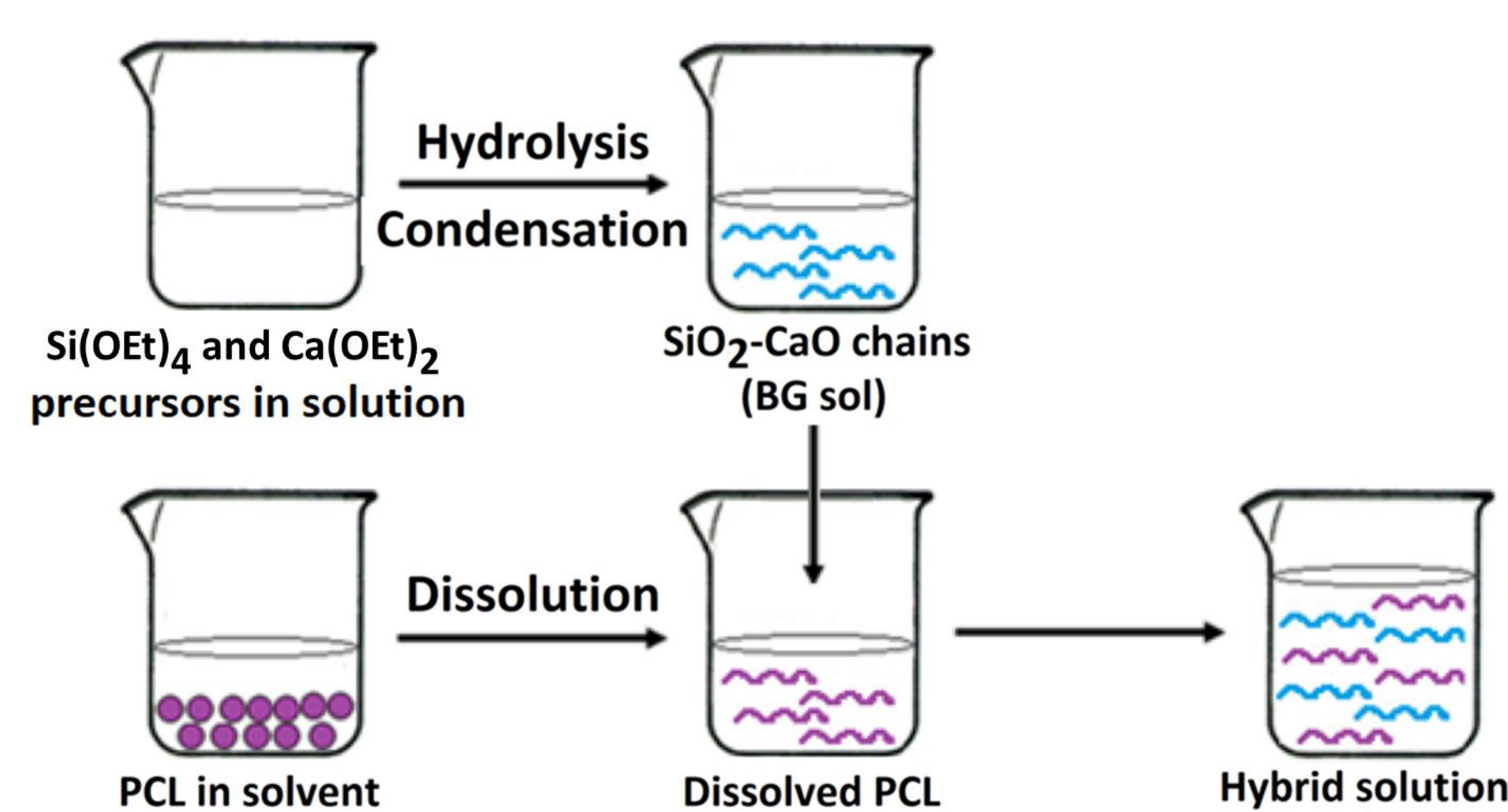


Introduction

Inorganic-organic hybrids appear as promising bone substitutes since they associate the bone mineral forming ability of bioactive glasses (BG) with the toughness of polymers. In such hybrids, the main challenge concerns the incorporation of calcium into the BG silicate network, which plays a major role in biomineralisation. Hybrids comprised of polycaprolactone (PCL, $M_n = 80,000$ g/mol) and SiO_2 -CaO BG were produced by a sol-gel process and built into porous scaffolds with controlled pore and interconnection sizes. PCL was chosen as the polymer because its slow degradation *in vivo* makes it a suitable candidate for bone filling. The calcium incorporation, apatite-forming ability, mechanical properties and degradation rate of the hybrid scaffolds were evaluated.

