



**HAL**  
open science

## Water dynamics in a mesoporous bioactive glass studied by NMR relaxometry

Abdelkarim Rjiba, Nizar Bchellaoui, Rachida Dorbez-Sridi, El-Eulmi Bendeif,  
Axel Gansmuller, Carole Gardiennet, Sabine Bouguet-Bonnet

► **To cite this version:**

Abdelkarim Rjiba, Nizar Bchellaoui, Rachida Dorbez-Sridi, El-Eulmi Bendeif, Axel Gansmuller, et al.. Water dynamics in a mesoporous bioactive glass studied by NMR relaxometry. Euromar 2018, Jul 2018, Nantes, France. hal-02271927

**HAL Id: hal-02271927**

**<https://hal.univ-lorraine.fr/hal-02271927v1>**

Submitted on 27 Aug 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Water dynamics in a mesoporous bioactive glass studied by NMR relaxometry



AbdelKarim Rjiba<sup>1</sup>, Nizar Bchellaoui<sup>1,2</sup>, Rachida Dorbez-Sridi<sup>1</sup>, El-Eulmi Bendeif<sup>3</sup>, Axel Gansmüller<sup>3</sup>, Carole Gardiennet<sup>3</sup>, Sabine Bouguet-Bonnet<sup>3</sup>

Sabine.Bonnet@univ-lorraine.fr

<sup>1</sup> LPCM FSM, Université de Monastir, Monastir, Tunisia

<sup>2</sup> LPQM, Université Paris-Saclay, Cachan

<sup>3</sup> CRM2, IJB, Université de Lorraine, Vandœuvre-lès-Nancy, France



## context and objectives

Mesoporous bioactive glasses (MBG) are nanostructured materials possessing a high bioactive response.

Many applications in tissue engineering and bone-tissue regeneration: formation of apatite-like layers (hydroxyapatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) at the surface of the bioglass when in contact with body fluids.

Body fluids are mainly composed of water → it is crucial to study and understand the dynamics of confined water in these MBG.

→ comparison of the dynamics when water is confined in two bioglasses having the same chemical composition but made with different methods

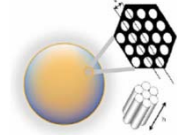
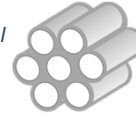
### 92S6 bioglasses

(92%  $\text{SiO}_2$ , 6%  $\text{CaO}$ , 2%  $\text{P}_2\text{O}_5$  mol%)

standard sol-gel technique

droplet based microfluidics

2D hexagonal mesoporous structure



microcapsules with a 2D hexagonal mesoporous organized shell

## material and methods

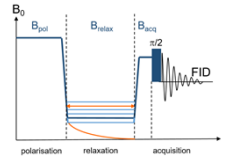
sample preparation	$S_{\text{BET}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	$d_p$ (nm)	particles size ( $\mu\text{m}$ )
sol-gel	376	0.66	5.7	~10
microfluidic	514	0.76	5.9	~8 (shell ~2 $\mu\text{m}$ thick)

Samples were prepared in 8 mm o.d. hermetically sealed capsules.



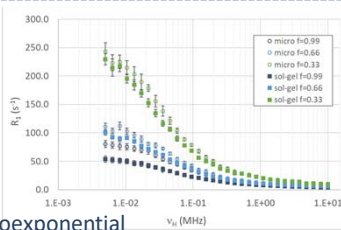
Bioglass powders were dried during one day at 150°C before hydration with the wanted volume of distilled water : filling degrees of 33%, 66% and 99% were used (corresponding to the percentage of the mesoporous volume).

Samples were then kept at 25°C during 1 night for complete equilibrium before  $^1\text{H}$  relaxometry measurement by Fast Field Cycling technique at 298K (Stelar SMARtracer relaxometer,  $^1\text{H}$  5kHz-10MHz).



