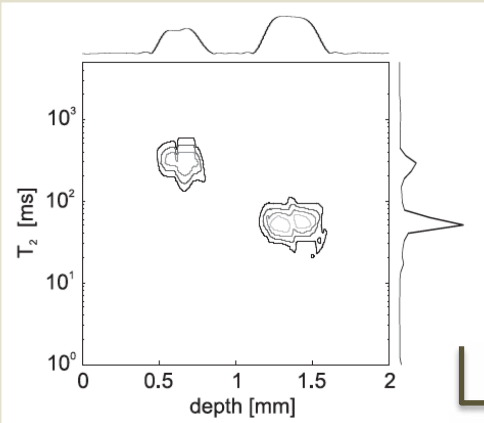


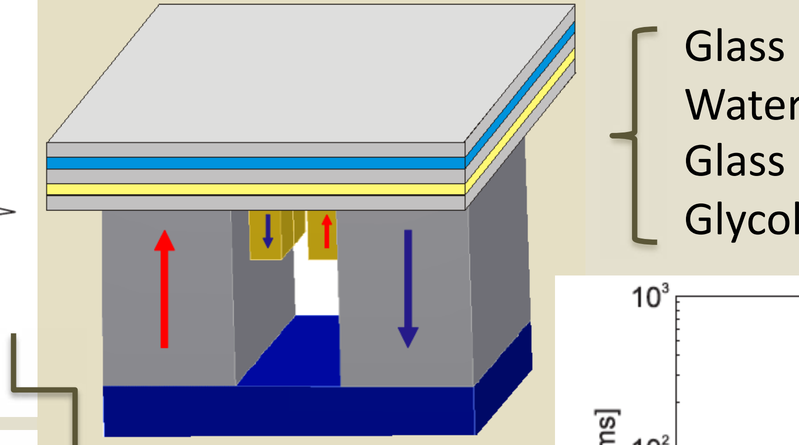
Measured field maps



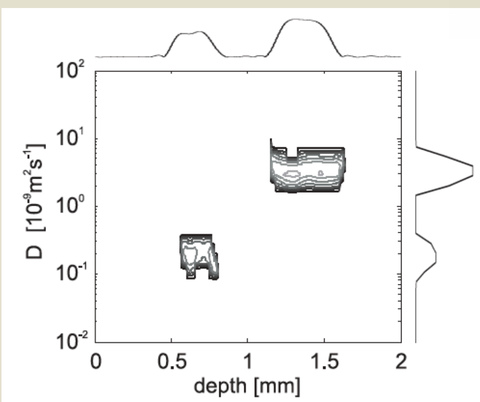
M. Van Landeghem, E. Danieli, J. Perlo, B. Blümich, F. Casanova, Single-sided NMR sensor for depth profiling human skin tissue, manuscript in preparation

2D / 3D Distributions from Bilayer Phantom

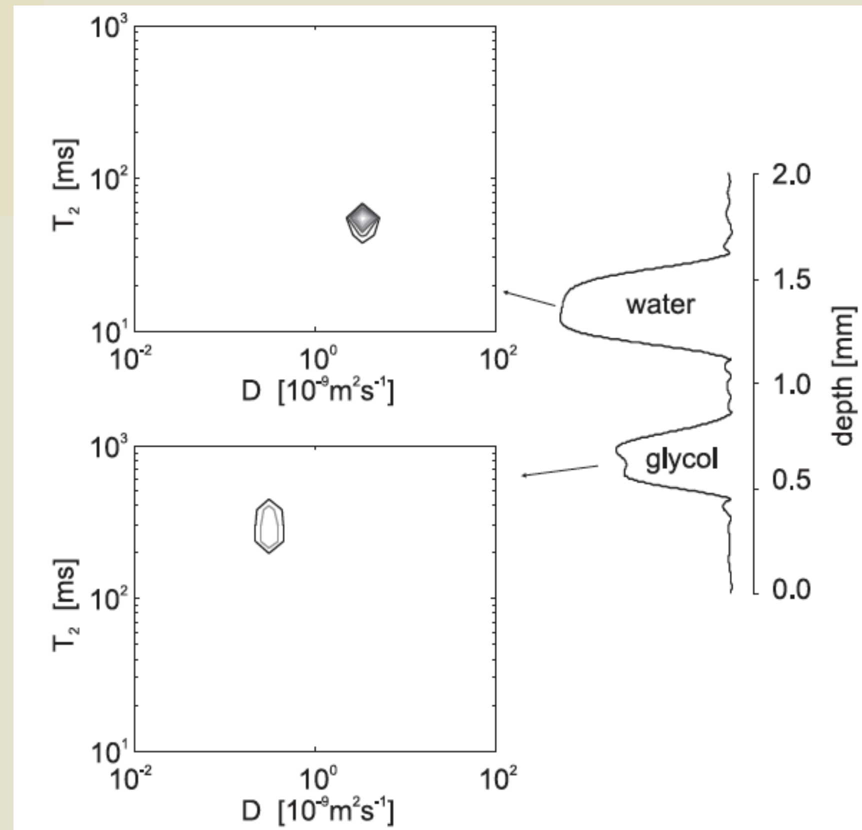




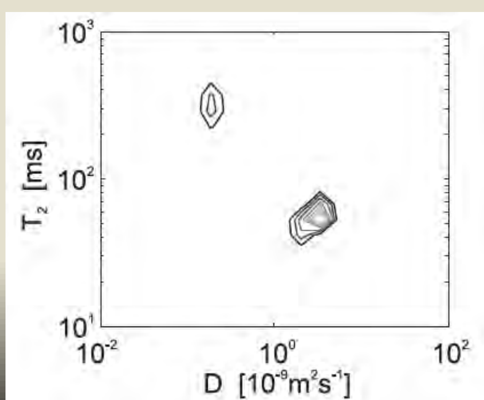
T_{acq} = 17 min



T_{acq} = 12 min



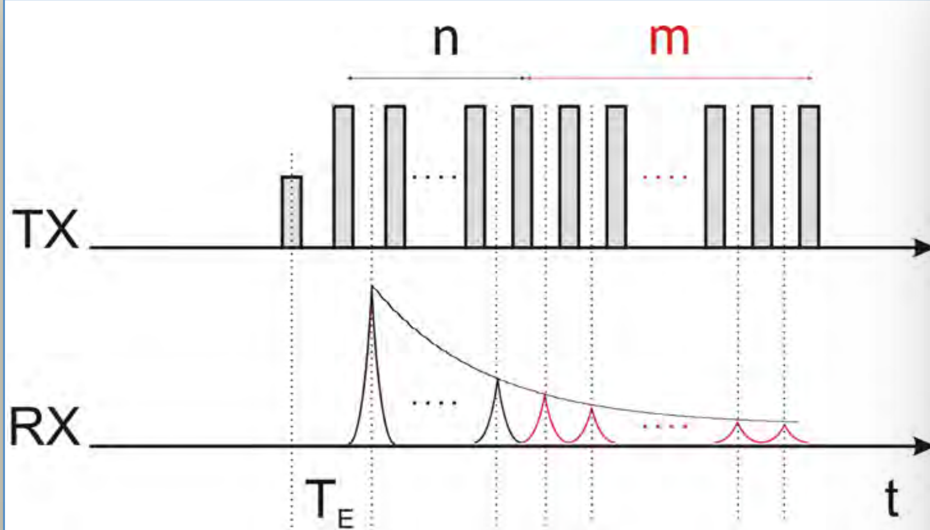
T_{acq} = 7 h



T_{acq} = 25 min

M. Van Landeghem, E. Danieli, J. Perlo, B. Blümich, F. Casanova, Single-sided NMR sensor for depth profiling human skin tissue, manuscript in preparation

