Structural, textural and acid-base properties of carbonates-containing hydroxyapatites

Lishil Silvester[a,b], Jean-François Lamonier[a,b], Rose-Noëlle Vannier[a,b,c], Carole Lamonier[a,b], Mickaël Capron[a,b], Anne-Sophie Mamede[a,b,c], Frédérique Pourpoint[a,b,c], Antonella Gervasini[d] and Franck Dumeignil[a,b,e*]

Supplementary information

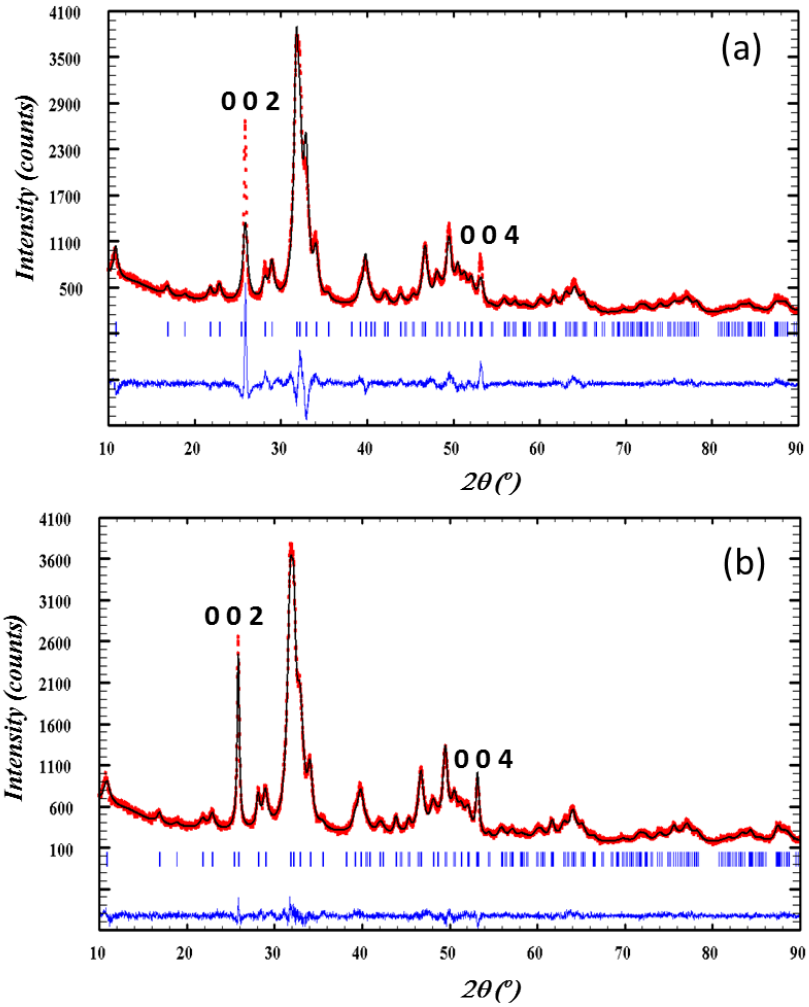


Fig.S1 Calculated X-ray diffraction profiles of Hap D (black lines) compared to experimental data (red dots) showing a poor agreement between calculated and experimental profiles for 002 and 004 Bragg peaks when an isotropic size-broadening model is used (a) and a good agreement when an anisotropic size-broadening model is used (b).

