OPAALE
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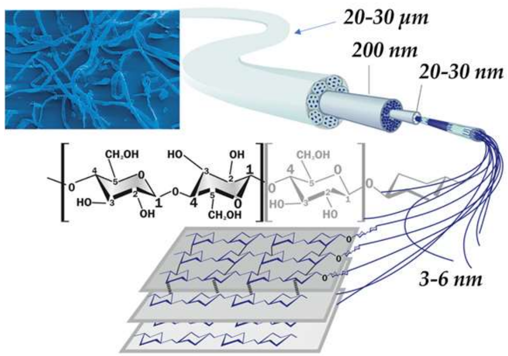
Multi-scale dynamics of water in bio-sourced materials. NMR and MRI approaches

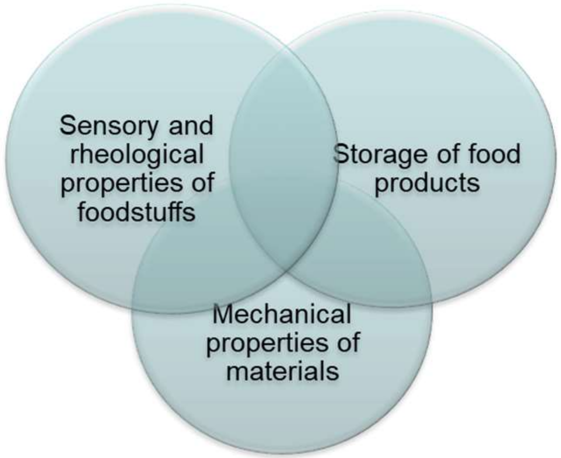
C. Rondeau-Mouro – UR OPAALE

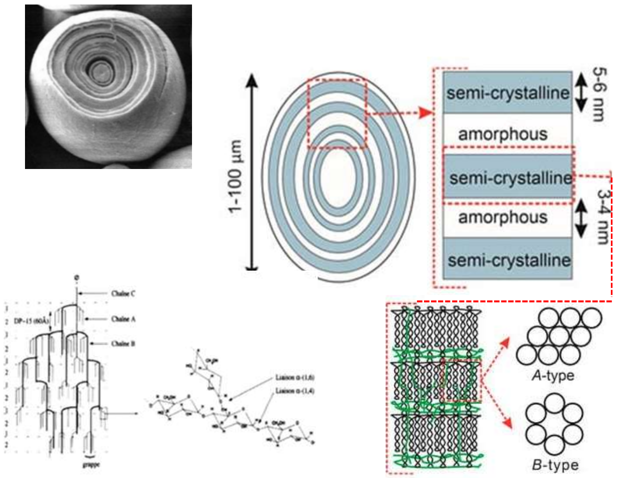
R. Kovrlija-Ferbus, E. Rakhshi, M. Cambert, S. Quellec, S. Challois

Role of water in food and material science

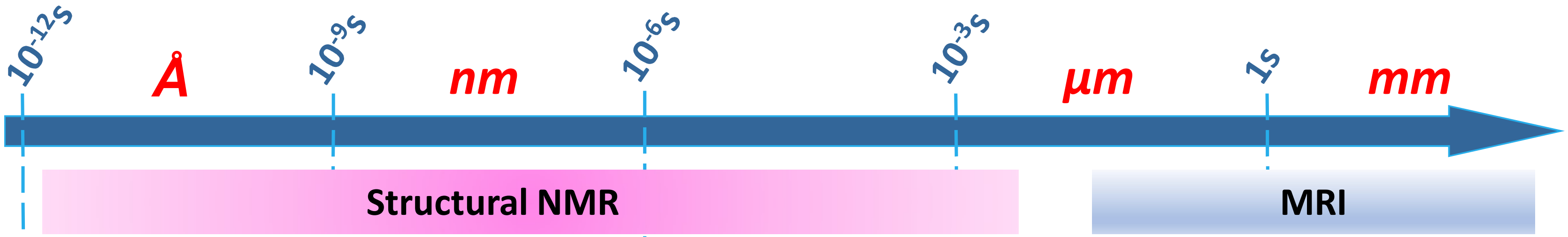
- Understand and quantify **water transfers** in bio-sourced products
- Investigate the **structure-fonction relationship of molecules** during transformation
- Innovation and optimization of **industrial processes** through the understanding of phenomena of transfer of matter at meso-, micro- and macroscopic scales (baking, water-uptake of materials)



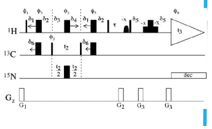


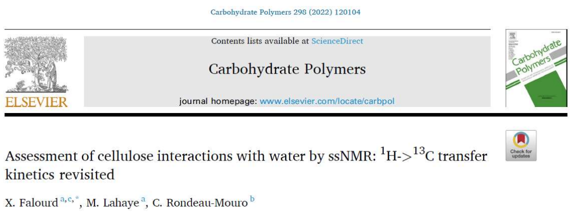


Time/length scales



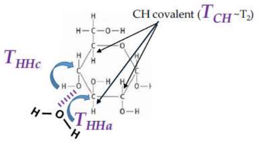
Structural water in biopolymers
ss-NMR
X. Falourd et al.

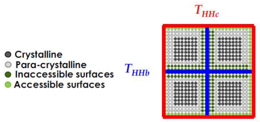


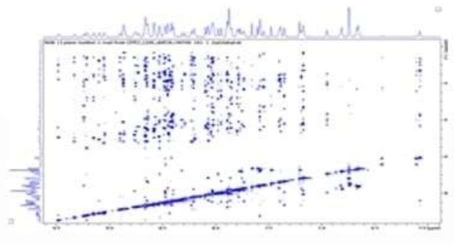

Carbohydrate Polymers 298 (2022) 120104
Contents lists available at ScienceDirect
Carbohydrate Polymers
journal homepage: www.elsevier.com/locate/carbpol

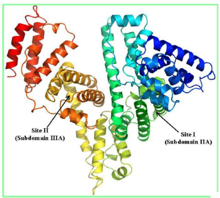
Assessment of cellulose interactions with water by ssNMR: ^1H->^{13}C transfer kinetics revisited