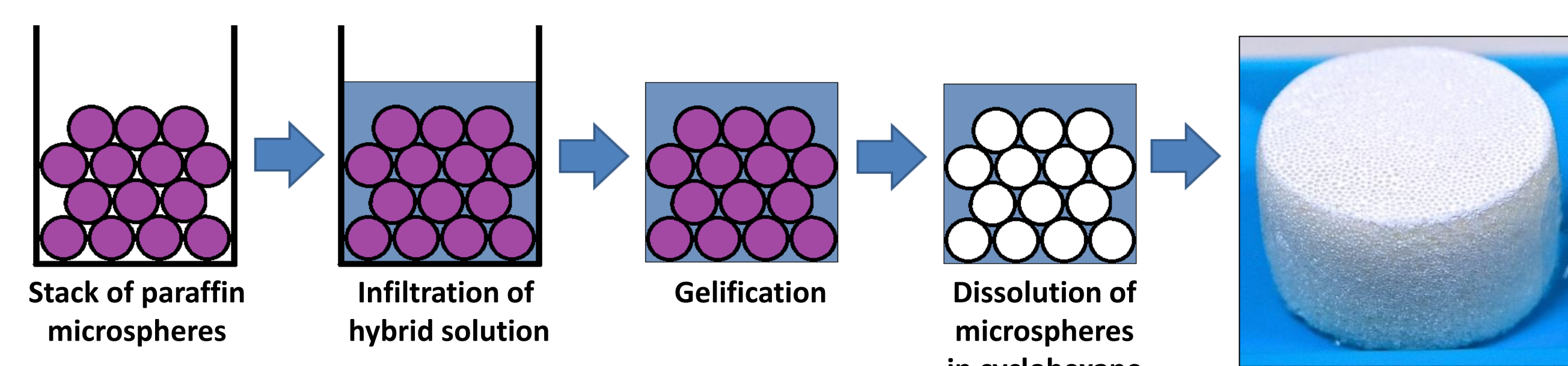
Synthesis of a hybrid solution

The presence of a polymer at an early stage of the sol-gel process forbids thermal treatments. When processing hybrid materials, calcium alkoxide precursors are preferred to salts as they allow effective calcium incorporation even at low temperatures. The composition is 70 wt % PCL – 30 wt % BG.