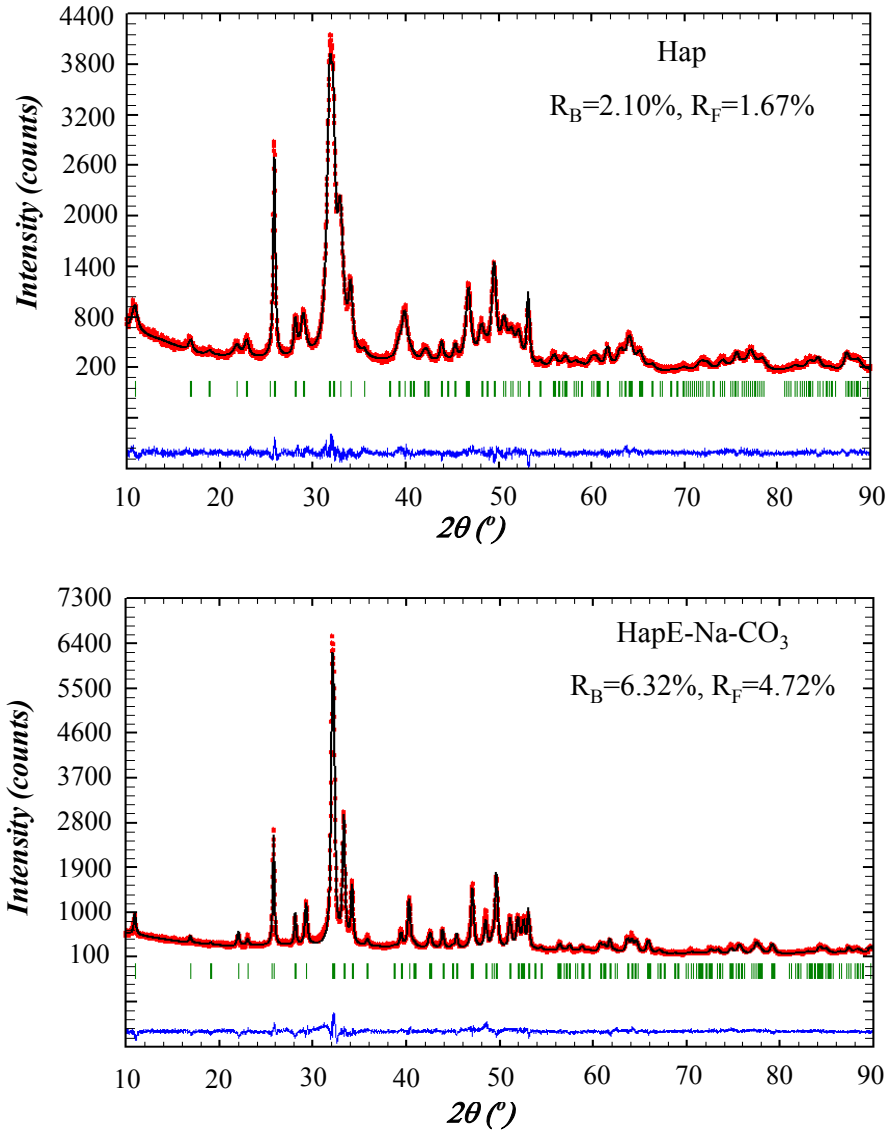


Fig.S2 Calculated X-ray diffraction profiles of Hap and HapE-Na-CO_3 samples (black lines) compared to experimental data (red dots) showing a good agreement between calculated and experimental profiles as shown by the difference in blue. R_B and R_F, the reliability factors, are given to attest the quality of the structure model.

