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Water dynamics in a mesoporous bioactive glass studied by NMR relaxometry



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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

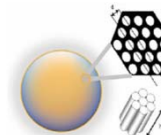
92S6 bioglasses

(92% SiO_2 , 6% CaO , 2% P_2O_5 mol%)

standard sol-gel technique

droplet based microfluidics

2D hexagonal mesoporous structure



microcapsules with a 2D hexagonal mesoporous organized shell

material and methods

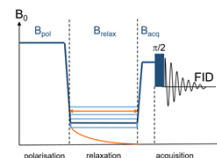
sample preparation	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_p ($\text{cm}^3 \cdot \text{g}^{-1}$)	d_p (nm)	particles size (μm)
sol-gel	376	0.66	5.7	~10
microfluidic	514	0.76	5.9	~8 (shell ~2 μm thick)

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



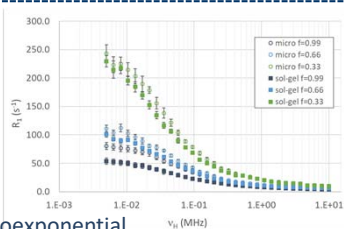
Bioglass powders were dried during one day at 150°C before hydration with the wanted volume of distilled water : filling degrees of 33%, 66% and 99% were used (corresponding to the percentage of the mesoporous volume).

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



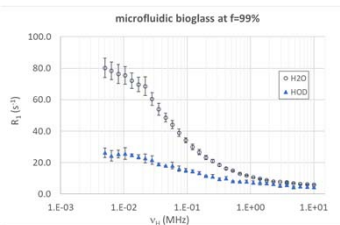
results and discussion

^1H 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 ^1H longitudinal relaxation rates were measured for H_2O protons (\circ) or residual protons (HOD \blacktriangle) in 99.9% D_2O .

→ HOD relaxation being purely intermolecular, the comparison of H_2O and HOD dispersion curves shows that the ^1H low-frequency relaxation of H_2O 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)

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

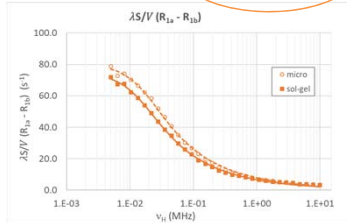
p_a : population in the adsorbed phase

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: $p_a = \frac{\lambda S}{V} \frac{1}{f}$

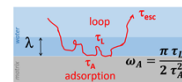
with λ adsorbed water layer width, S porous surface area and V the porous volume

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



$R_{1a}(\omega_H)$ 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

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

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

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.