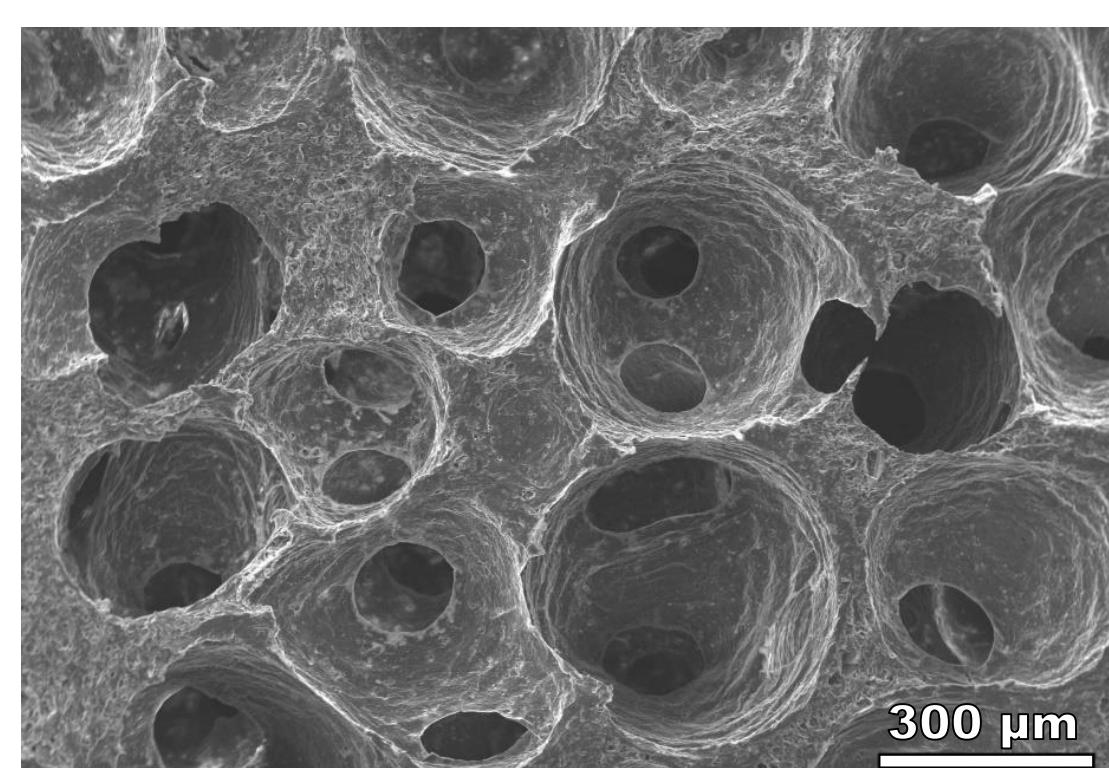


Building scaffolds

The sol-gel foaming process is the most common way to build scaffolds from a sol, but it requires an excess of water to operate. Calcium alkoxides are extremely reactive towards water and its introduction causes a rapid gelation of the sol. Here we found a convenient way of generating a 3D-interconnected macroporous structure at ambient temperature and without adding water. A porogen leaching method is employed.