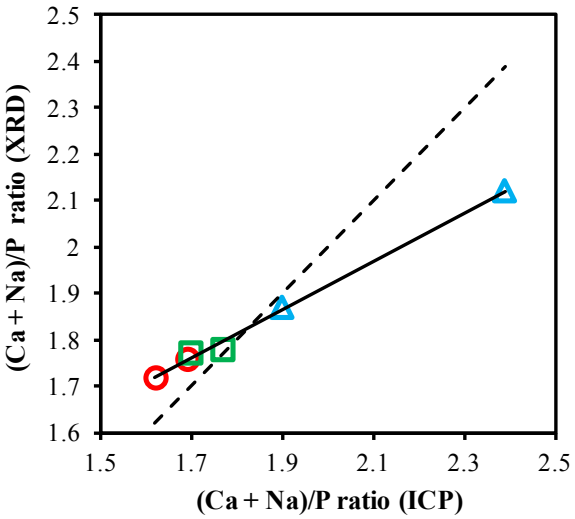
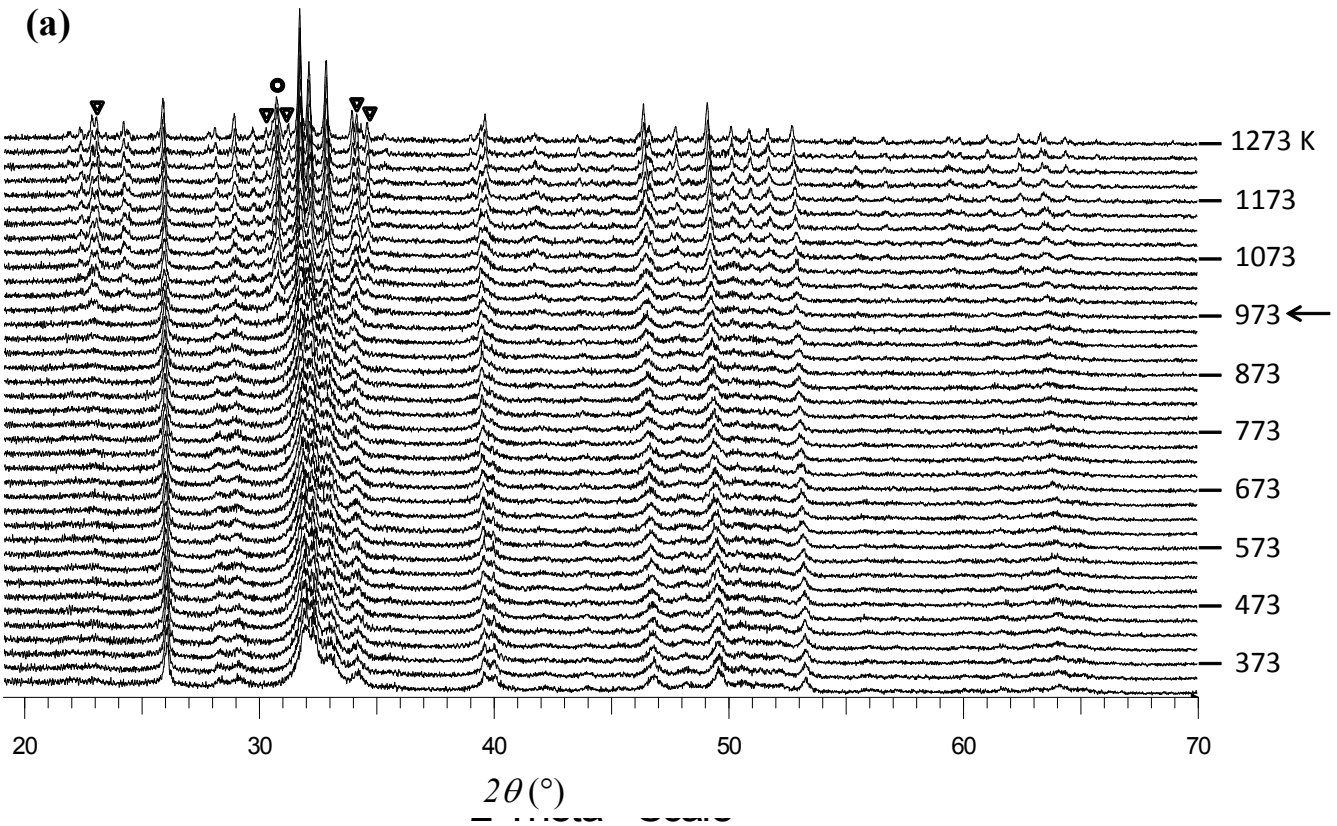


Fig.S3 (Ca + Na)/P ratio calculated from XRD refinement as a function of the ICP (Ca + Na)/P ratio (circles representing HapD and Hap, squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3). The dashed line represents the theoretical perfect correlation (1 to 1).