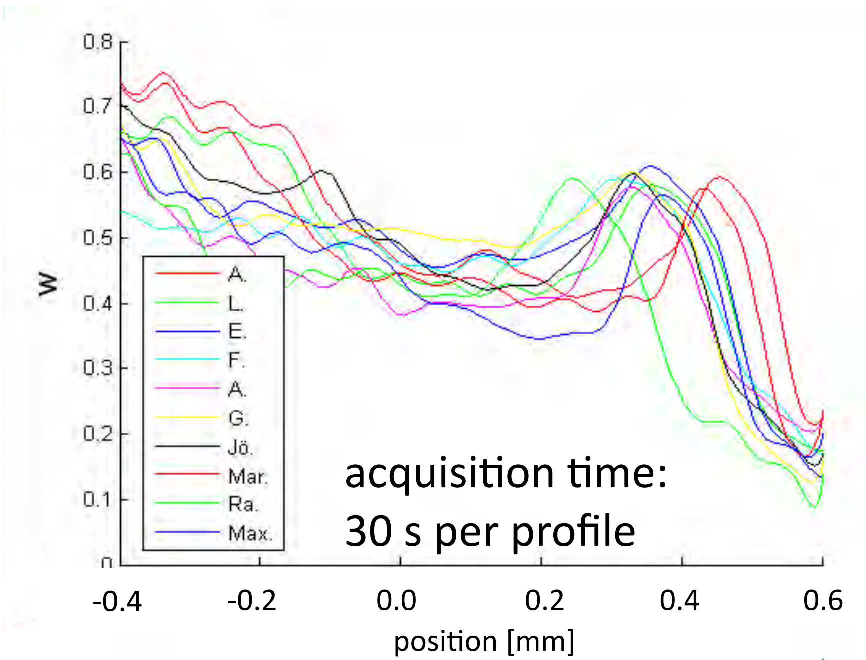
1D Profiles of the Palm of the Hand



CPMG sequence and echo counts

$$w = \frac{\sum_{m=m_i}^{m_f} s(m\,T_E)}{\sum_{n=n_i}^{n_f} s(n\,T_E)}$$

Definition of relaxation weigthed amplitudes *w*

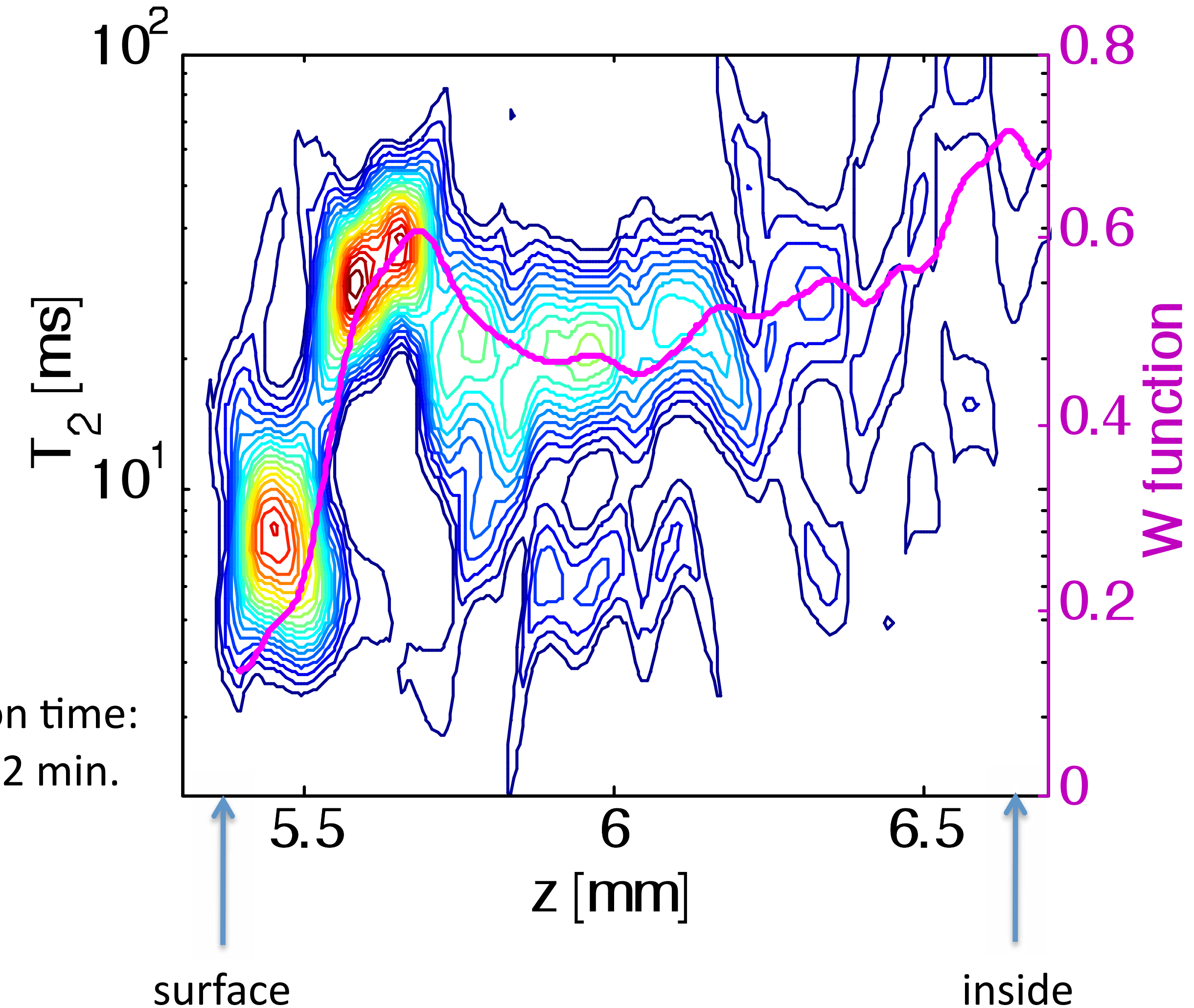


inside

surface

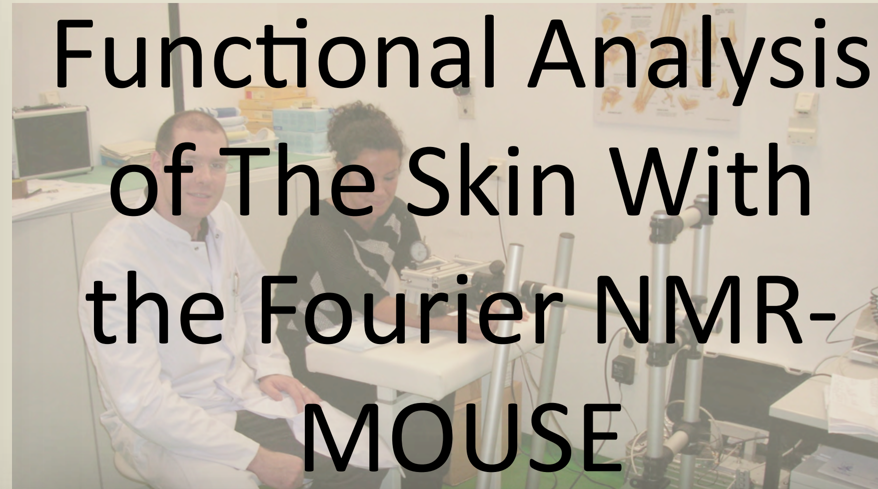
Different individuals have different skin profiles

Depth-Resolved T_2 distributions versus the *w* function

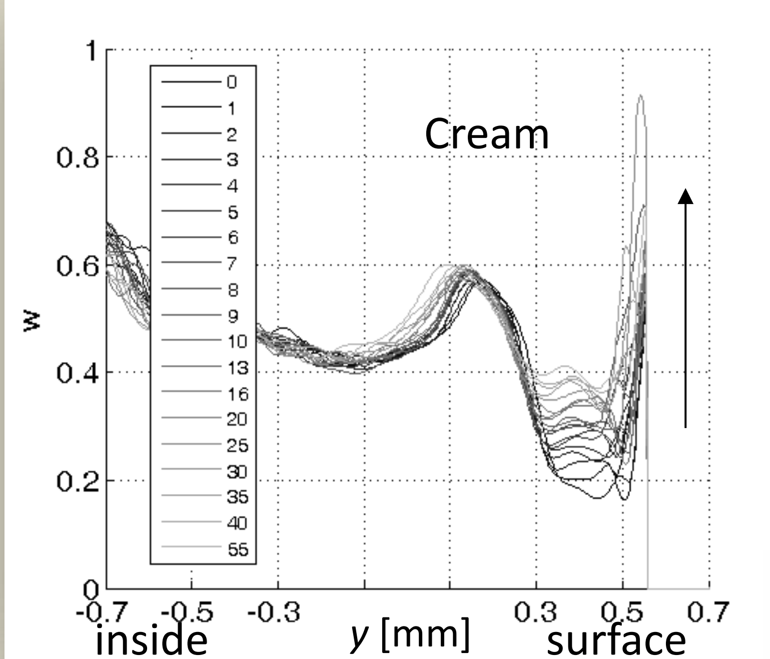


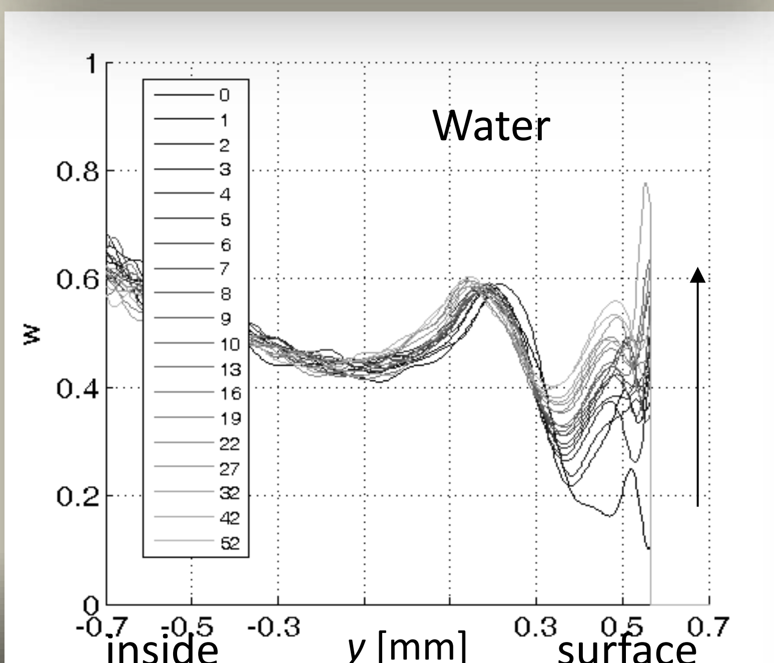
acquisition time:
less than 2 min.

