



	Experiment title: <i>Structural and reactivity analysis of new bioactive glasses using atomic Pair Distribution Function (PDF)</i>	Experiment number: MA-3925
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Report:

The aim of this study is the investigation of the structural properties of confined physiologic liquids inside two mesoporous glasses having the same chemical composition ($\text{SiO}_2\text{-CaO-P}_2\text{O}_5$ with a molar ratio of $\text{Si/Ca/P} = 92/6/2$) but different structural features. The first bioglass was prepared by a conventional Sol-Gel process (named hereafter 92S6 sol-gel) and the second one was prepared following a new elaboration process of mesoporous bioactive silica hollow microspheres using droplet-based microfluidics (named hereafter 92S6 Microfluidic). In order to follow the structural changes induced by the amount of confined water, samples were prepared with three different water loadings (30, 60, and 100 vol%). These ratios were chosen based on additional DSC measurements. To compare our PDF results to those obtained from the calorimetric measurements, we carried out variable temperature total X-ray scattering data. We collected data at four temperatures (290K, 253K, 233K and 190K) using a large area, high energy single-photon counting detector, Pilatus3 2M CdTe and a high energy monochromatic beam (68.5 keV, $\lambda = 0.18099 \text{ \AA}$). Data obtained were integrated and truncated at a finite maximum value of $Q_{\text{max}} = 17 \text{ \AA}^{-1}$ beyond which the signal-to-noise ratio became unfavorable. All the differential experimental atomic pair distribution functions (d-PDF) were obtained by using the PDFgetX2 software.

Comparison of the differential pair distribution function (d-PDF) of water confined in 30%92S6, 60%92S6, and 100%92S6 and that of the bulk water clearly shows the confinement effect on the structural organization (**fig 1**). The d-PDF diagram of bulk water exhibits two main peaks at 2.8, and 4.5 \AA corresponding to the distances of the first and second $\text{O}_w\text{-O}_w$ neighbors, respectively. The main peak at 2.8 \AA due to the oxygen-oxygen correlation term is observed in all samples whatever the hydration level. At low water content, 30 vol% (**fig.1**), the second neighbors are totally distorted and are distributed on two sites localised at 4 \AA and 4.9 \AA . This distortion is less pronounced when increasing the hydration ratio to 60 vol % (**fig.1**) and the structure of confined water shows two peaks at the same positions compared to the bulk water (2.8 and 4.5 \AA). This feature has been also observed in similar system reported in the literature and can be attributed to either the local hydrogen-bonded network modification or to the contribution from substrate-water terms arising from specific interactions at the bioglass interface. For high hydration levels, 100 vol %, we find a behavior closer to the bulk water.

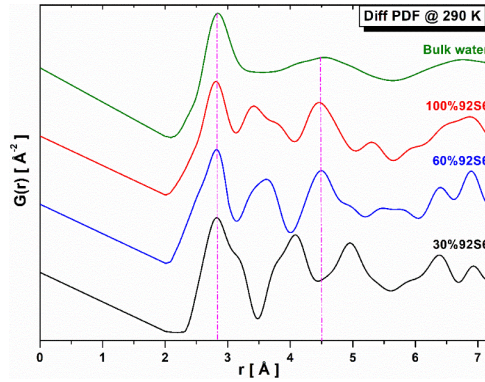


Fig 1. Differential X-ray pair distribution function, d-PDF, of water confined in 30%92S6, 60%92S6, and 100%92S6 compared with that of bulk water at 290 K. Vertical lines indicate positions at 2.8, and 4.5 Å.

In order to affirm the attribution of the observed PDF peaks we investigated them by studying the structure as a function of temperature using total X-ray scattering coupled to PDF analysis. Fig.2 shows the d-PDF of water in 100%92S6 (top left corner), 60%92S6 (top right corner), at 290, 253, 243, 233, and 200 K. The d-PDF of water in 30%92S6 (bottom) is also shown at 290, 253, and 200 K. For water in 60%92S6, and 100%92S6, the d-PDF diagrams show that with decreasing the temperature, the peak intensities of the first and second neighbors' pair correlations at 2.8, and 4.5 Å increase, accompanied by a shift of the first neighbors to shorter distances 2.71 Å. The peak at 3.75 Å is not strongly affected by the temperature. On the other hand, the peak intensity at ~ 3.3, and ~ 3.4 Å for 100%92S6, and 60%92S6 respectively, decreases gradually with decreasing temperature. At 200 K, this peak disappears completely, indicating that non-hydrogen bonded water diminishes with decreasing temperature, converting into hydrogen bonded water.

For water in 30%92S6, the intensities of the d-PDF peaks exhibit less changes with temperature compared to 60 and 100 vol% loading samples. This observation is consistent with previous studies where it was reported that the first two monolayers of the confined water with a thickness of 3-5 Å around the pore wall are ascribed as non-freezable pore water. These results are consistent with the DSC thermal analysis and show that the network of interactions of water molecules undergoes interesting structuring with the formation of stronger hydrogen bonds at low temperatures.