5



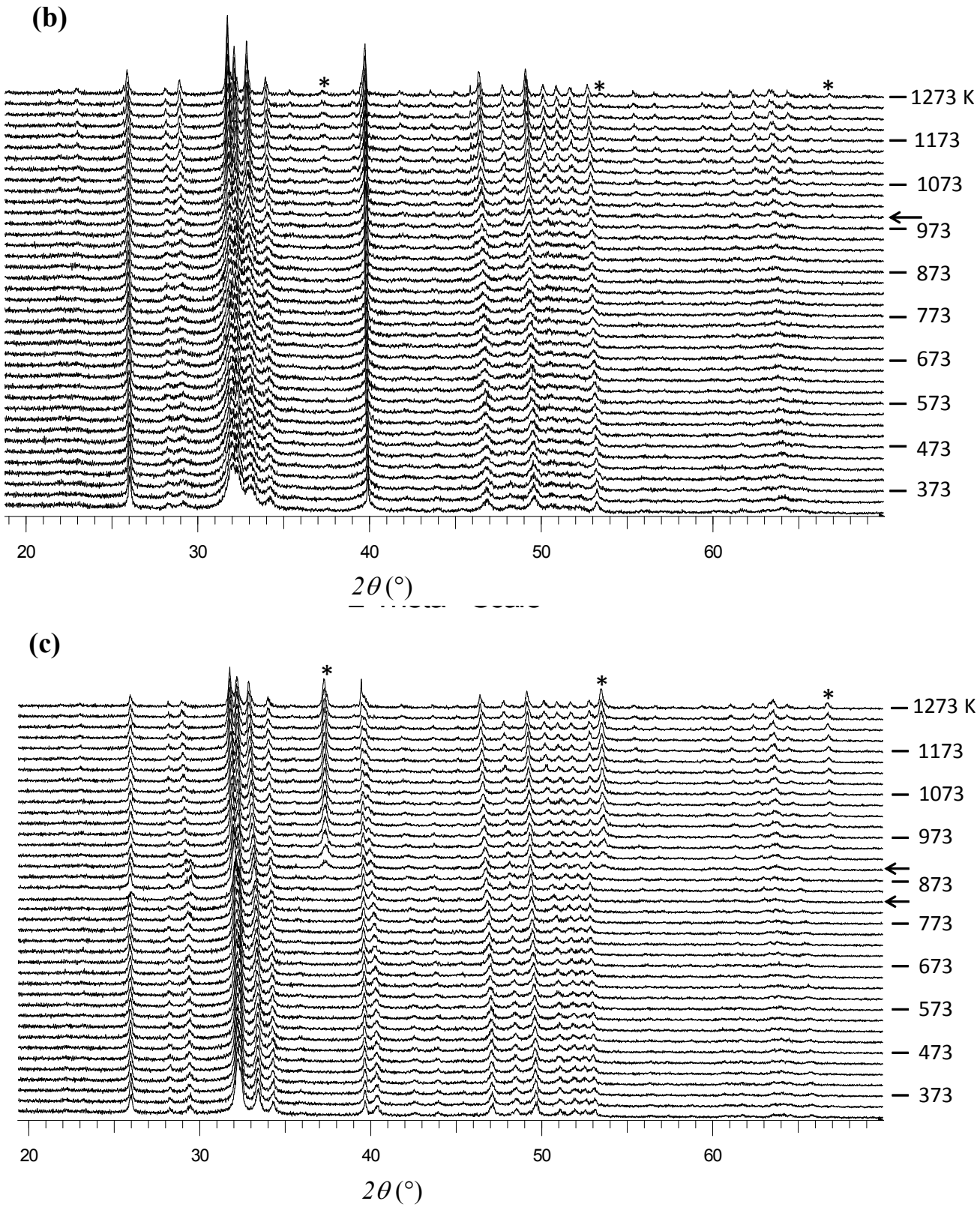


Fig.S4 XRD patterns of *(a)* HapD [arrow pointing the temperature for the appearance of $Ca_3(PO_3)_2$ phases mainly at $2\theta = 30°$ & 34.5°], *(b)* Hap-CO_3 [arrow representing the formation of CaO phase at $2\theta = 37°$] and *(c)* HapE-Na-CO_3 [arrow at 823 K showing the reconstruction of apatite structure and the formation of CaO phase for $2\theta = 37°$, 53.5° & 66.5° at 898 K] collected during temperature increase under air.

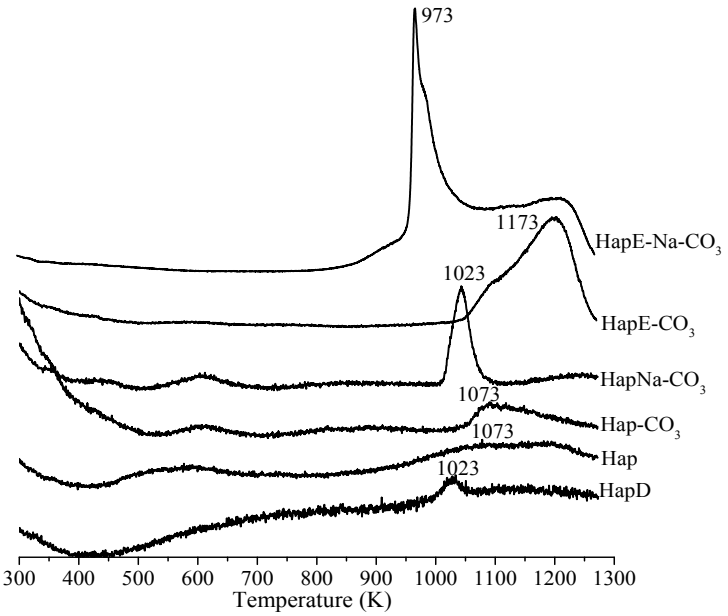


Fig. S5 Derived TGA curves of apatite solids obtained using MS with m/z = 44 showing the CO_2 loss.