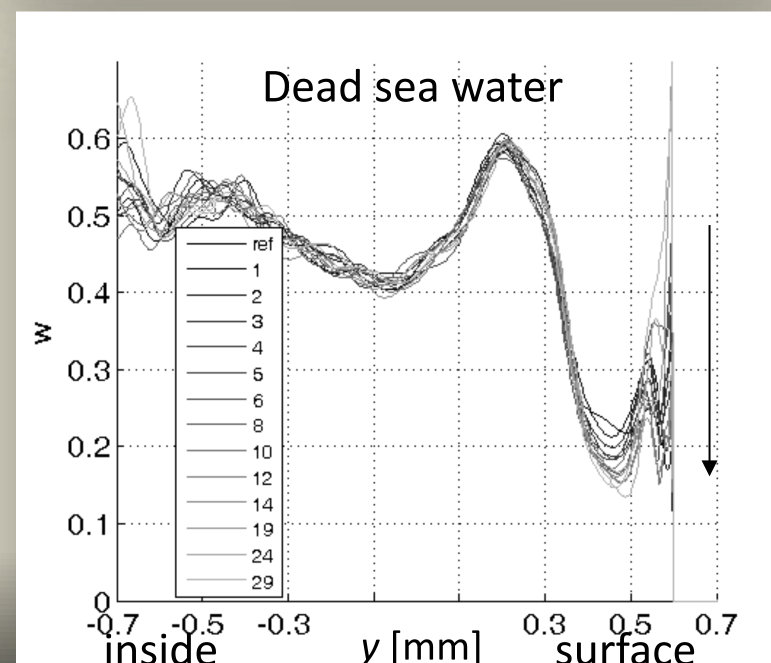
Functional Analysis of The Skin With the Fourier NMR-MOUSE



- Gradient 10 times smaller: 80 kHz/ mm
- Single-shot profiles across 1 mm depth
- 30 s accquisition time per profile





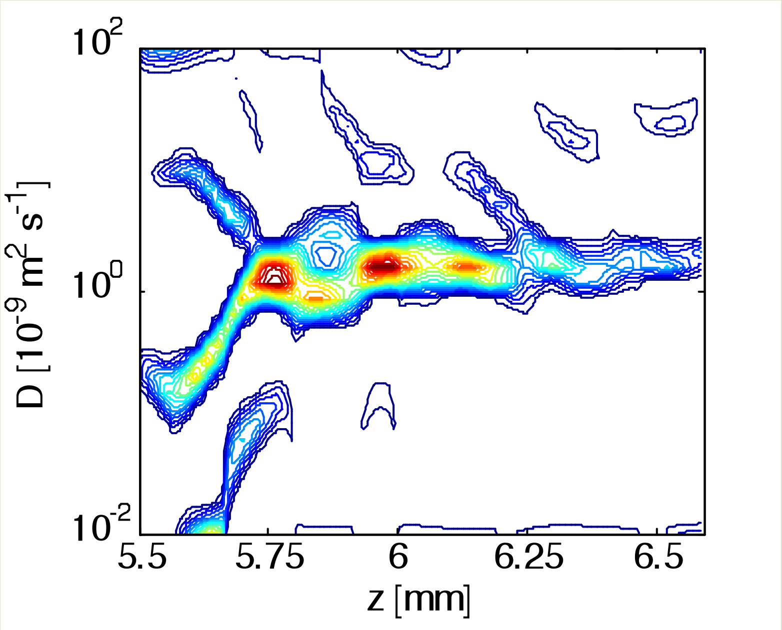


Maxime van Landeghem, Ernesto Danieli, Federico Casanova

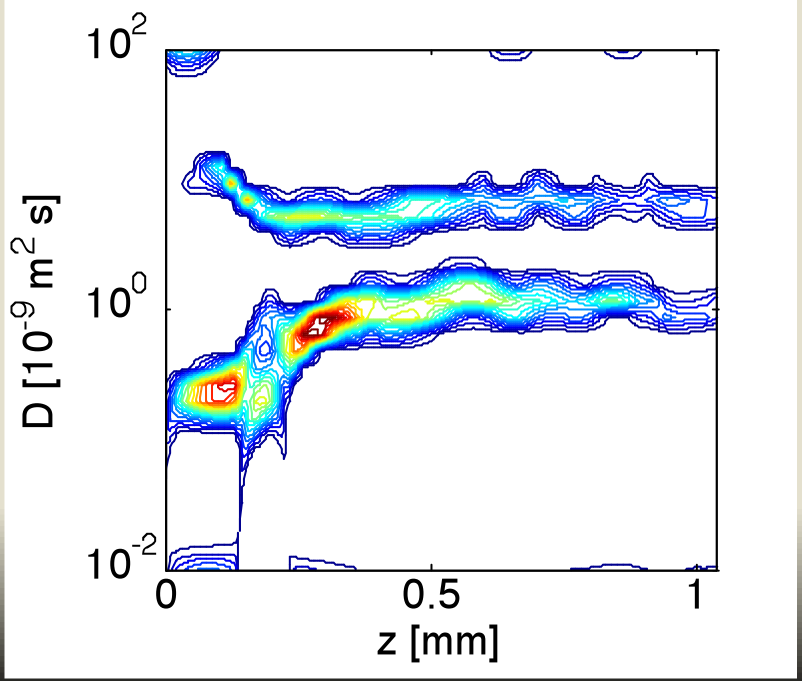
D Distributions Versus Depth

acquisition time:
less than 10 min.