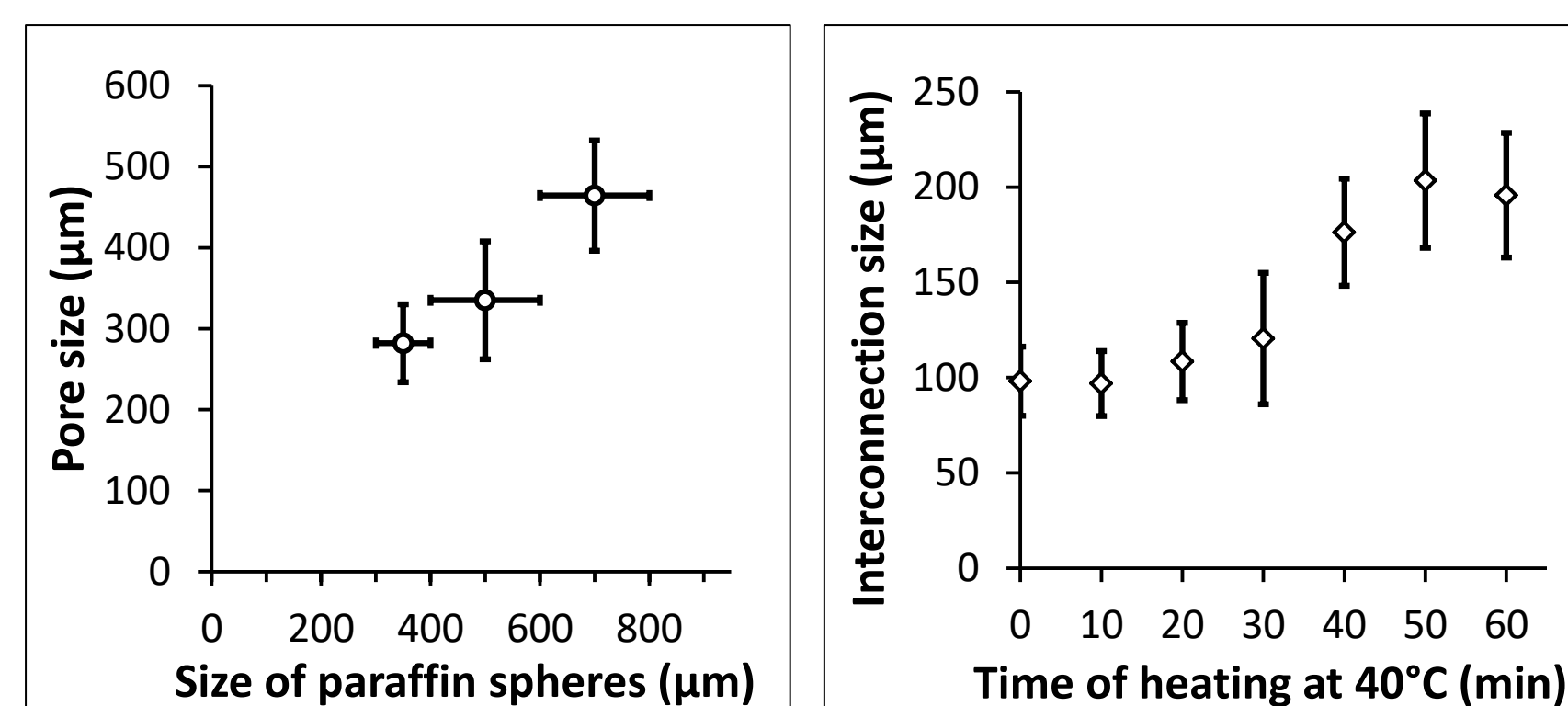


Structure



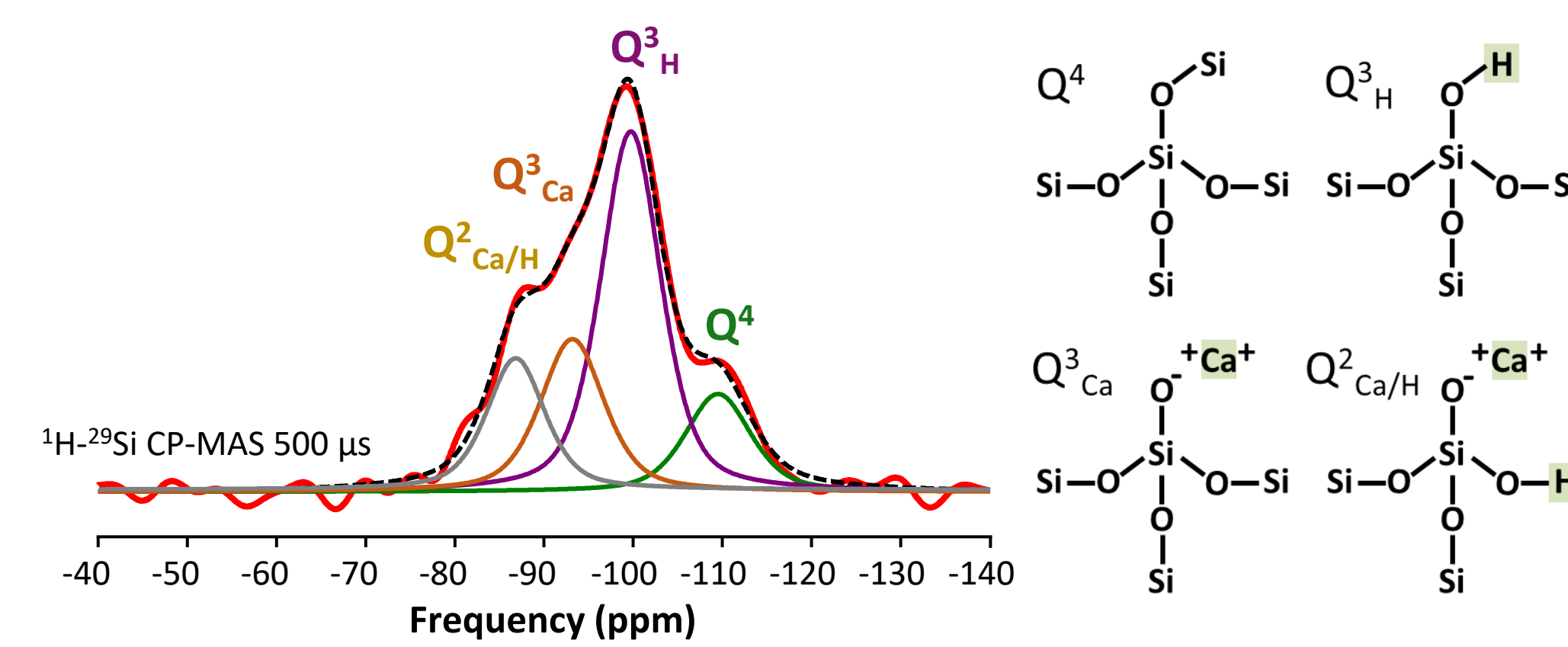
→ Well defined and highly interconnected pores

Control of the porosity



→ Widening of interconnections by partial fusion of paraffin spheres at 40°C
→ Tuneable porosity