X. Falourd[a,c,*], M. Lahaye[a], C. Rondeau-Mouro[b]

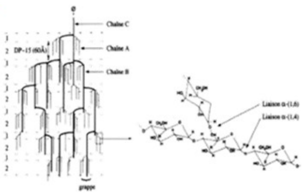


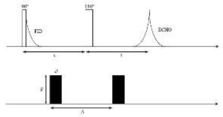


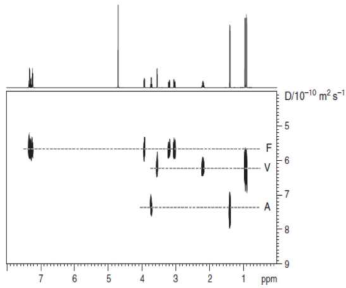


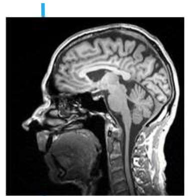


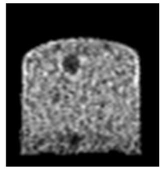
Proteins
Polysaccharides



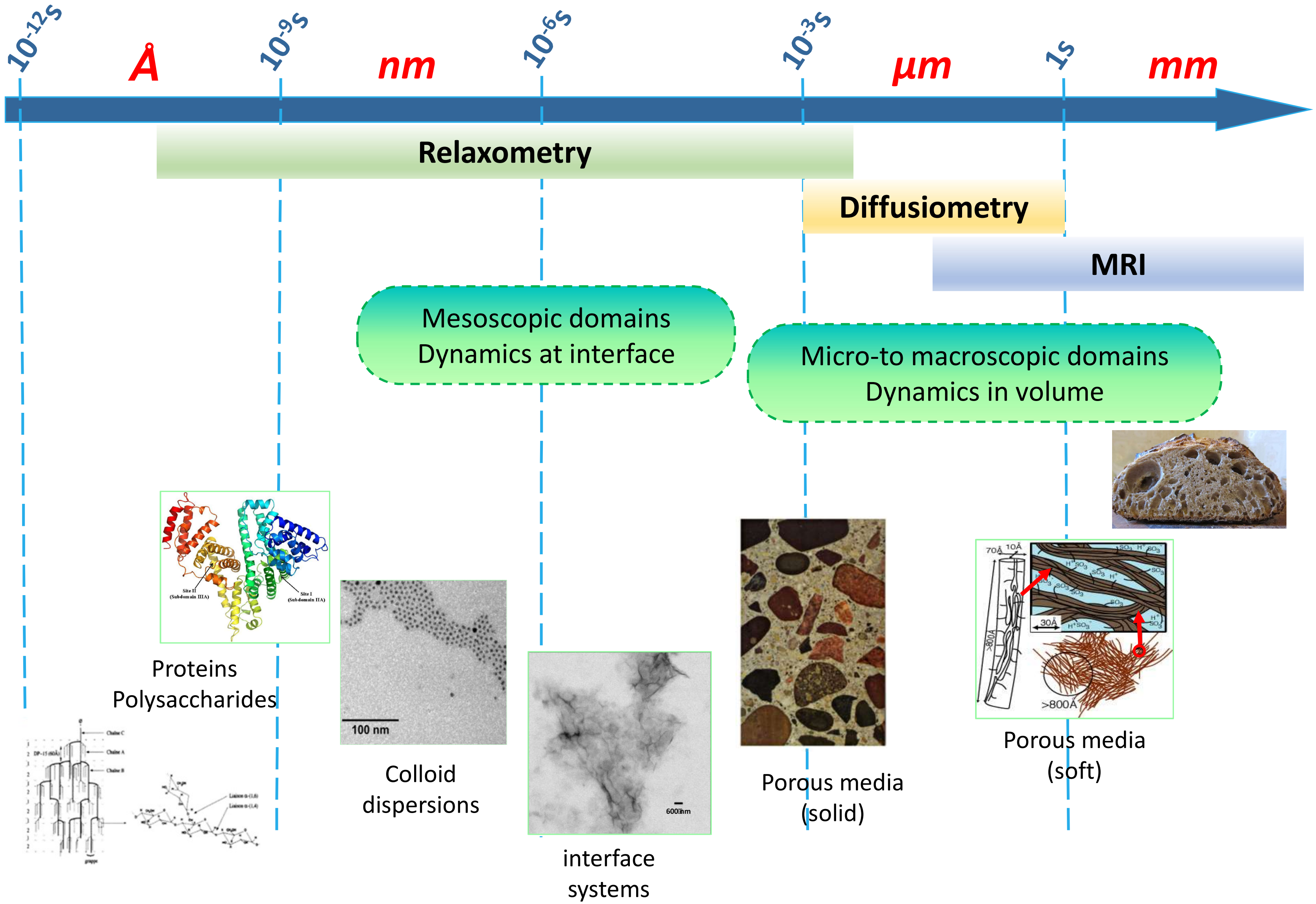








Time/length scales

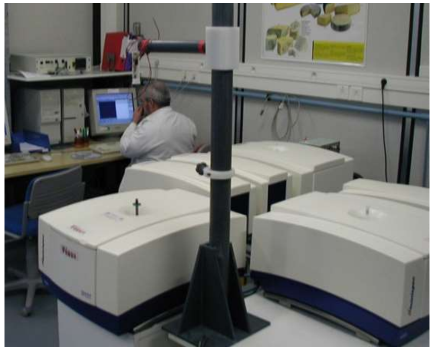


Facilities

Low-field (proton NMR !)

NMR

0,47 - 0,23 T



minispec Bruker (20 MHz)

0,47T 0,3T

NMR MOUSE Magritek

PHENIX

Sorbonne Paris

Spinmaster Stelar

MRI

0,2 T

Concerto Siemens

1,5 T

Avanto Siemens

High-field

PRISM

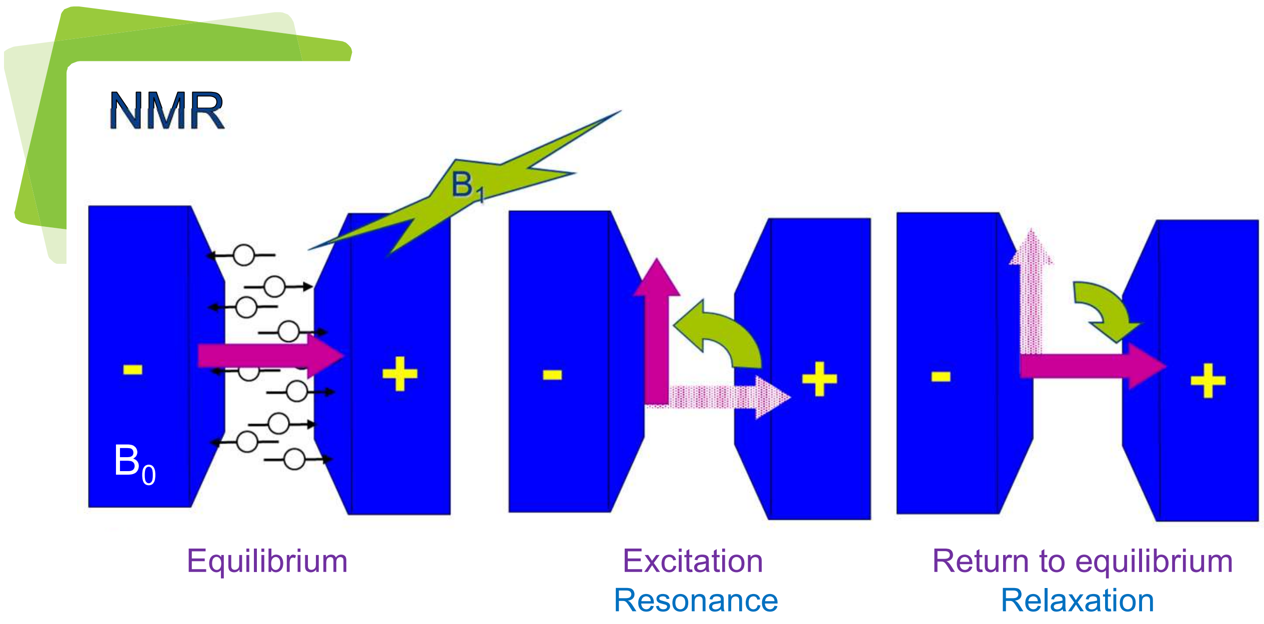
Imagerie et spectroscopie multi-modales

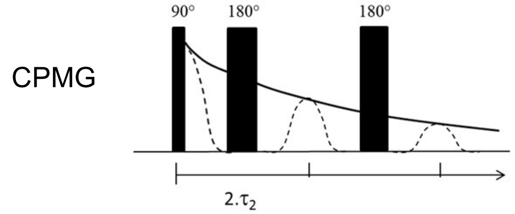
Université Rennes & Angers,
CNRS, INRA Rennes