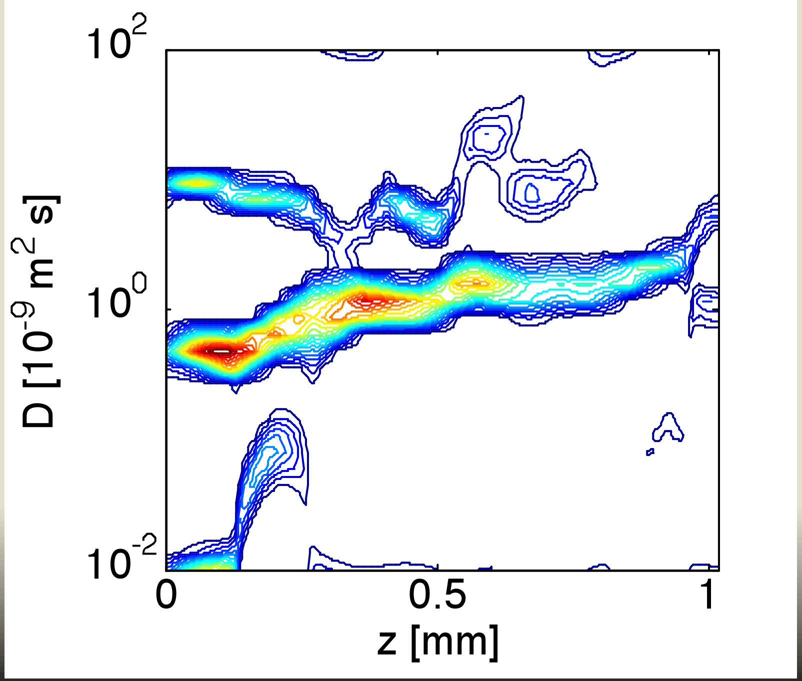
Reference



Saturated with cream

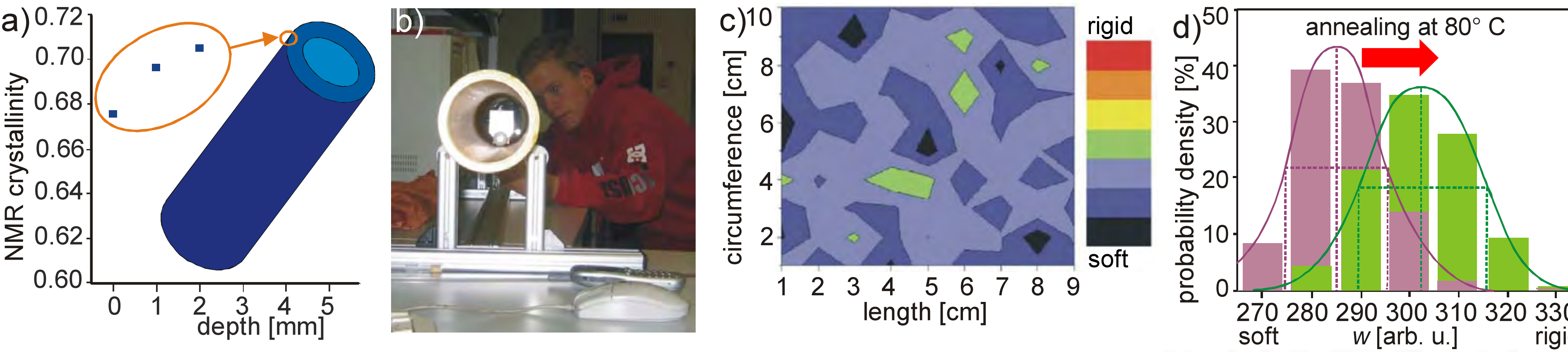


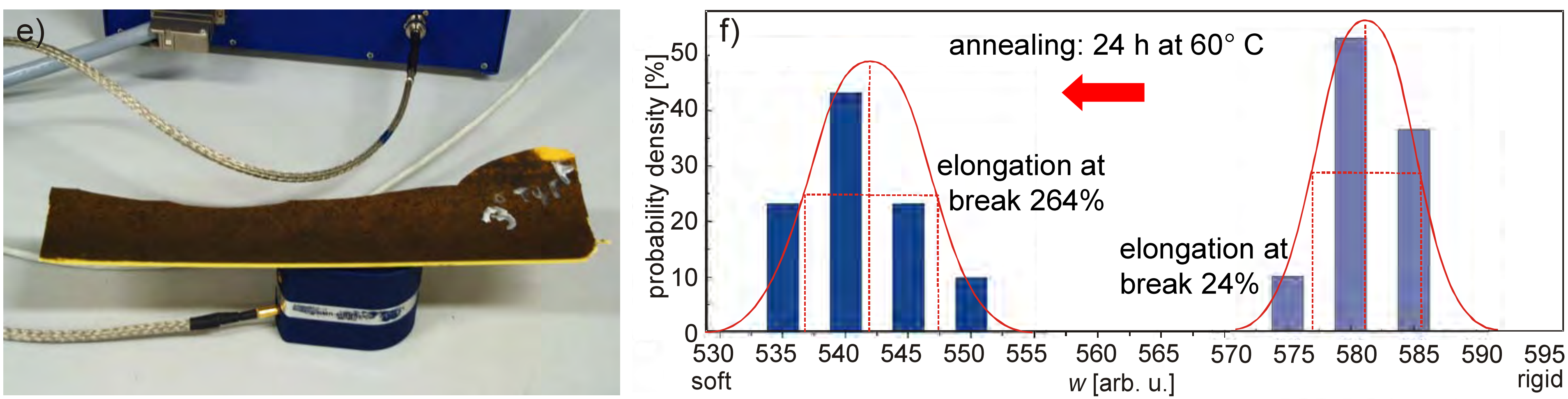
Saturated with water



Aging and Annealing of PE

PE100 pipes





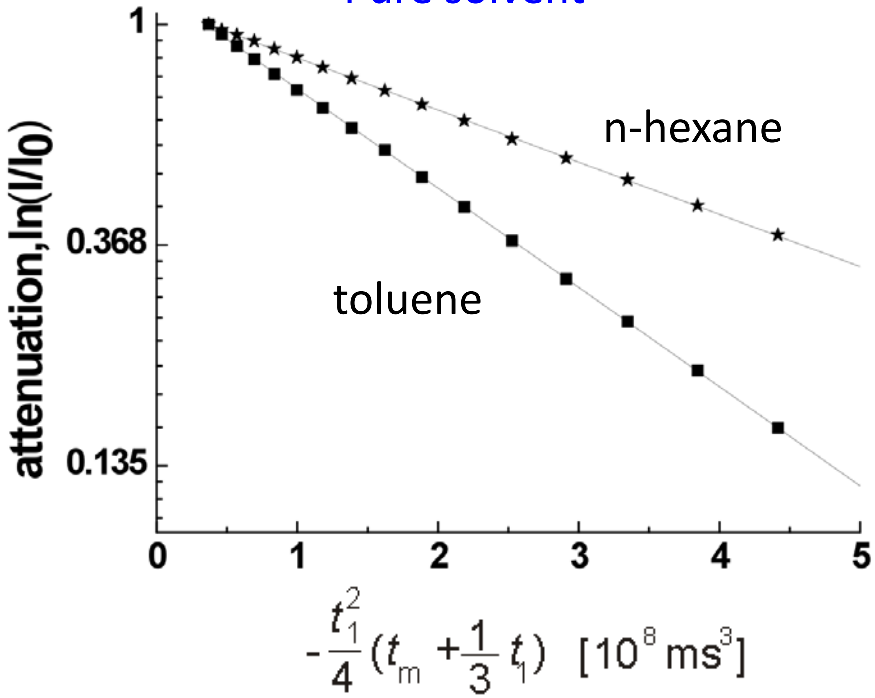
LDPE steel pipe shell, 20 – 30 years in the ground

Blümich, F. Casanova, J. Perlo, *Mobile Single-Sided NMR*, **Prog. Nucl. Magn. Reson. 52** (2008) 197-269

Self-Diffusion of Solvents in PE Samples

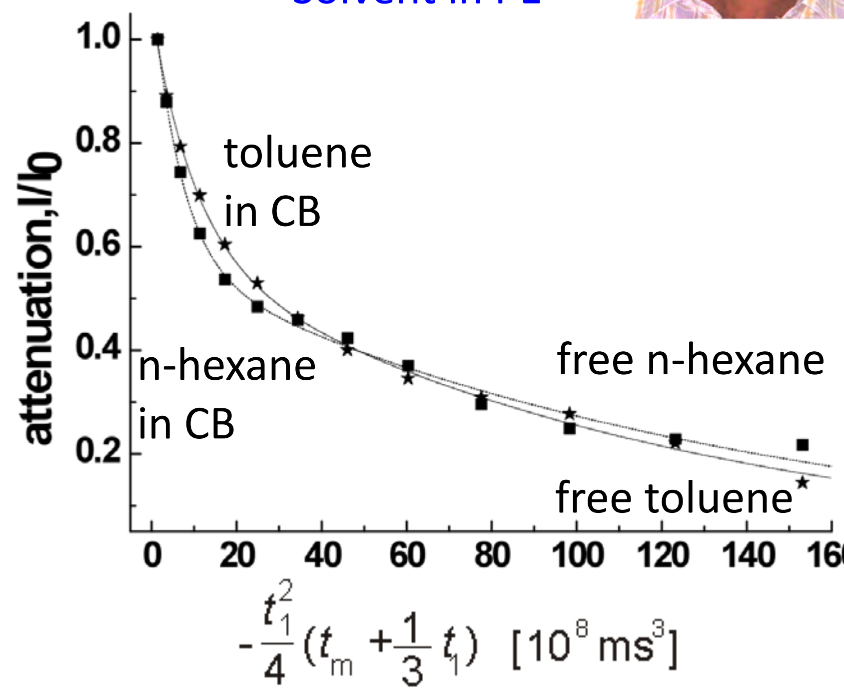
Rance Kwamen

Pure solvent



$$D_0(n-hexane) = 4.5 \times 10^{-9}\ m^2/s$$
$$D_0(toluene) = 2.37 \times 10^{-9}\ m^2/s$$