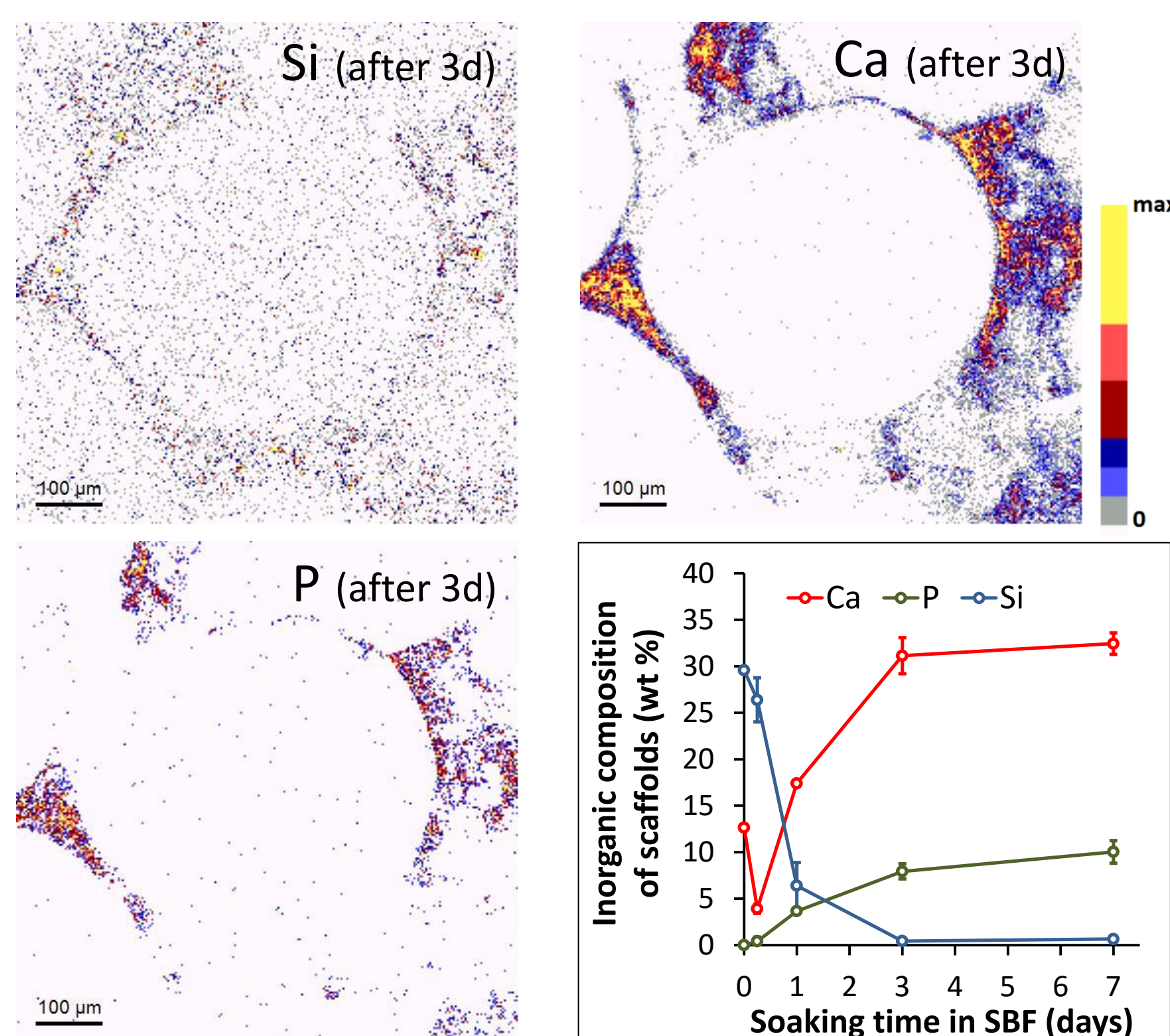
Calcium incorporation : NRM study



Q^3_{Ca} and $Q^2_{Ca/H}$ species ⇒ incorporation of Ca ions