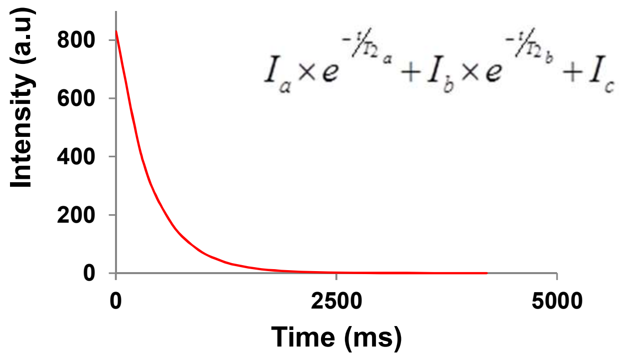
11,7 T

MRµI

500 MHz Bruker



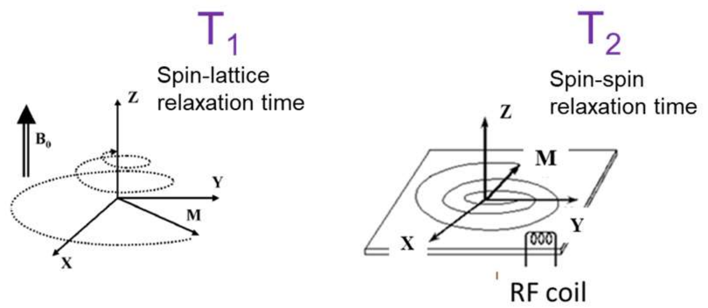




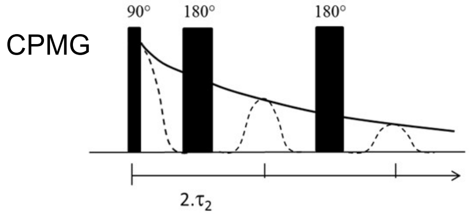
$$I_a \times e^{-t/T_{2a}} + I_b \times e^{-t/T_{2b}} + I_c \times e^{-t/T_{2c}}$$

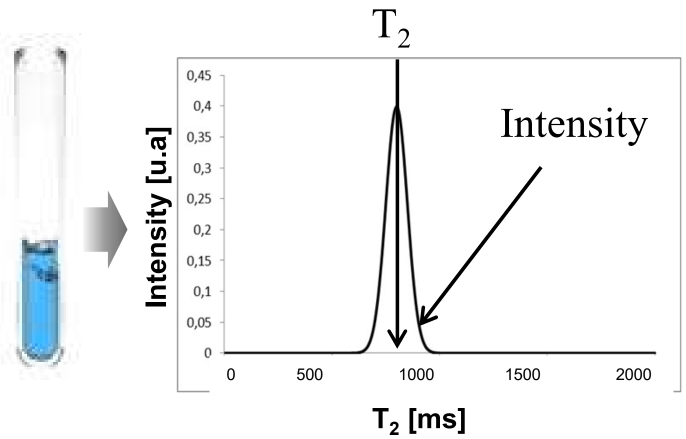
Mobility of atoms and molecules

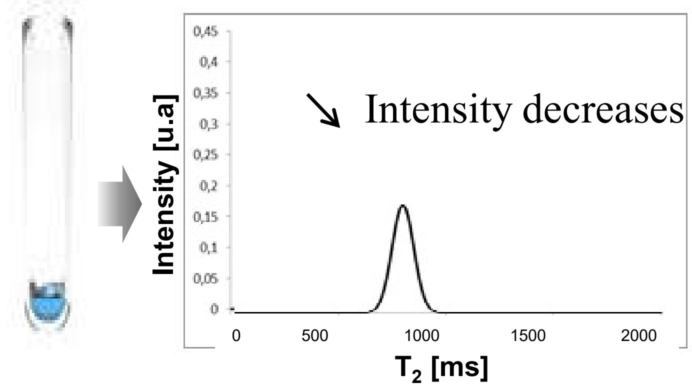
- according to their nature, their chemical environment and physical state (in solvent, polycrystalline powder, aggregated in vesicles, etc.)
- depending on their form (aliphatic chain or globular protein)
- according to their interactions with other molecules



BASICS OF TD-NMR







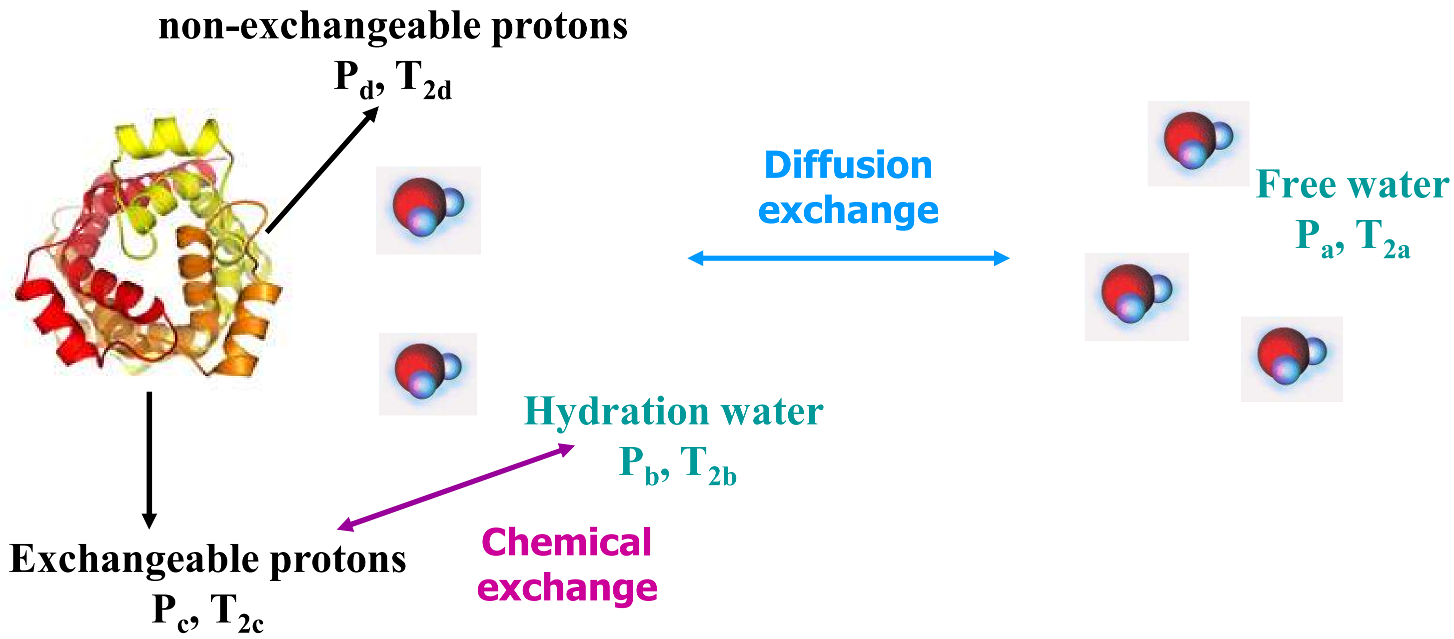
T_2 ⟷ Water mobility

Signal intensity ⟷ Water amount

NMR is a non-invasive and quantitative method

Proton relaxation times depend on the **nature of molecules**, their **size**, their **physical state** (liquid/soft/solid), their **environment** (compartment/interactions)