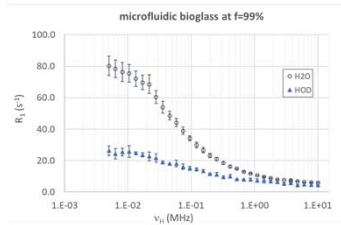
## results and discussion

$^1\text{H}$  longitudinal relaxation rates as a function of the magnetic field (dispersion) as a tool to evaluate the dynamical behavior of the fluid embedded in bioglass



monoexponential recovery curves for all  $R_1$  measurements → **two-phase fast exchange model**

### measurements with deuterated water



The microfluidic bioglass was filled at 99% with protonated or heavy water, and  $^1\text{H}$  longitudinal relaxation rates were measured for  $\text{H}_2\text{O}$  protons ( $\circ$ ) or residual protons (HOD  $\blacktriangle$ ) in 99.9%  $\text{D}_2\text{O}$ .

→ HOD relaxation being purely intermolecular, the comparison of  $\text{H}_2\text{O}$  and HOD dispersion curves shows that the  $^1\text{H}$  low-frequency relaxation of  $\text{H}_2\text{O}$  is mainly due to **intramolecular** dipolar interactions modulated by molecular reorientations.

### dispersion as a function of the filling factor for comparing slow dynamical processes in confinement

**two-phase fast exchange model** : exchange between bulk-like water et water adsorbed at the pore surface is fast compared to the longitudinal relaxation → measurement of an averaged relaxation rate

longitudinal relaxation rate in the adsorbed phase

longitudinal relaxation rate in the bulk phase (extreme narrowing, independent of the magnetic field)

$$R_1(\omega_H) = p_a R_{1a}(\omega_H) + (1-p_a) R_{1b}$$

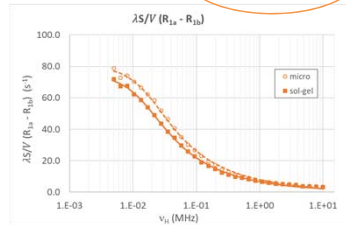
$p_a$  : population in the adsorbed phase

When the filling factor increases,  $p_a$  decreases and  $R_1$  tends toward  $R_{1b}$ .

The population in the adsorbed phase can be assumed to vary with the filling factor  $f$  as:  $p_a = \frac{\lambda S}{V} \frac{1}{f}$

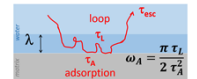
with  $\lambda$  adsorbed water layer width,  $S$  porous surface area and  $V$  the porous volume

$$R_1(\omega_H) - R_{1b} = \frac{\lambda S}{V} (R_{1a}(\omega_H) - R_{1b}) \frac{1}{f}$$



$R_{1a}(\omega_H)$  can thus be retrieved with the linear evolution of  $R_1$  as a function of  $1/f$  (with  $R_{1b} = 0.41 \text{ s}^{-1}$  from an independent measurement)

$S/V$  values are obtained from nitrogen adsorption/desorption isotherms, and dispersion curves are analyzed according to Levitz's model\*



intermittent Brownian dynamics near a flat surface

$$J(\omega) \propto \left( \frac{\omega}{\omega_A} \right)^{0.5} + \frac{\omega}{\omega_A} + \frac{1}{2} \left( \frac{\omega}{\omega_A} \right)^{1.5}$$

$$R_{1a}(\omega) = K_d (J(\omega) + 4J(2\omega))$$

sample preparation	$\tau_{\text{esc}}$ ( $\mu\text{s}$ )	$\tau_l$ (ps)	$\tau_A$ (ps)	$\lambda$ ( $\text{\AA}$ )
sol-gel	6.2	12	21	3.3
microfluidic	5.1	12	21	3.7

faster escaping to the bulk for water confined in the microfluidic bioglass

same dynamical behavior for the adsorbed molecule

The apparent shift of experimental dispersion curves is mainly due to different  $S/V$  ratio for the two samples.

## conclusion

Low-field relaxometry allowed us to analyze water slow dynamics in confinement in both bio-glasses: adsorbed water has the same behavior in the mesoporous channels of both systems (made with microfluidic or sol-gel methods), but the microcapsule organization enhances slightly the rate of escaping of water molecules towards the bulk.