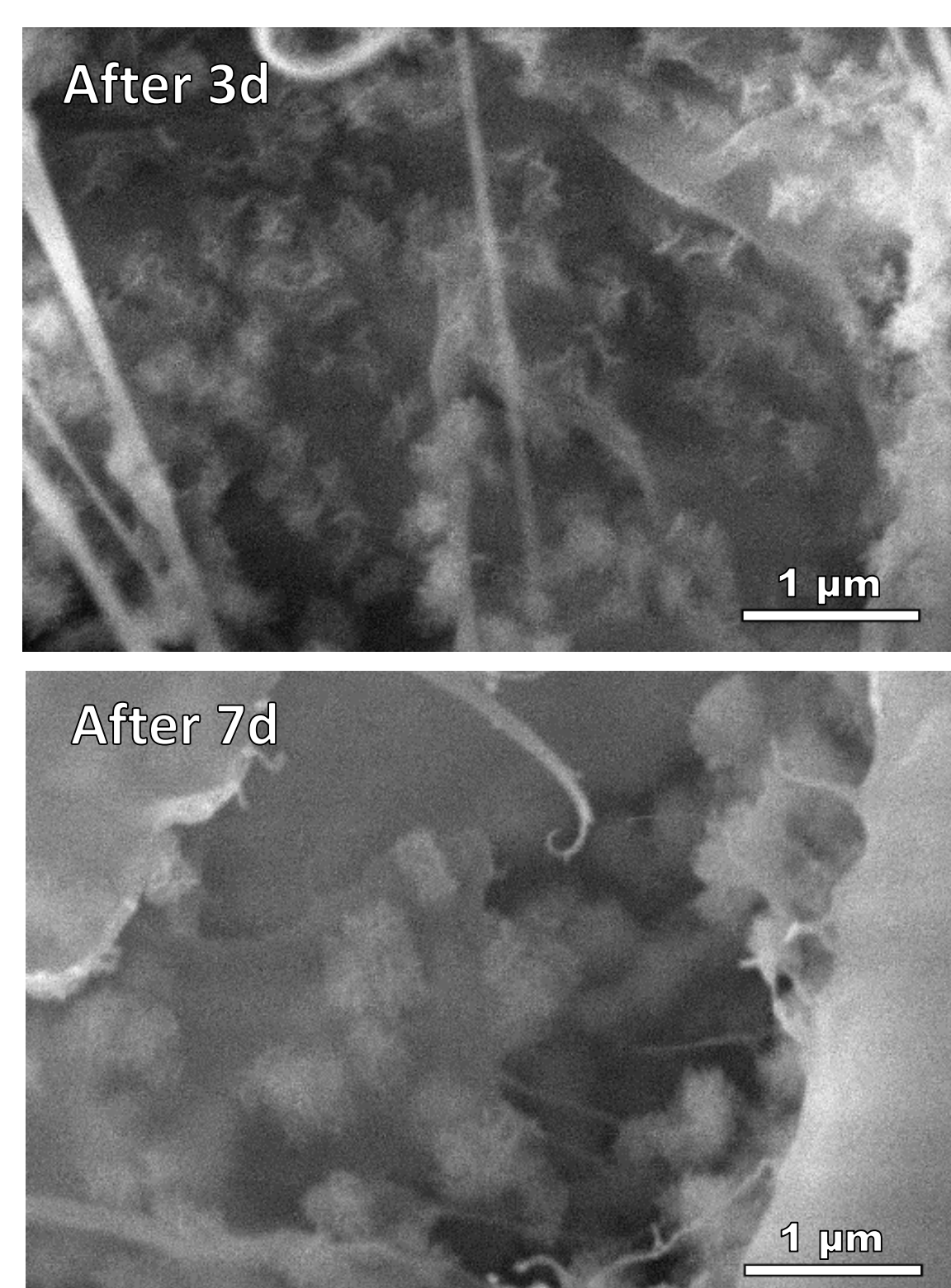
Bioactivity assay : characterisation of hybrid scaffolds after immersion in Simulated Body Fluid (1 mL/mg)

