- on the other hand, PxC1 and PxC2 glasses exhibit almost the same type of behavior, but to a much more significant degree: the layers go from 20 µm for phosphorus ratios of 1% and 2% to 40 µm for higher ratios of phosphorus,
- finally, the thickness of the HCA layer for PxA1, PxA3, and PxB3 glasses, increases little or not at all, and remains at approximately 20 µm, while the phosphorus doping of these glasses has considerably improved the nucleation time of HCA.

The glasses for which the doping by phosphorus does not allow increasing the deposit rate of the HCA layer show an increase in the thickness of this layer.

The glasses with the thickest HCA layers are:

P4Cl: 40.32% SiO_2-22.56% CaO-33.12% Na_2O-4% P_2O_5,
P5C2: 42.75% SiO_2-22.325% CaO-29.925% Na_2O-5% P_2O_5.

The bioactivity of the SiO_2-CaO-Na_2O-P_2O_5 system depends on the ratios of Si/Ca and Si/Na and on the phosphorus content.

Three behaviors of bioactivity were highlighted in the quaternary:

- high phosphorus glasses, which form the HCA layer very quickly (6 h) with average thicknesses (20–30 µm): P6A1, P6A3, and P6B3,
- high phosphorus and sodium glasses, which form a thicker HCA layer (40 µm) in slower times (16 h for P4C1, 14 h for P5C2),
- finally, glasses with limited bioactivity: with an HCA formation time of 2 to 3 days and a thickness of around 20 µm. These are the most silica-rich glasses (PxB5).

Bioglass 45S5 develops 30 µm of HCA at 10 days of soaking in SBF. It begins to form the HCA layer at 12 h of soaking. According to the quaternary study, it is closely related to the domain defined by PA1, PA3, and PB3 glasses.

3.2.4 Correlation Between Glass Structure and Bioactivity (Mercier et al., 2011; Pardini, 2007)

The previous study has allowed the influence of silicon, calcium, sodium, and phosphorus ratios on the mechanism of bioactivity to be studied using infrared spectroscopy to detect the formation of apatite. The study has thus allowed the chemical composition of the bioactive glasses to be linked to their bioactivity. In order to better understand this evolution, a study of their structures by NMR spectroscopy was carried out to correlate the structure with the bioactivity of these bioactive glasses.

Figure 3.5 represents the ^{29}Si MAS-NMR spectra of PxB3 ($0 \leq x \leq 6$), PxB5 ($0 \leq x \leq 5$), and PxC1 ($0 \leq x \leq 4$) glasses. All the spectra show that the bioactive glasses of the SiO_2-CaO-Na_2O-P_2O_5 system are highly depolymerized due to the modifying oxides (CaO and Na_2O). Indeed, these glasses are constituted of several silicates of Q^n entities, which ensure the cohesion of the glasses. The PxB5 glasses present predominantly Q^2 and Q^3 entities, whereas Q^1 and Q^2 are the major entities for the PxC1 and PxB3 series.