Water-macromolecule mixture



→ Depending on the rate of chemical and diffusion exchanges,

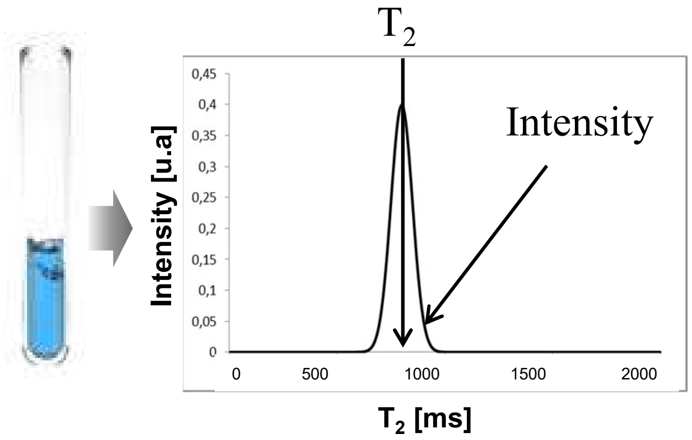
mean value of T_2

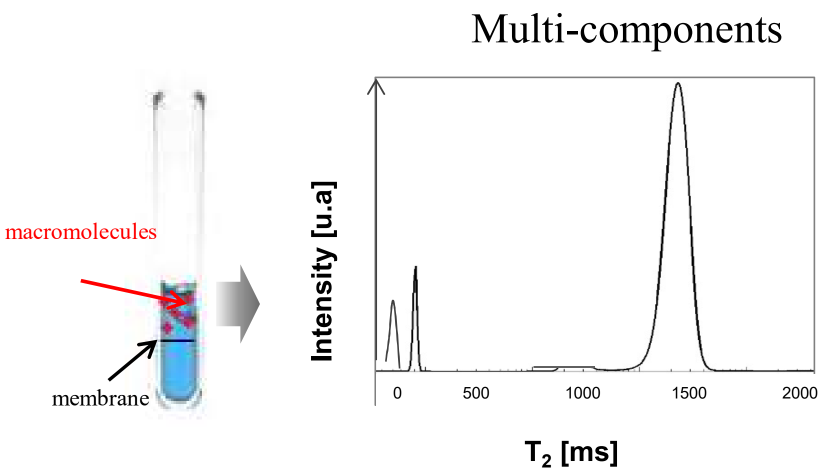
$$M(t) = (P_a + P_b + P_c + P_d).e^{-\left(\frac{P_a}{T_{2a}} + \frac{P_b}{T_{2b}} + \frac{P_c}{T_{2c}} + \frac{P_d}{T_{2d}}\right)}$$

several T_2 values

$$M(t) = P_a e^{-\frac{P_a}{T_{2a}}} + P_b e^{-\frac{P_b}{T_{2b}}} + P_c\, e^{-\frac{P_c}{T_{2c}}} + P_d\, e^{-\frac{P_d}{T_{2d}}}$$

Water NMR relaxation in **slow chemical and diffusion exchange** between compartments

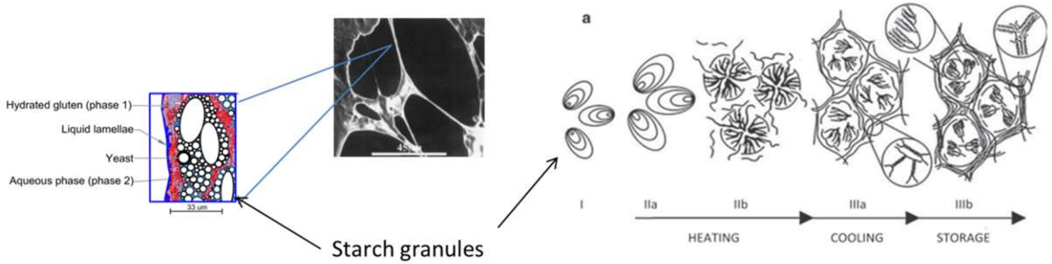


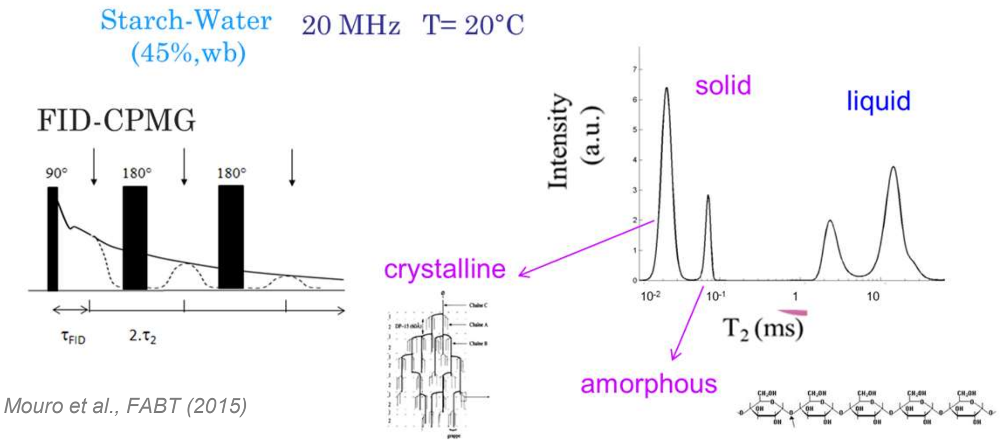


Signal intensity ⟷	Water amount
T_2 ⟷	Water mobility
Multi-components ⟷	Chemical exchanges and/or Compartmentation

Time-domain NMR

Water state at molecular scale

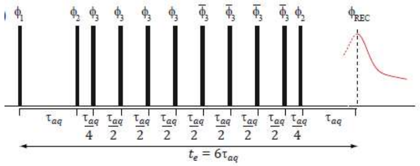




C. Rondeau- Mouro et al., FABT (2015)

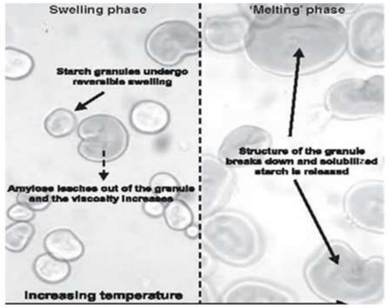
Coupling of FID and CPMG sequences to quantify the liquid and solid phases in sample

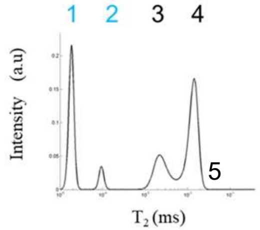
- getting a **better time resolution** in the microsecond T_2 range
- making possible the **quantitation of changes** of each T_2 component whatever is the physical state of molecules