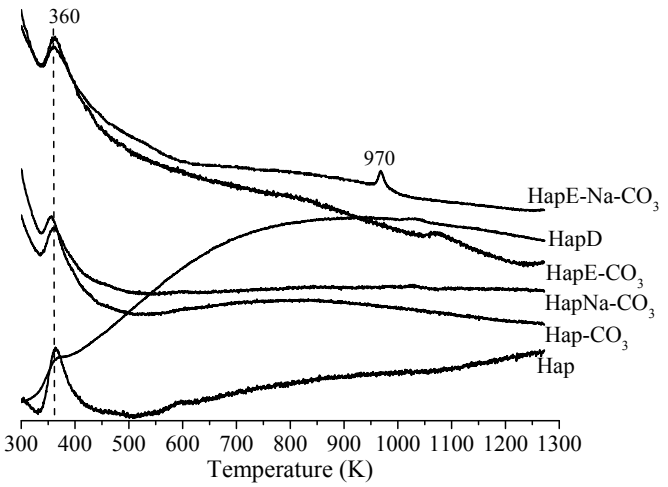


Fig. S6 Derived TGA curves of apatite solids obtained using MS with m/z = 18 showing the H_2O loss.

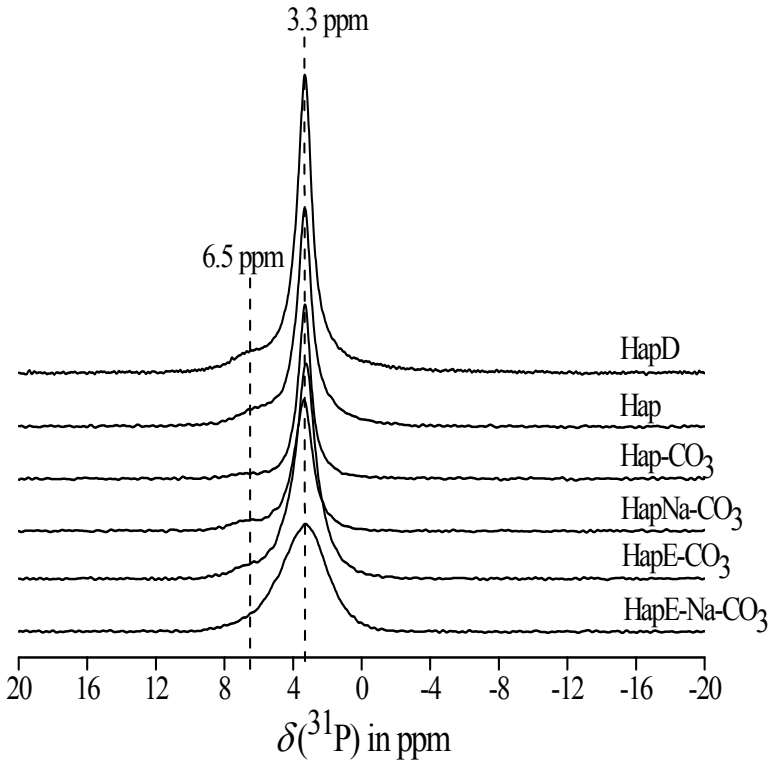


Fig. S7 ^{31}P CP MAS-NMR spectra of the hydroxyapatite solids.

