

CaO and Na<sub>2</sub>O). The two effects of the introduction of phosphorus (complexation of phosphorus by the modifiers and repolymerization of the silicate network) come into play and the silica layer allows the phosphorus-modifier complexes to pass into the SBF. A medium quantity of phosphorus-calcium complexes prepares the crystallization of the HCA in the amorphous CaP layer, developed from SBF. The higher the phosphorus ratio is (Ca is always available), the more P-Ca complex there is in the amorphous CaP layer to crystallize the HCA.

A1 (42% SiO<sub>2</sub>-34.5% CaO-23.5% Na<sub>2</sub>O) is rich in modifiers and especially in calcium. The effect of phosphorus-calcium complexation in the glass is preponderant, which improves the crystallization rate of HCA. In fact, the rapidity of crystallization is greater the more phosphorus is present in the glass.

In conclusion, bioactivity depends on both the phosphorus ratio and the composition of the other compounds of the glasses. The glasses rich in silica (>50 mol%) do not modify their bioactivity in terms of nucleation time of HCA with the addition of phosphorus. Sodium-rich glasses, which are already very bioactive without phosphorus, are also little influenced by the addition of phosphorus. On the other hand, the invert glasses (with a silica ratio ranging from 42 to 50 mol%) and with a Na<sub>2</sub>O ratio lower than 31 mol%, present a layer of crystallized apatite more rapidly if they contain phosphorus. The two most bioactive compositions are P6B3 and P6A3, forming the HCA in 6h. Their molar compositions are respectively:

P6B3: 44.18% SiO<sub>2</sub>-24.91% CaO-24.91% Na<sub>2</sub>O-6% P<sub>2</sub>O<sub>5</sub>,

P6A3: 44.18% SiO<sub>2</sub>-27.73% CaO-22.09% Na<sub>2</sub>O-6% P<sub>2</sub>O<sub>5</sub>.

In comparison, Bioglass 45S5 contains slightly more silica (46.1%) and slightly less phosphorus (2.6%). It is normal that it only develops the HCA layer after 12h of soaking, its phosphorus ratio being lower.

After studying the bioactivity in terms of nucleation time of the HCA layer, the influence of phosphorus on the thickness of this layer after soaking for a fixed time was analyzed.

### 3.2.3.2 Bioactivity in Terms of Thickness

In the case of each of the phosphorus glasses, the evolution of the surface was studied after 10 days of soaking. Only the results obtained for the P5C2 glass are presented. It is the glass which has the greatest amount of phosphorus added to the most bioactive glass of the ternary SiO<sub>2</sub>-CaO-Na<sub>2</sub>O.

P5C2 is part of the group of phosphorus glasses that exhibits the HCA layer after between 10 and 16h (medium bioactivity observed by infrared spectroscopy), whereas C2 of the ternary is the most bioactive (12h).

Table 3.5 shows the thicknesses of the HCA layer of the phosphorus glasses after 10 days of soaking. The values obtained for the corresponding glasses without phosphorus are also noted.