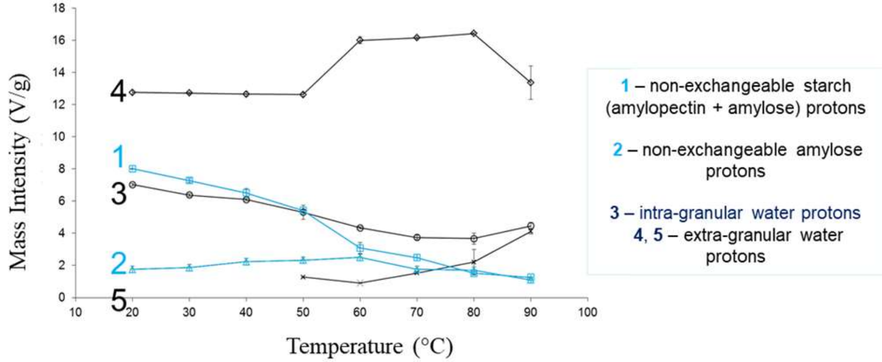


Alternative to the FID : Magic Sandwich Echo

A. Pines et al. J. Magn. Reson. (1972)
S. Matsui, J. Magn. Reson. (1992)

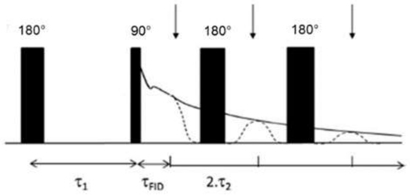






C. Rondeau- Mouro et al., FABT (2015)

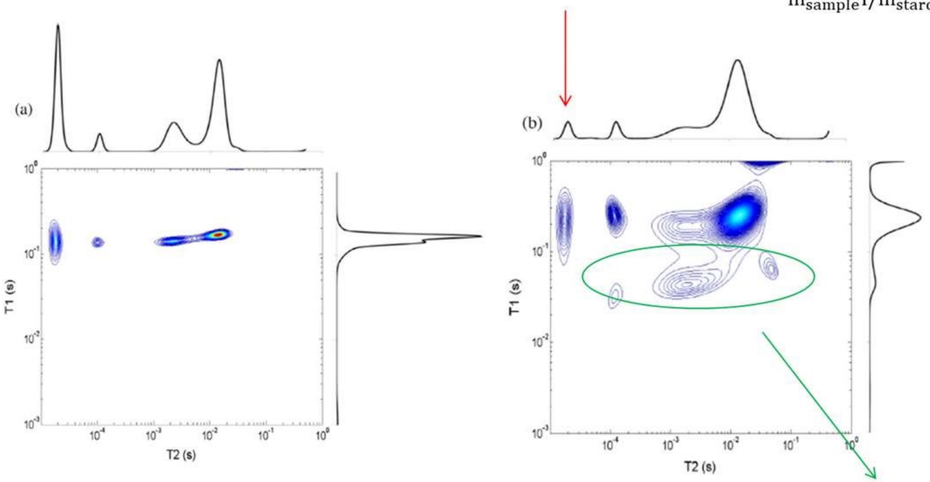
Bi-dimensional TD-NMR



IR-FID-CPMG

wheat starch-water at 45 % wc

$$SC\ (\%) = \frac{I_{T_2(1)} + I_{T_2(2)}}{m_{sample} I / m_{starch}}$$



20°C

90°C

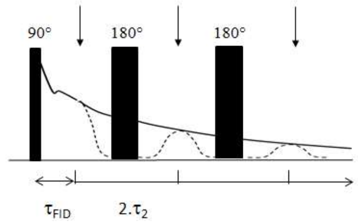
Cross relaxation

Solid Content = 59.1 ± 1.3 %

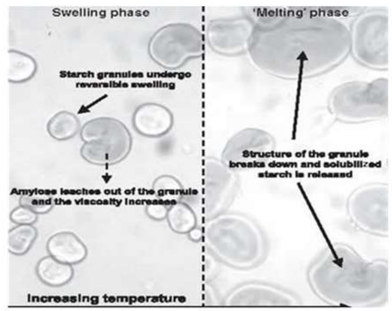
Starch gelatinisation →

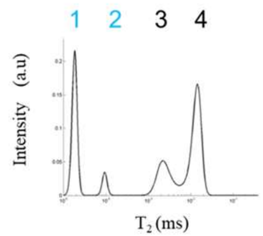
Solid Content = 20.4 ± 1.7 %

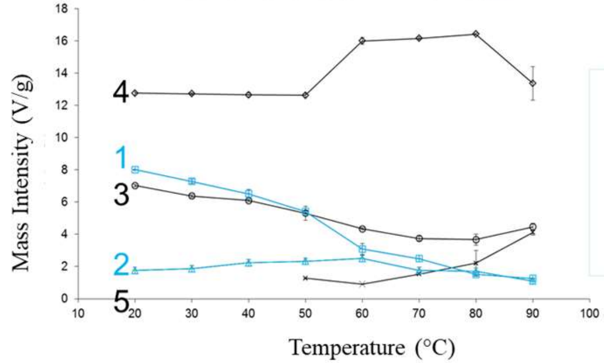
R. Kovrlija, C. Rondeau-Mouro, Food Chemistry (2017)
R. Kovrlija, C. Rondeau-Mouro, FABT (2016)
C. Rondeau-Mouro et al., J. Magn. Reson. (2016)



FID-CPMG







1 – non-exchangeable starch (amylopectin + amylose) protons

2 – non-exchangeable amylose protons

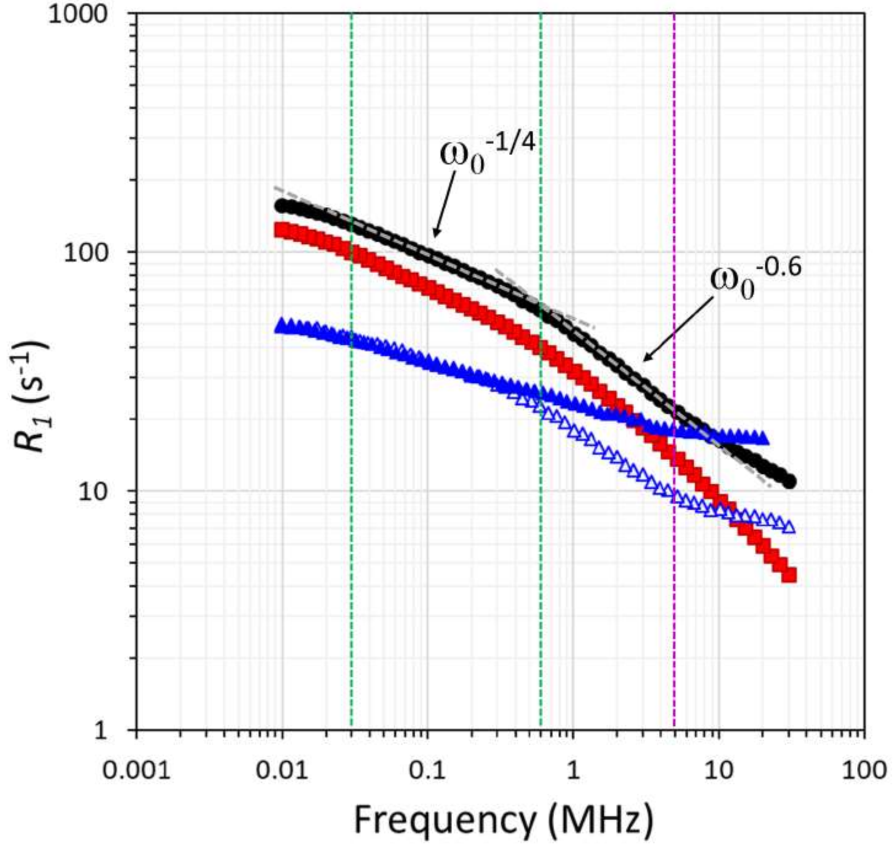
3 – intra-granular water protons

4, 5 – extra-granular water protons

C. Rondeau- Mouro et al., FABT (2015) ; E. Rakhshi et al. Magn. Res. Chem. (2022)

FFC experiments on dough upon heating

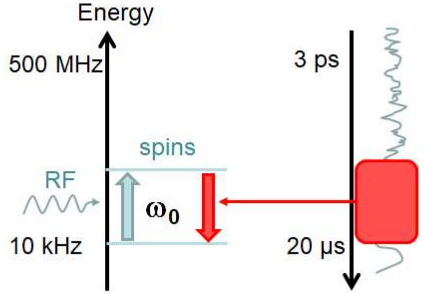
Nuclear Magnetic Relaxation Dispersion (NMRD) profile



$$\tau_C \sim (2\pi\omega)^{-1}$$

Anne-Laure Rollet, Paris Sorbonne

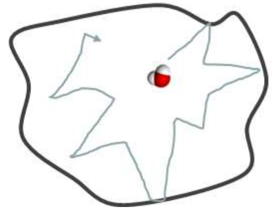
Stimulated process



Relaxation stimulated by the magnetic field fluctuations due to spin motions with correlation time τ_c

$$\omega_0\tau_c=1$$

Decreasing the magnetic field $B_0=\omega_0/\gamma$ leads to a drastically increase in the spatial window explored by molecules