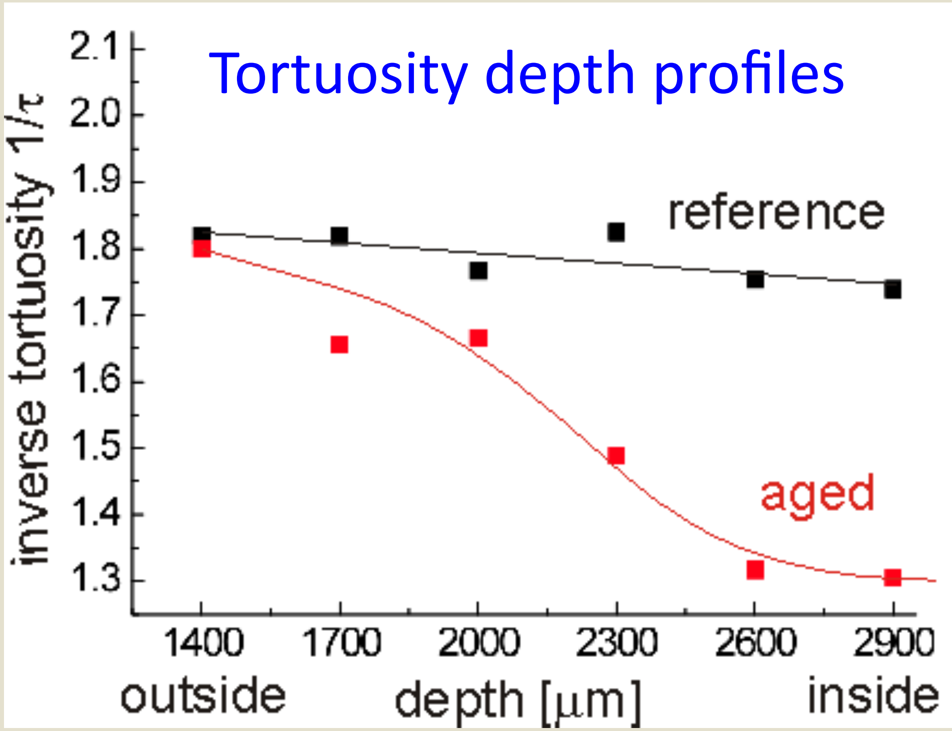
Solvent in PE



$$D_0(hexane/CB) = 7.35 \times 10^{-11}\ m^2/s$$
$$D_0(toluene/CB) = 8.5 \times 10^{-11}\ m^2/s$$

Stimulated echo for measurements of diffusion by unilateral NMR

Aged PE Pipes: Solvent Diffusion and Relaxation

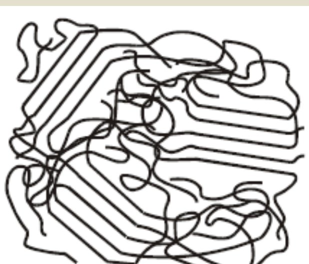


low crystallinity

large elongation at break

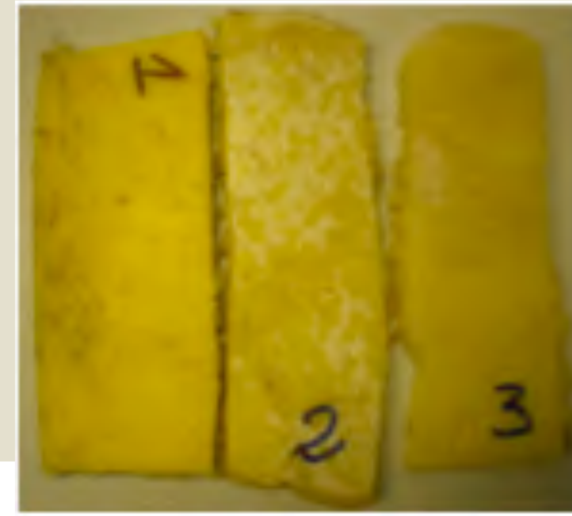
high crystallinity

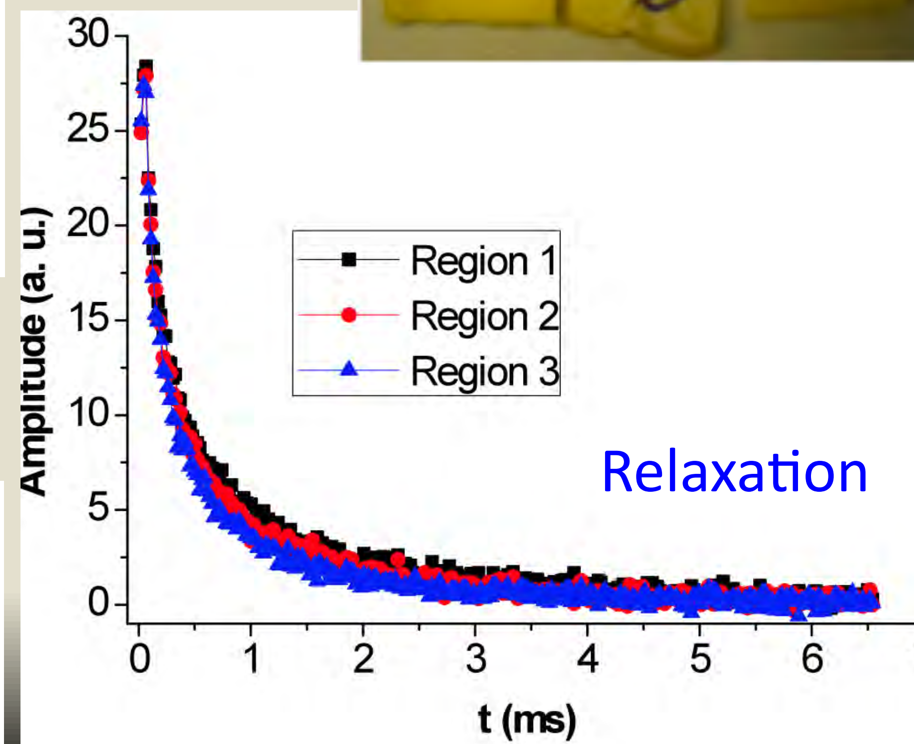
low elongation at break



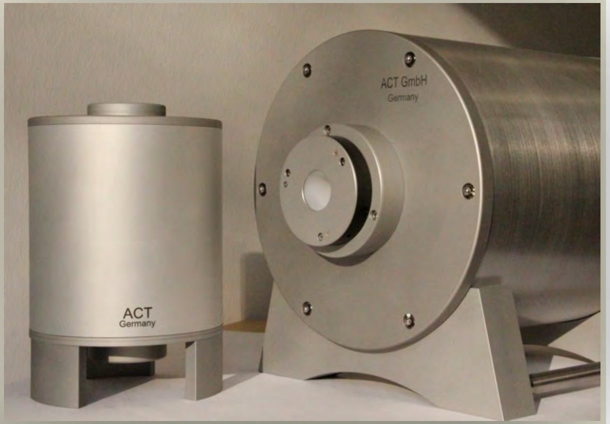
The solvent molecules diffuse in the amorphous regions