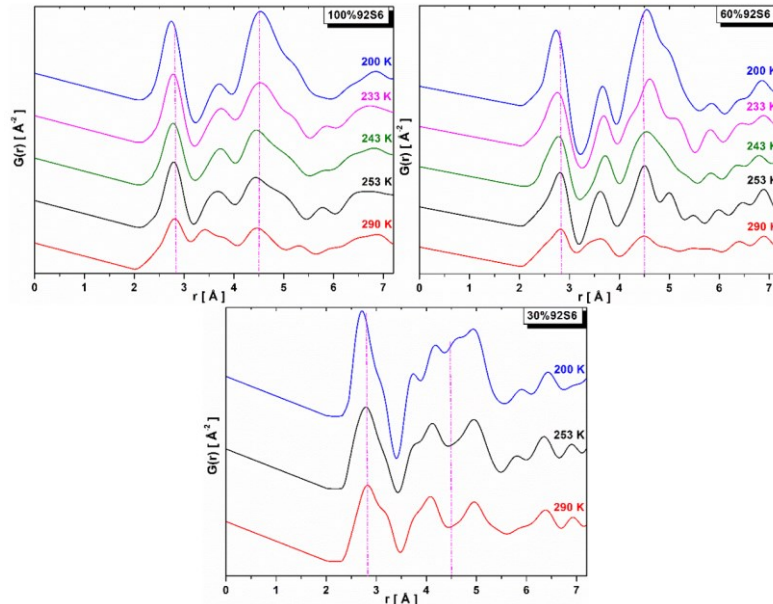


Fig 2. Variable temperatures differential X-ray pair distribution function, d-PDF, of water confined in: 100%92S6 (top left); 65%92S6 (top right), and 30%92S6 (bottom). Vertical lines indicate positions at 2.8, and 4.5 Å.

To validate the structural properties obtained from experimental PDFs, we compared the experimental results to those of theoretical calculations based on Monte Carlo simulations. This work was done using EPSR software (Empirical Potential Structure Refinement). The resulting PDFs (**fig.3**) show that our simulation results are in very good agreement with the experiments. The structural model can be described as being formed by a dynamic monolayer of about 4 Å thickness for low liquid content (30%92S6). By increasing the hydration ratio, a radial filling process is set up until the total filling of the pore. Thus, the liquids confined in the center of the pores show structural parameters that are quite similar to those of the bulk liquids.

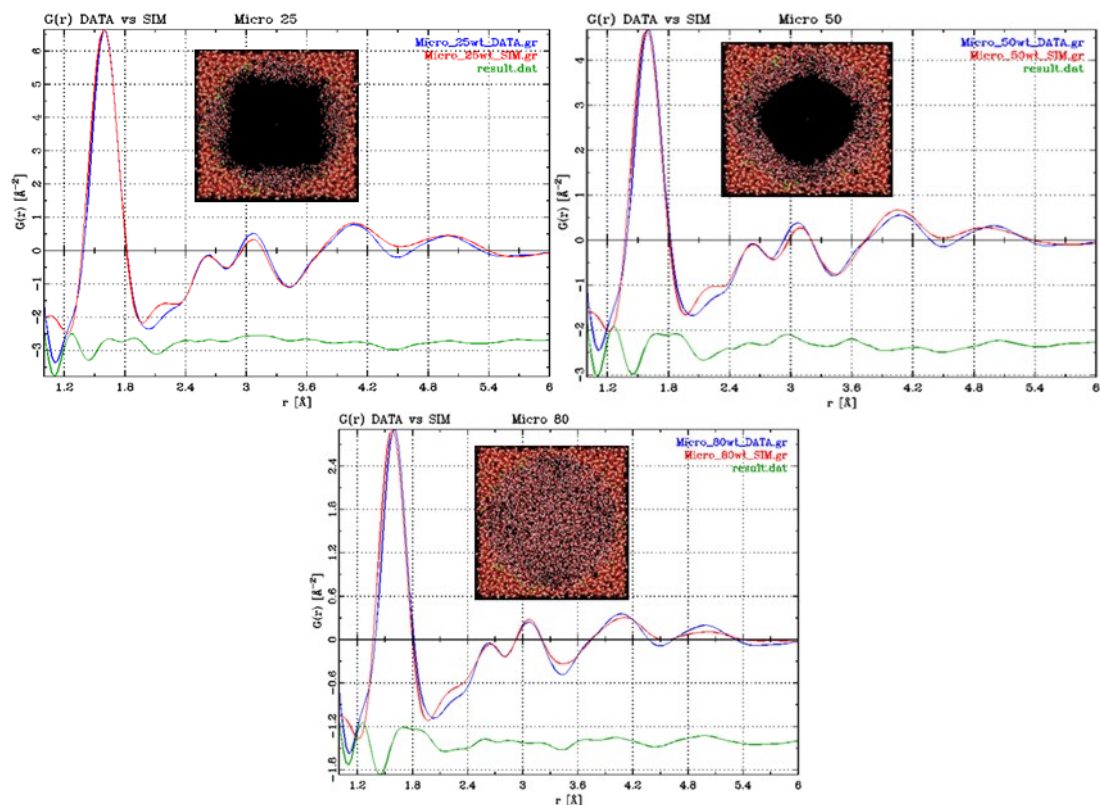


Fig 3. Comparison of experimental and simulated PDFs for the different investigated systems.

All these results allow us to validate our theoretical and experimental approaches and to continue our investigations on these challenging nanomaterials.

Publications:

- 1- *Structural study of water confined in bioactive glasses using experimental and theoretical Pair Distribution Function*
H. Khoder, D. Schaniel, S. Pillet & E-E. Bendeif
Acta Cryst, A: Foundation and Advances. **2020**, (Submitted)
- 2- *Imprinting isolated single iron atoms onto mesoporous silica by templating with metallosurfactants.*
Y. Berro, S. Gueddida, Y. Bouizi, C. Bellouard, E-E. Bendeif, A. Gansmuller, A. Celzard, V. Fierro, D. Ihiwakrim, O. Ersen, M. Kassir, F. El Haj Hassan, S. Lebègue, M. Badawi, N. Canilho & A Pasc.
Journal of Materials Chemistry A. **2020**, (under revision)