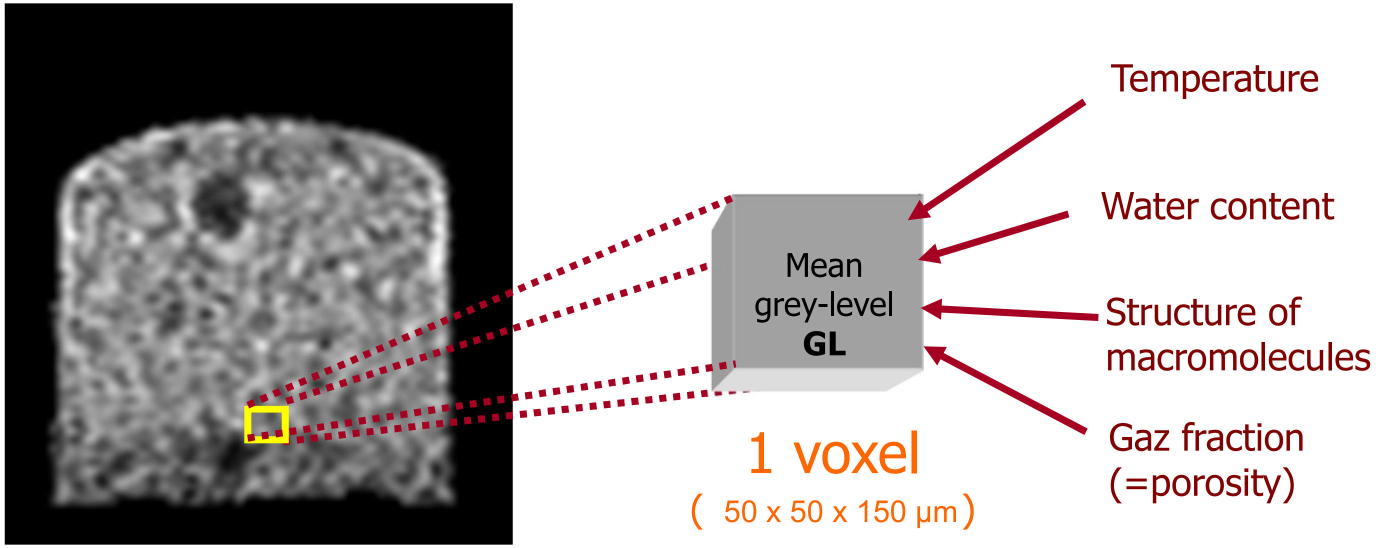


Long time motions
Molecular diffusion

Korb, J.-P., & Bryant, R. G. (2001). The physical basis for the magnetic field dependence of proton spin-lattice relaxation rates in proteins. *The Journal of Chemical Physics, 115*(23), 10964–10974. https://doi.org/10.1063/1.1417509

Study of the water interaction with macromolecules (gluten and starch)

MRI to analyze structures and processes with a spatial resolution



MRµI

- to study dynamical mechanisms (water uptake, heating, freezing, storage …)
- to explicit the relationship between the MRI signal and local quantities (porosity, water content …)

➢ conception of computer codes

11.7 T

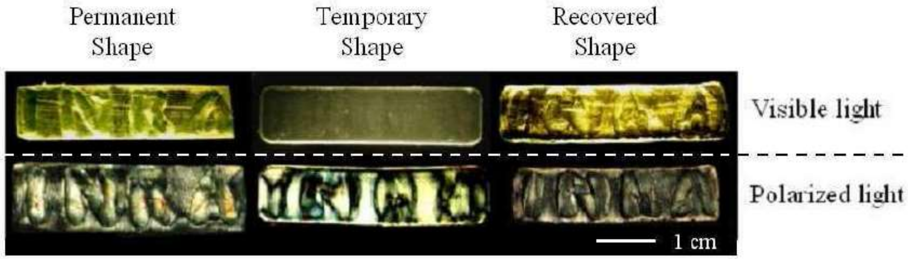
Transport diffusion of water by micro-imaging

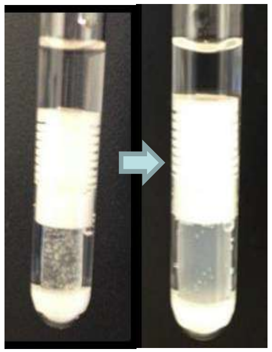
11.7 T

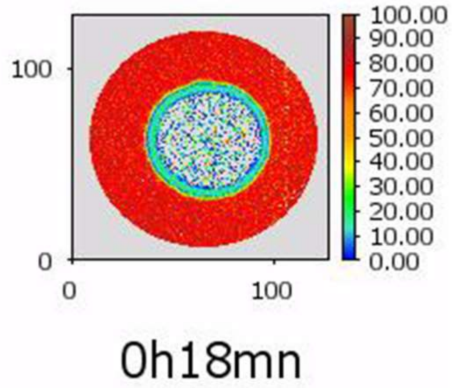
MSME
ΔTE of 5 ms, 32 echoes
TR= 1.5 s, AQ=15min
128 × 128, FOV 10 × 10 mm
Resolution = (78 × 78 µm²)* 500 µm

Potato starch-glycerol blends, 4mm Ø

Shape-memory property :



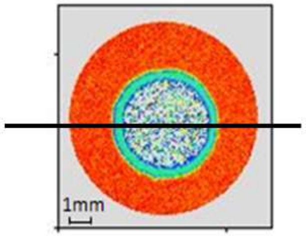


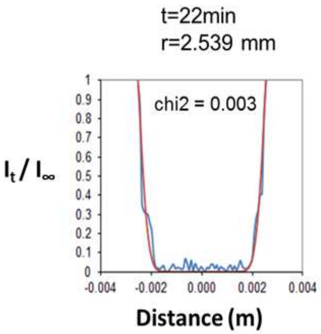


T_2 (ms)

Collaboration with D. Lourdin, UR BIA, INRAE Nantes, France

Initial transport diffusion of water





$D_i = (5.5 \pm 1.5) \times 10^{-11}$ m²/s

Crank defined diffusion models for several sample geometries, such as plane sheet, infinite cylinder or sphere.

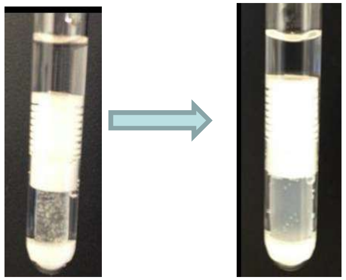
Concentration of water in a disc :

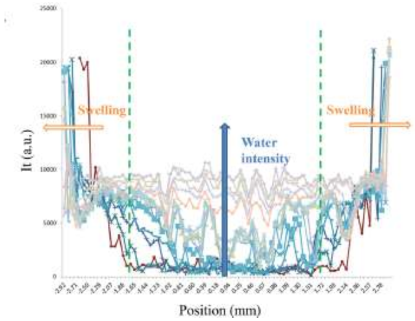
$$\frac{C - C_0}{C_\infty - C_0} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1} e^{-D(2n+1)^2\pi^2 t/4l^2} \cos\frac{(2n+1)\pi x}{2l} \quad (2)$$

Crank J. 1975. The mathematics of diffusion. Clarendon Oxford

$$\bar{D} > D_i$$

decrease in gradient driving force when the sample is increasingly hydrated



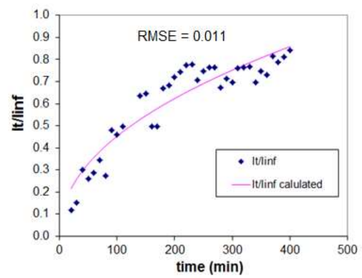


Average diffusion coefficient

$$\frac{I_t}{I_\infty} = k\, t^n$$

$$\bar{D} = \left(\frac{\pi k r}{4}\right)^2 = (2.00 \pm 1.06) \times 10^{-10} m^2/s$$

Signal intensity at 1.72 mm from the center



n = 0.48 ± 0.03

Case I kinetics - Fickian Diffusion (n~1/2)

𝒱 water diffusion << 𝒱 starch relaxation

R. Kovrlija, C. Rondeau-Mouro, Food Chemistry (2017)
C. Chevigny ey al. Biomacromolecules (2018)

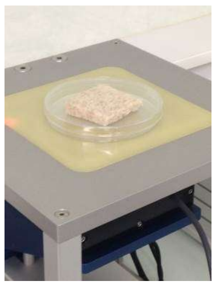
MOUSE
Mobile Universal Surface Explorer

Light and portable open unilateral NMR sensor with a permanent magnet (0.47 T, 0.31 T), a surface RF coil and a highly uniform gradient perpendicular to the scanner surface (**23.5 / 7.3 T/m)**