Differently aged PE samples

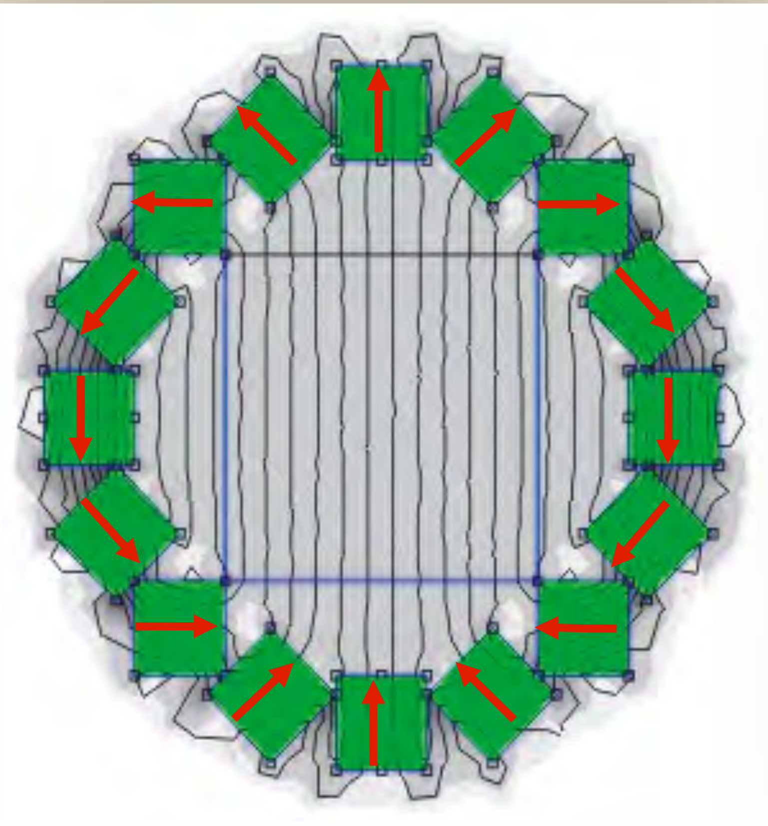




Halbach Magnets



n = 16



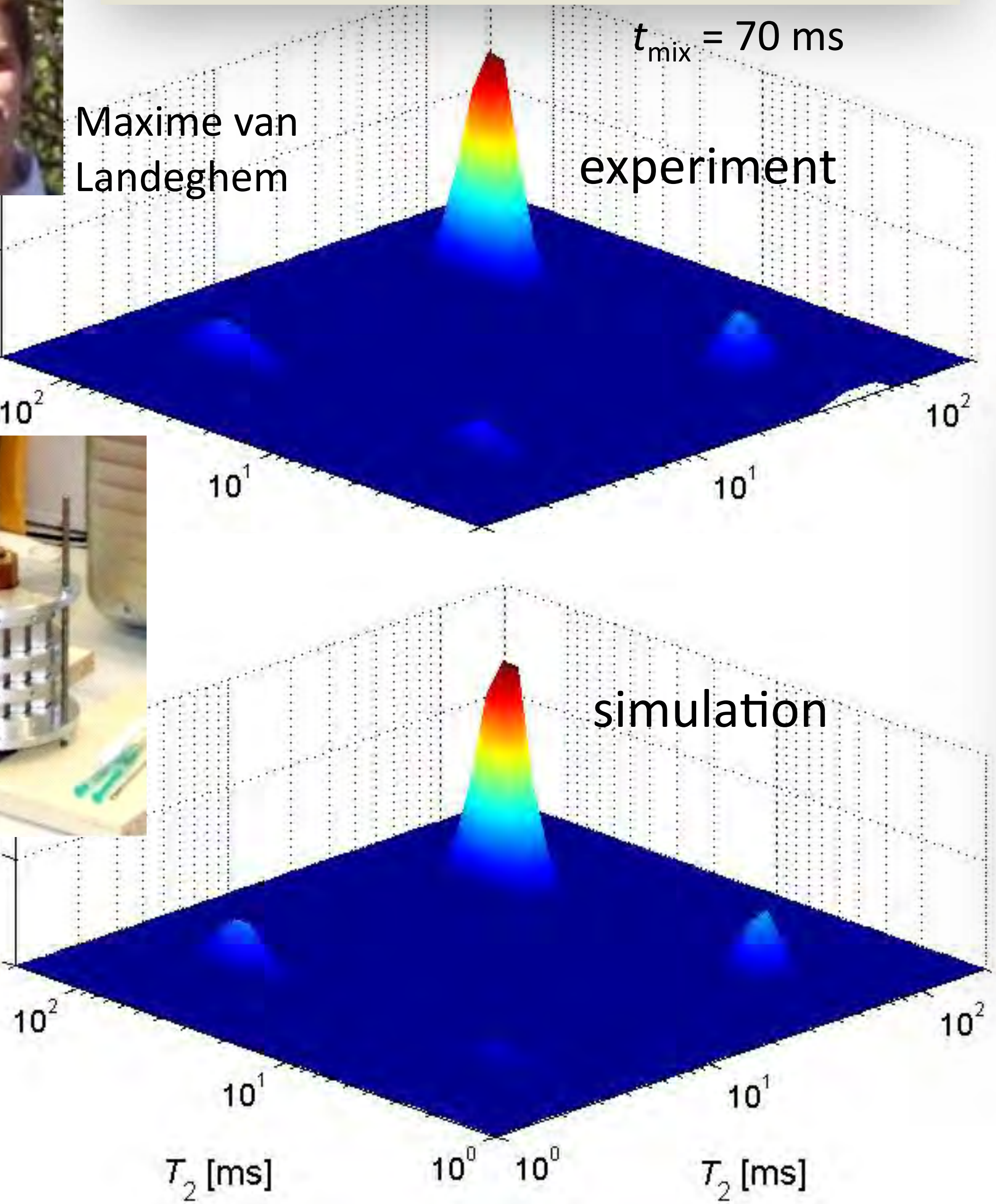
K. Halbach, *Design of permanent multipole magnets with oriented rare earth cobalt material*, **Nucl. Instrum. Methods 169** (1980) 1–10; H. Raich and P. Blümler, *Design and construction of a dipolar Halbach array with a homogeneous field from identical bar magnets: NMR Mandhalas*, **Concepts Magn. Reson. B23** (2004) 16-25

2D Exchange NMR of Water in Silica Particles

Maxime van Landeghem

Pulse sequence: CPMG(t_1) - t_{mix} – CPMG(t_2)

t_{mix} = 70 ms



Fit results

Parameter	Value
M^A	5.5
M^B	18.4
T_2^A	3.9 ms
T_2^B	103.5 ms
T_1^A	610.0 ms
T_1^B	630.0 ms
k	1/(110 ms)

M. Van Landeghem, A. Haber, J.-B. d'Espinose de Lacaillerie, B. Blümich, *Analysis of Multi-Site 2D Relaxation-Exchange NMR*, **Concepts Magn. Reson. 36A (2010)** 153-169

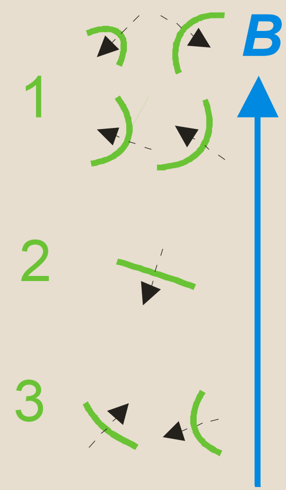
n-site exchange: $\boldsymbol{M}(t) - \boldsymbol{M}_0 = \exp\{-(\mathbf{R}+\mathbf{K})(t - t_0)\} [\boldsymbol{M}(t_0) - \boldsymbol{M}_0]$

Distance Constraints from Exchange Rates

a working hypothesis

molecular diffusion in a fluid-filled pore

curvatures define relaxation times ??



distances between relaxation centers from exchange rates

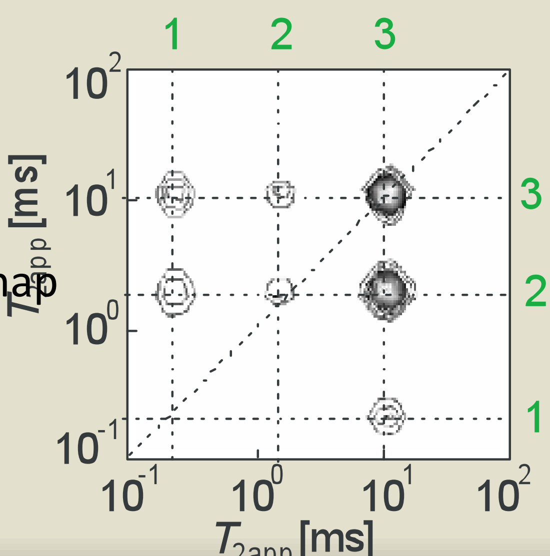
$$(\Delta \boldsymbol{R})^2 = 6\, D\, t_D$$

$$k_{12}^{-1} = 400 \text{ ms} = (\Delta \boldsymbol{R}_{12})^2 / 6\, D_{H_2O}$$

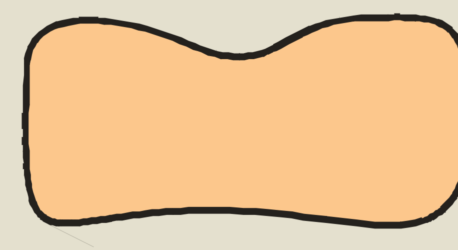
$$k_{13}^{-1} = 20 \text{ ms} = (\Delta \boldsymbol{R}_{13})^2 / 6\, D_{H_2O}$$

$$k_{23}^{-1} = 3000 \text{ ms} = (\Delta \boldsymbol{R}_{23})^2 / 6\, D_{H_2O}$$