- Quantitative chemical mapping by PIXE



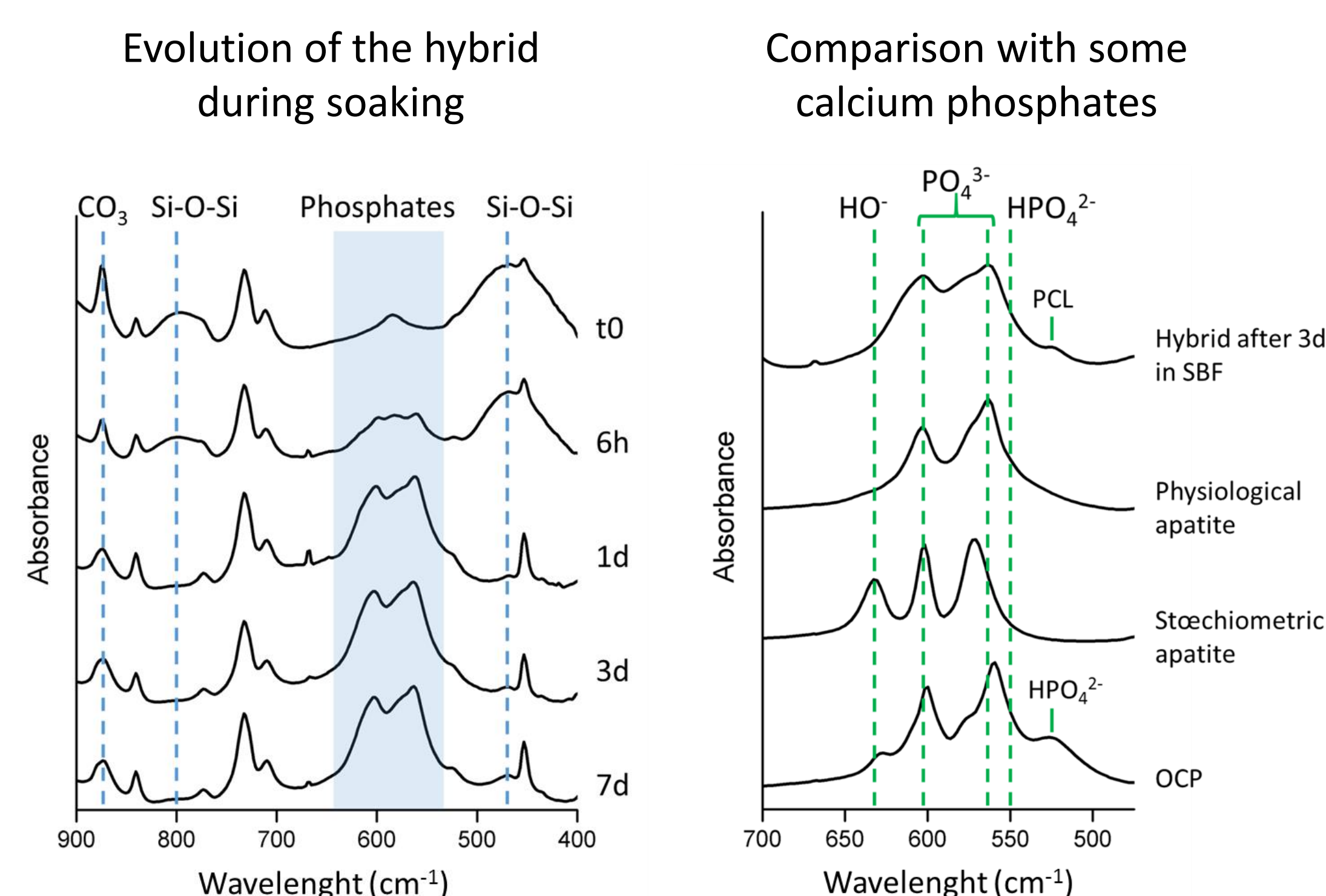
→ After 3 days of immersion in SBF, the inorganic phase of the hybrid turns into a calcium phosphate

- FEI MEB observations



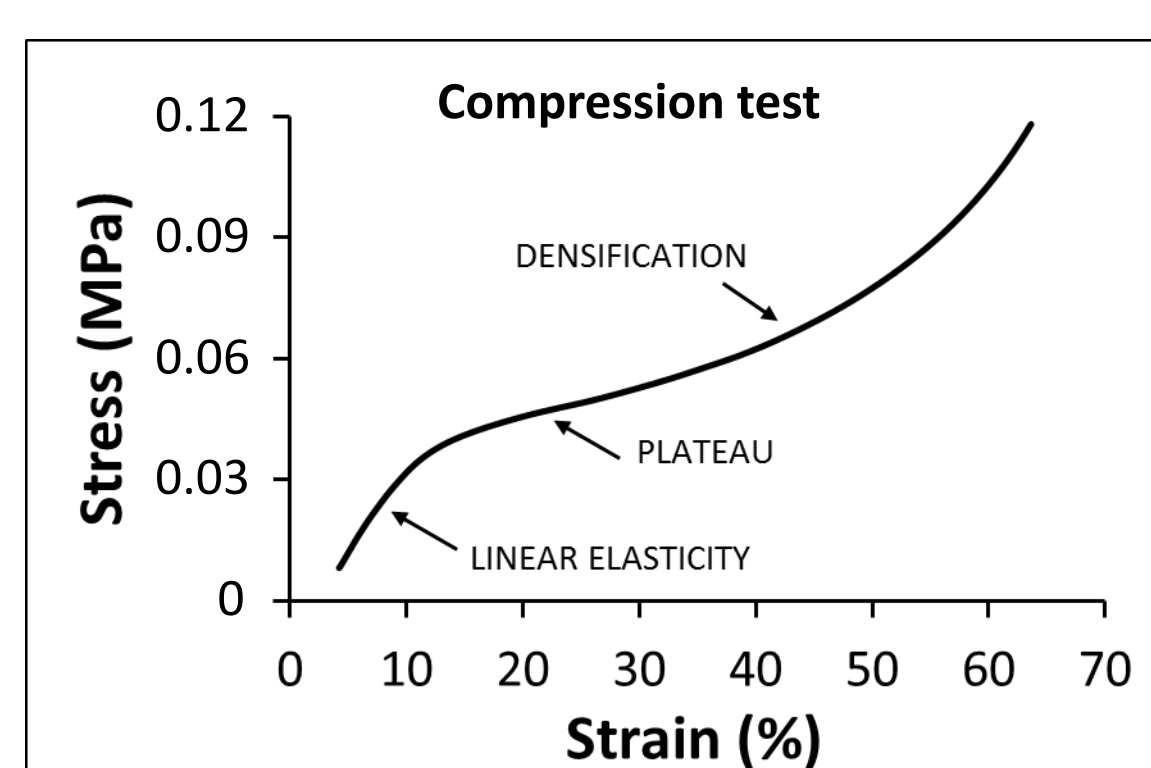
→ Rapid growth of precipitates with a needle shape typical of apatite