A flat sensitive volume is excited and detected by the surface RF coil placed on the top of the magnet

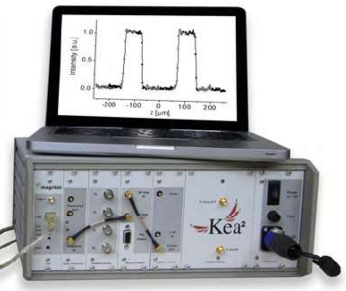
The high precision lift automatically moves the sensor to profile the sample as a function of the depth

Max depth = 5 / 25 mm, resolution 10 / 150 µm, RF size = 13x13 mm / 40x40 mm

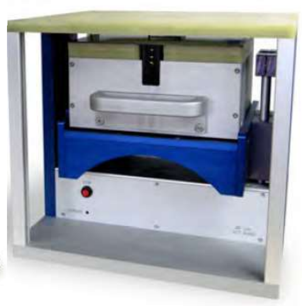


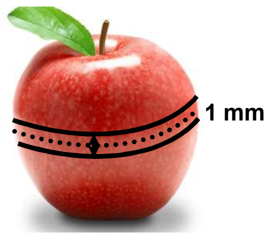
PM5

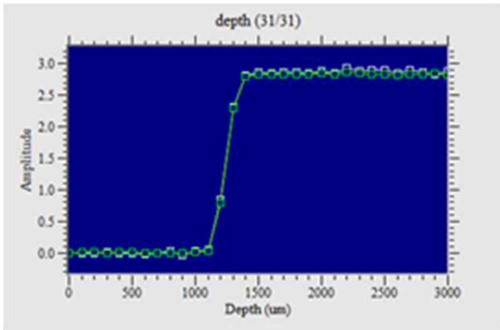
Magritek

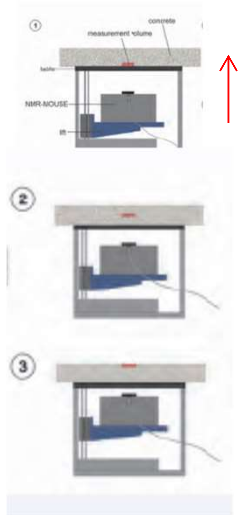


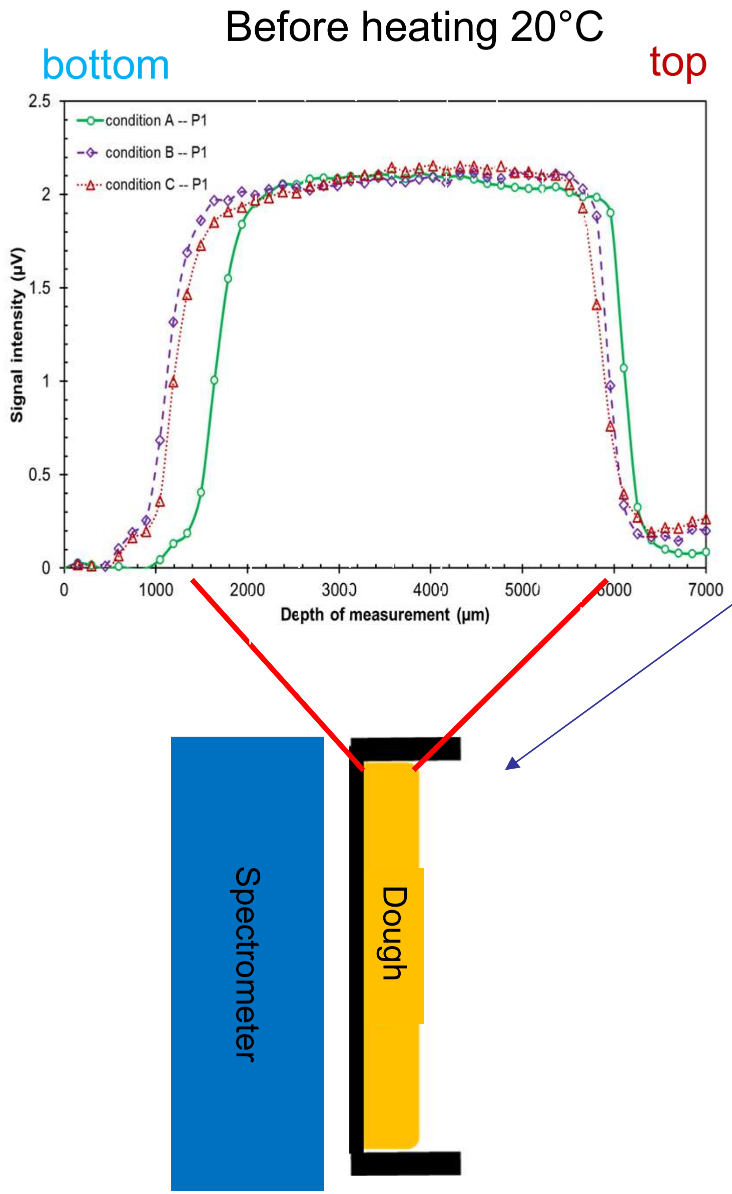
PM25

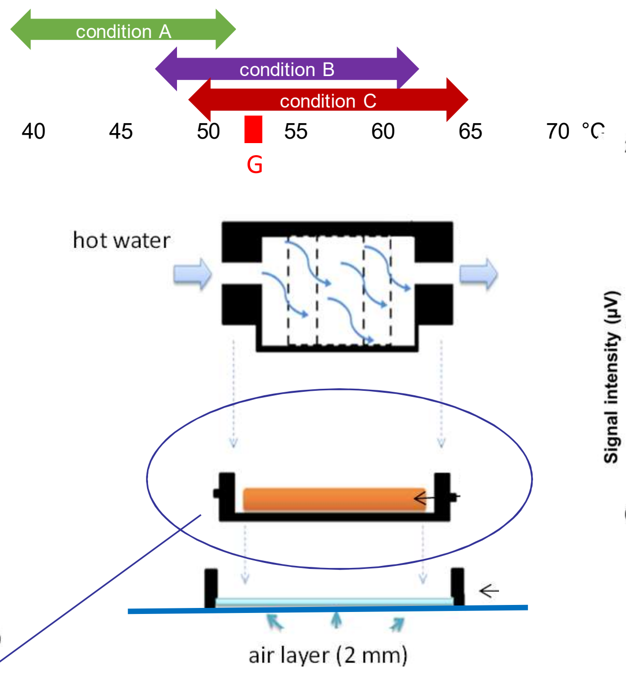


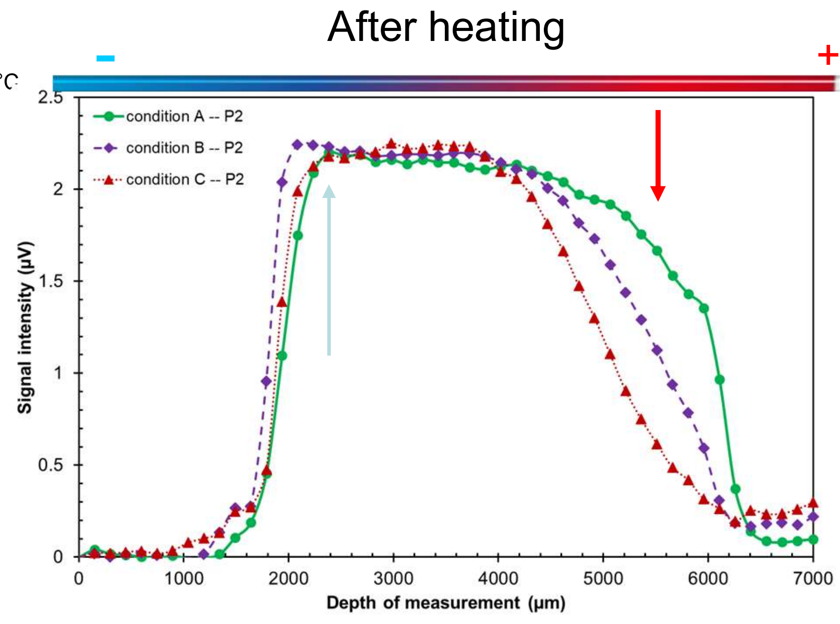


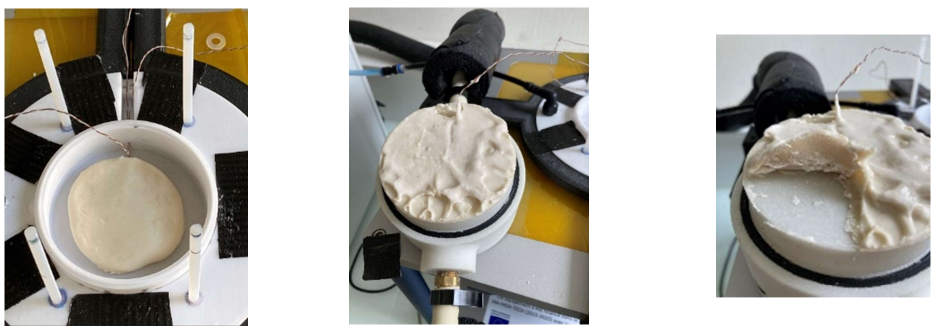












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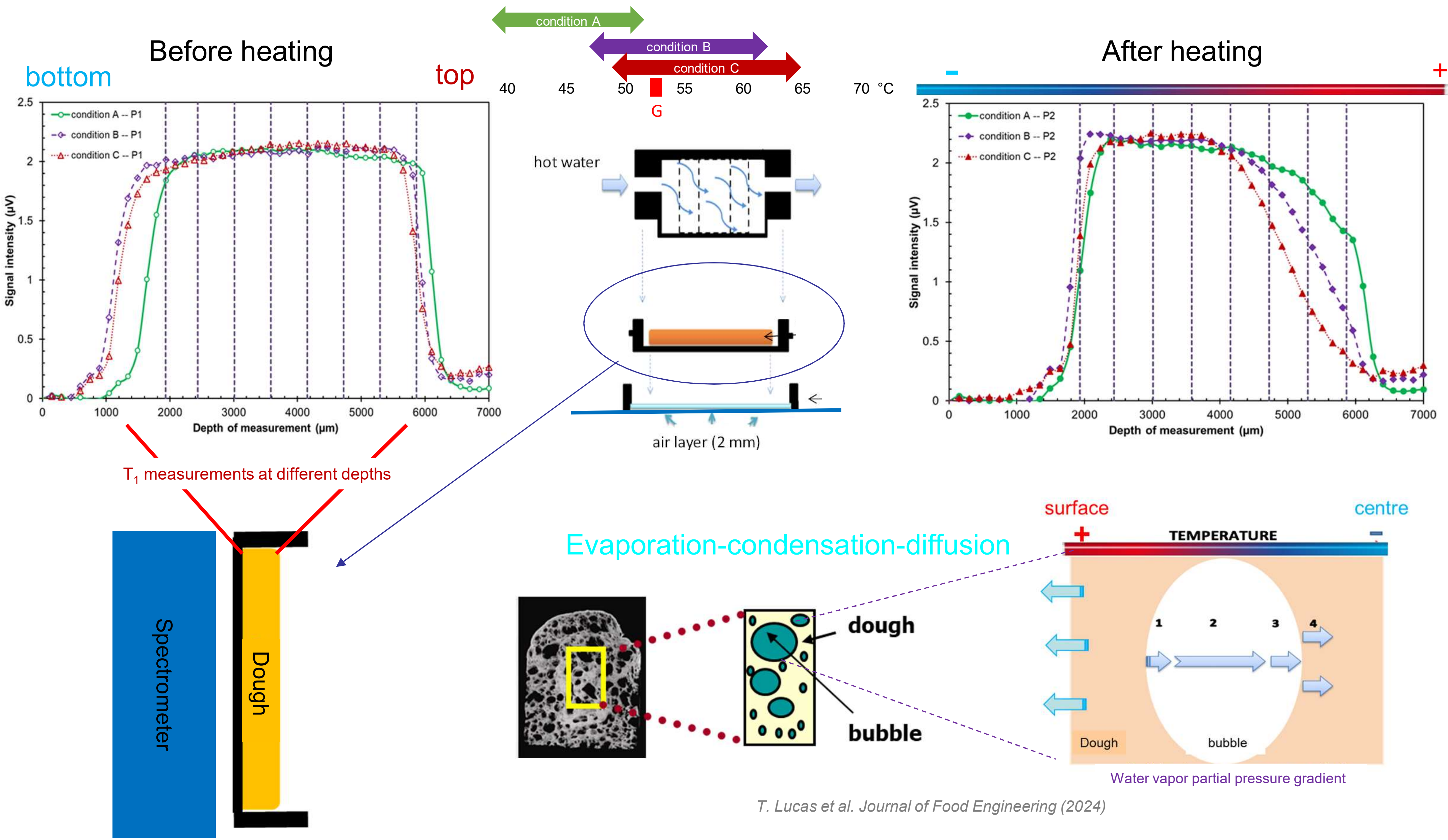

Before heating
bottom
top
condition A
condition B
condition C
40 45 50 55 60 65 70 °C