simulated relaxation exchange map

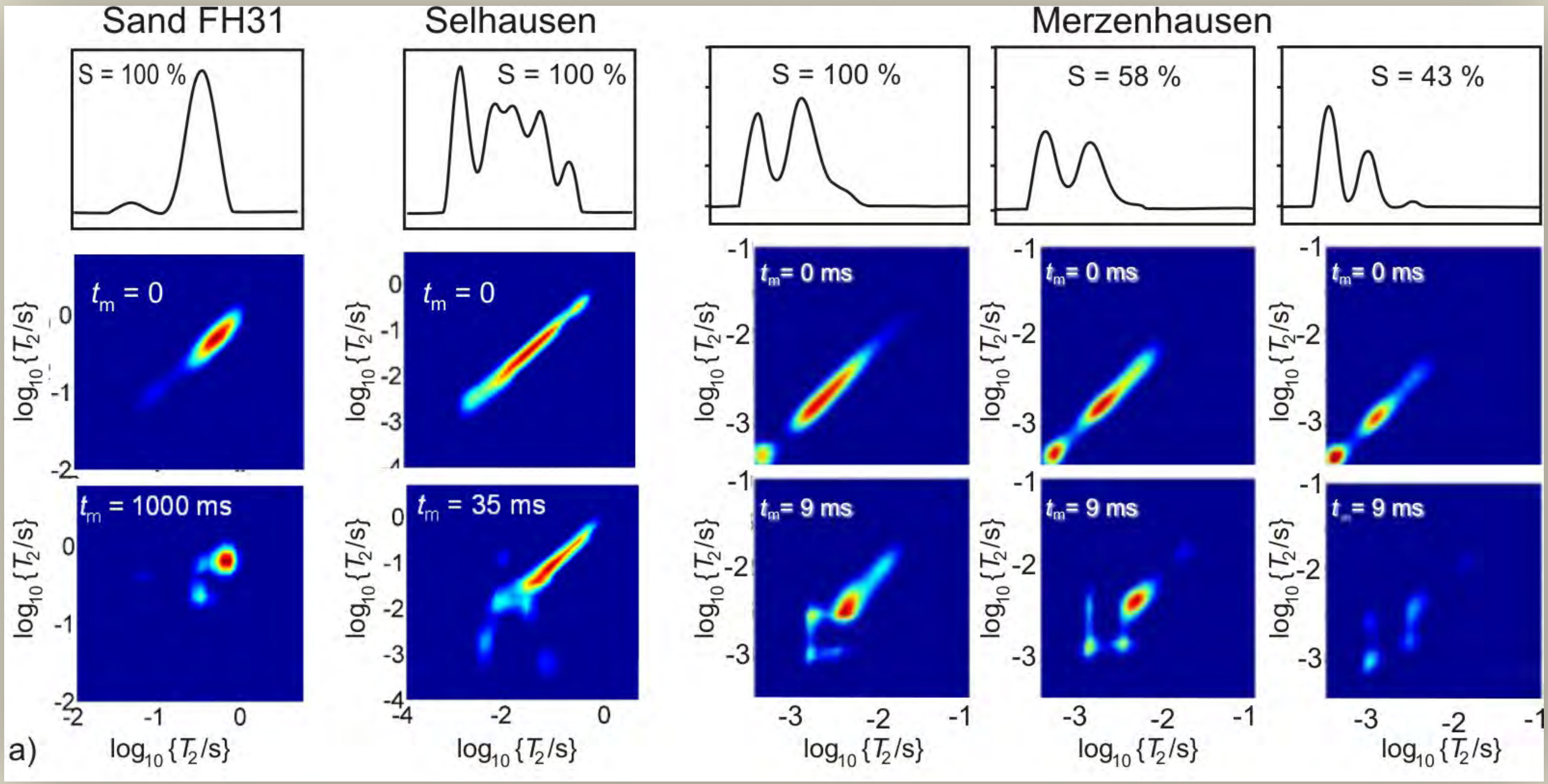


model of average pore to study drying processes



M. Van Landeghem, A. Haber, J.-B. d'Espinose de Lacaillerie, B. Blümich, *Analysis of Multi-Site 2D Relaxation-Exchange NMR*, **Concepts Magn. Reson. 36A** (2010) 153-169

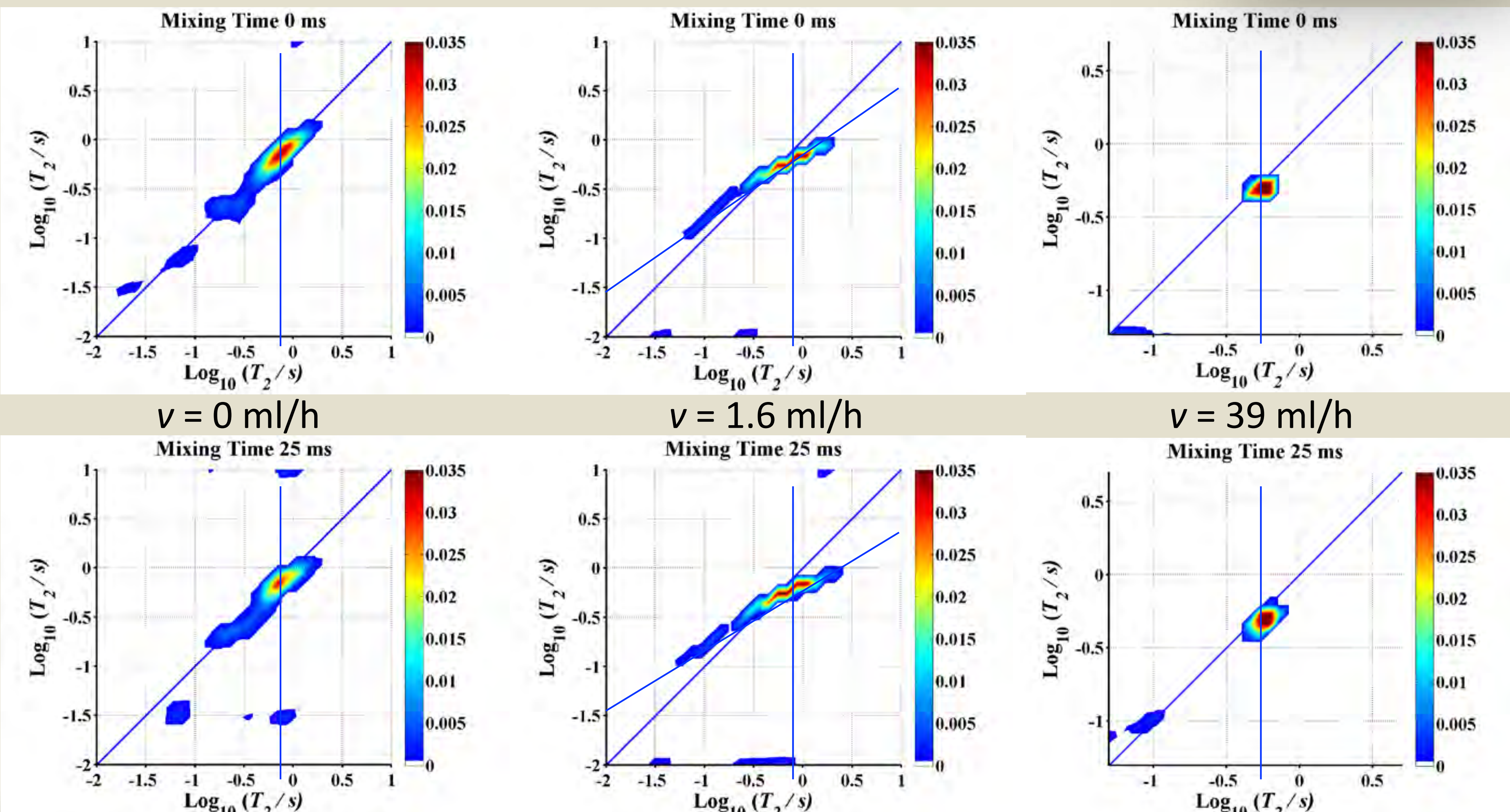
T_2 Distributions of Sand and Soil



B. Blümich, F. Casanova, M. Dabrowski, E. Danieli, L. Evertz, A. Haber, M. Van Landeghem, S. Haber-Pohlmeier, A. Olaru, J. Perlo, O. Sucre, *Small-Scale Instrumentation for NMR of Porous Media,* special issue on Physics of Magnetic Resonance of Porous Media, **New Journal of Physics 13** (2011) 015003 1-15

TR32

T_2 Exchange NMR of Diffusion and Advection



B. Blümich, F. Casanova, M. Dabrowski, E. Danieli, L. Evertz, A. Haber, M. Van Landeghem, S. Haber-Pohlmeier, A. Olaru, J. Perlo, O. Sucre, *Small-Scale Instrumentation for NMR of Porous Media,* special issue on Physics of Magnetic Resonance of Porous Media, **New Journal of Physics 13** (2011) 015003 1-15

Modelling Diffusion and Advection

Julia Kowalski

Bloch-Torrey equation: Diffusion and Advection

$$\frac{\partial}{\partial t}\mathbf{M} = \underbrace{\gamma \mathbf{M} \times \mathbf{B}}_{\text{precession}} + \underbrace{\mathbf{R}\left(\mathbf{M} - \mathbf{M}_0\right)}_{\text{relaxation}} + \underbrace{\nabla \cdot \mathbf{D} \nabla \mathbf{M}}_{\text{self-diffusion}} - \underbrace{\nabla \cdot \mathbf{v} \mathbf{M}}_{\text{advection}}$$