- FTIR spectroscopy



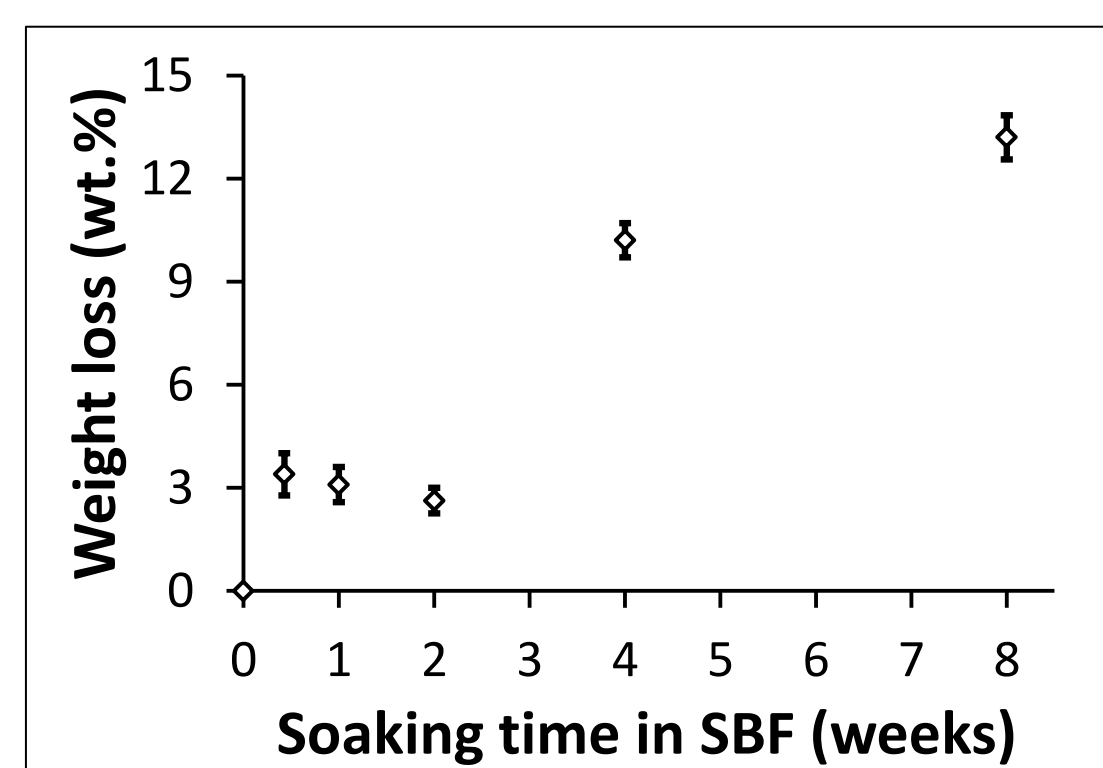
→ The hybrid scaffold quickly forms a calcium phosphate that appears to be a physiological apatite

Mechanical properties



→ PCL effectively introduces plasticity
→ Hybrid scaffolds are highly flexible

Degradation rate in SBF



→ Slow degradation *in vitro*

Conclusion

Despite the difficulties that arise from the synthesis of BG-based hybrid scaffolds, we were able to build BG-PCL hybrid scaffolds with well incorporated calcium. The process is relatively simple and allows the control of both the pore and interconnection sizes. The hybrid induces the rapid precipitation of apatite *in vitro*, which indicates its potential bioactivity. The addition of PCL effectively introduces plasticity and the hybrid scaffolds can be implanted into sites subjected to cyclic loads. Because of their apatite-forming ability, plasticity and slow degradation, BG-PCL hybrid scaffolds appear as promising bone substitutes.