G
After heating
condition A -- P1
condition B -- P1
condition C -- P1
Signal intensity (µV)
Depth of measurement (µm)
condition A -- P2
condition B -- P2
condition C -- P2
hot water
air layer (2 mm)
T1 measurements at different depths
Spectrometer
Dough
Evaporation-condensation-diffusion
surface
centre
TEMPERATURE
dough
bubble
Dough
bubble
Water vapor partial pressure gradient
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ACKNOWLEDGEMENTS

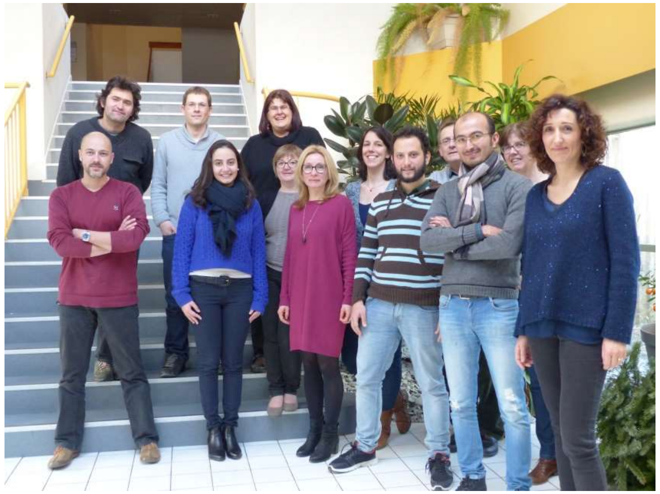
Ruzica Ferbus-Kovrlija PhD
Elham Rahkshi PhD
Stéphane Quellec
Sylvain Challois
UR OPAALE, Rennes

Pierre-Antoine Eliat
Fanny Noury
PF PRISM, Rennes
Collaboration in image acquisition

Denis Lourdin
UR BIA, Nantes
Starch blend production

Jean-Michel Roger & Silvia Mas Garcia
UMR ITAP, 34196, Montpellier
Image processing using chemometrics

MRIFood team



THANK YOU FOR YOUR ATTENTION