5

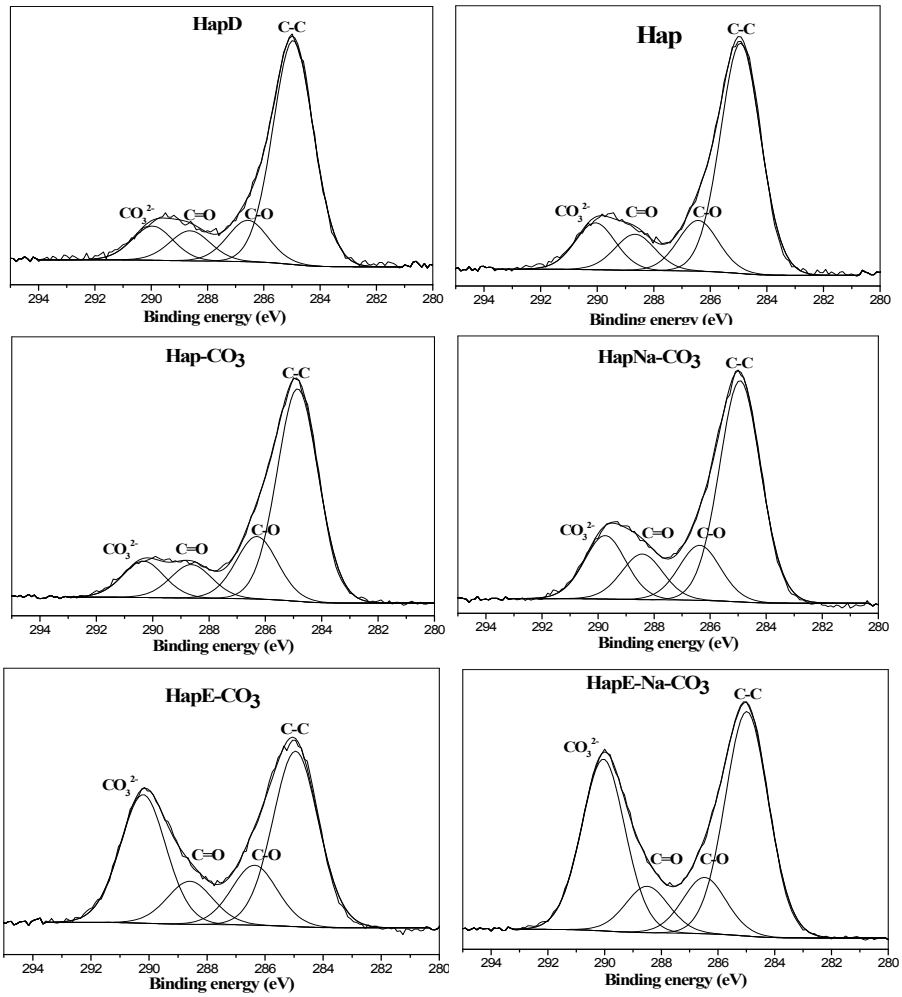


Fig.S8 C1s photopeak of the samples.

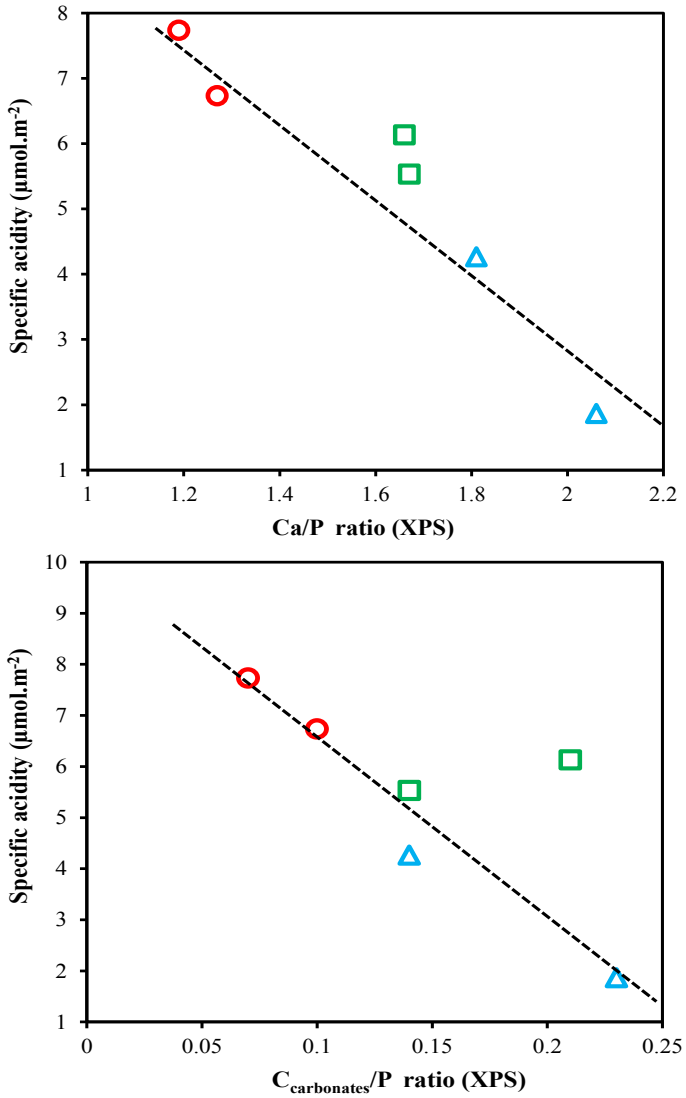


Fig.S9 Specific acidity of the solids as a function of the surface Ca/P and the $C_{carbonate}$/P ratios (circles representing HapD and Hap, squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).