Introduction of dimensionless parameters

$$\mathbf{t} = \mathbf{T}_2^c \tilde{\mathbf{t}} \quad \mathbf{x} = \mathbf{L}\tilde{\mathbf{x}} \quad \mathbf{y} = \mathbf{L}\tilde{\mathbf{y}} \quad \mathbf{z} = \mathbf{L}\tilde{\mathbf{z}} \quad \mathbf{M} = \mathbf{M}_0 \tilde{\mathbf{M}}$$

$$\frac{\partial}{\partial t}\mathbf{M} = \mathbf{R}\left(\mathbf{M} - \mathbf{e}_z\right) + \mathbf{N}_d \triangle \mathbf{M} - \mathbf{N}_v \mathbf{e}_v \nabla \mathbf{M}$$

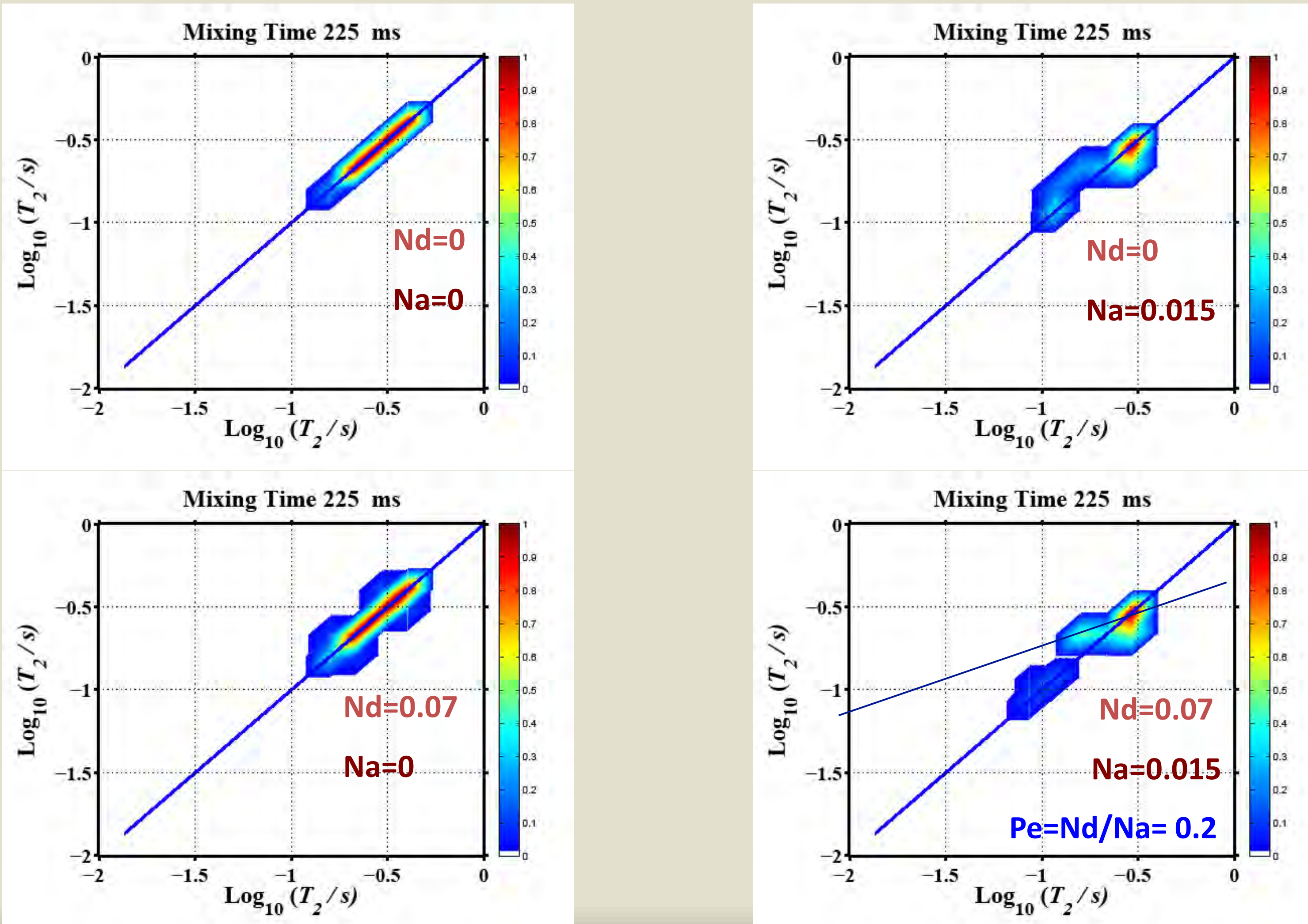
Typical experimental parameters

Diffusion number	Advection number
$Nd = DT_2^c / L^2$	**$Na = vT_2c / L$**
$Nd \approx 0.5 - 3$	$Na \approx 0 - 200$

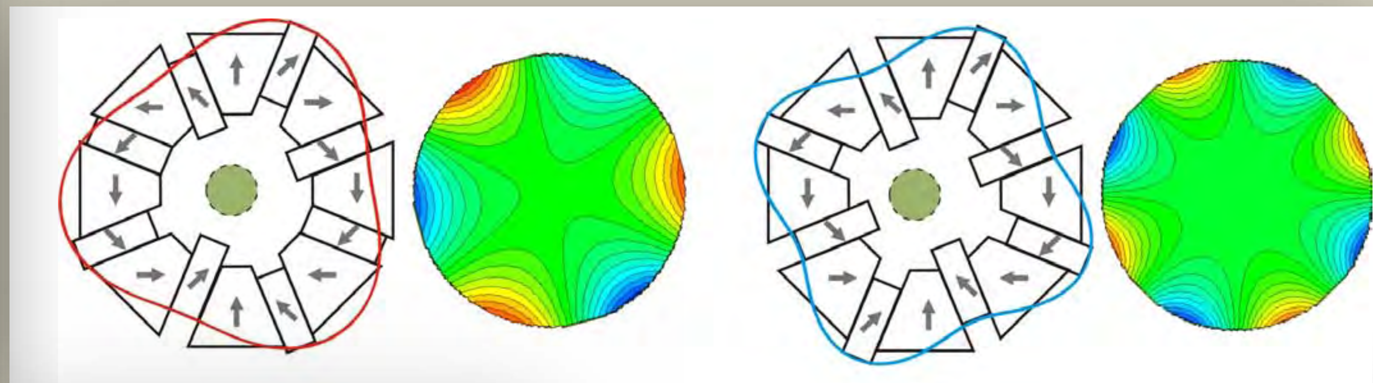
Peclet number: $Pe = Na/Nd$

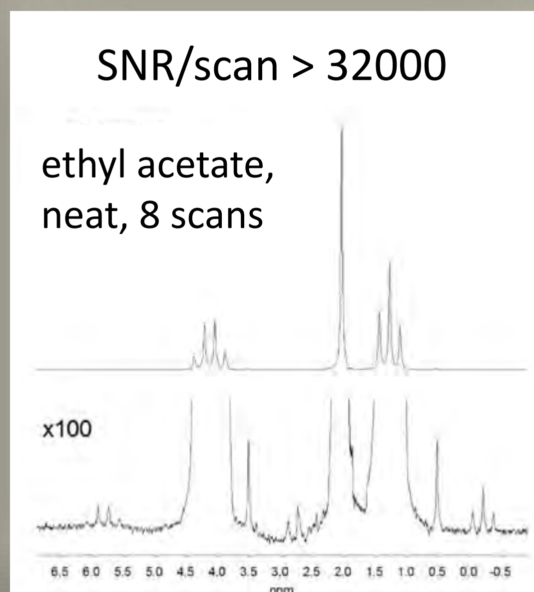
isotropic self-diffusion:	$2.2 \cdot 10^{-9} m^2/s$
static field:	$B = (0, 0, B_0)$
transverse relaxation rate:	$100 - 700$ ms
constant pump flow rate:	1-700 ml/h
void volume fraction:	35 %
average particle size:	0.2 mm

Modelling Diffusion and Flow Exchange



High Homogeneity, Large Volume, Small Magnet





Commercial 40 MHz temperature controlled desktop ^{1}H NMR spectroscopy

E. Danieli, J. Perlo, B. Blümich, F. Casanova, *Small Magnets for Portable NMR Spectrometers*, **Angew. Chem. Int. Ed. Eng. 49** (2010) 4133-4135

Thank You

€€€: DFG
BMBF FCI
GIF Humboldt
DAAD