

## Electronic Supplementary Information

### *In situ* study of thermal crystallization of amorphous calcium phosphates

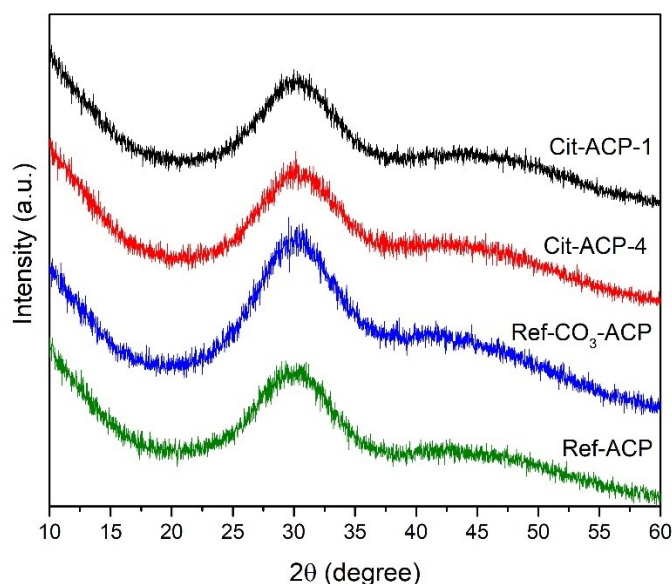
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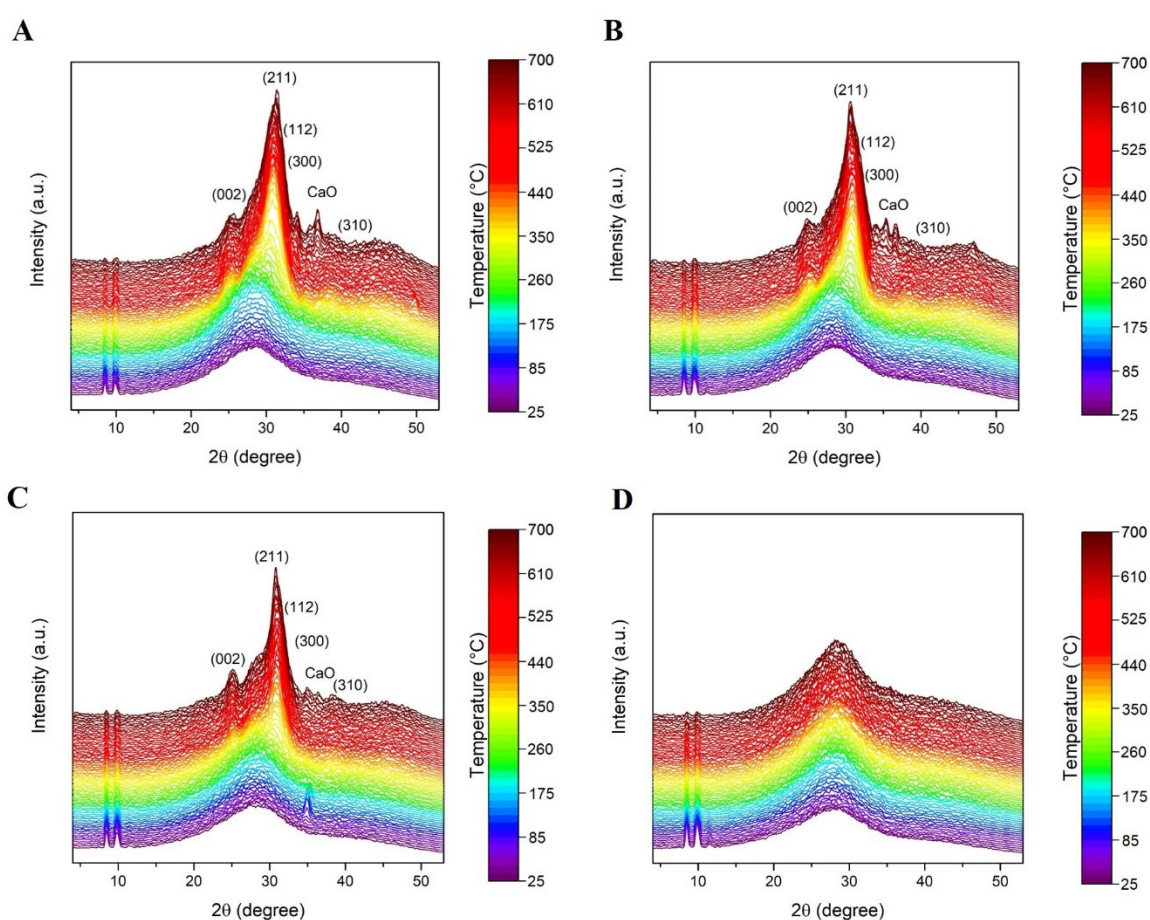
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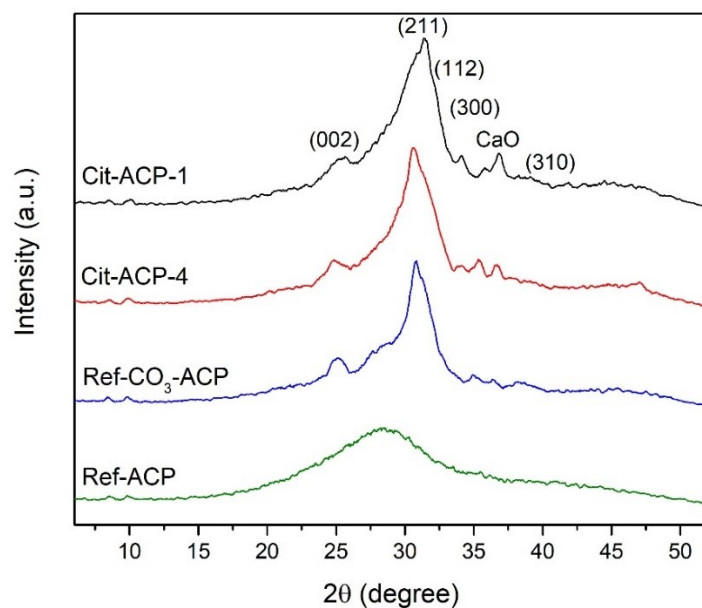


**Supplementary Figure 1.** PXRD patterns of ACP samples.

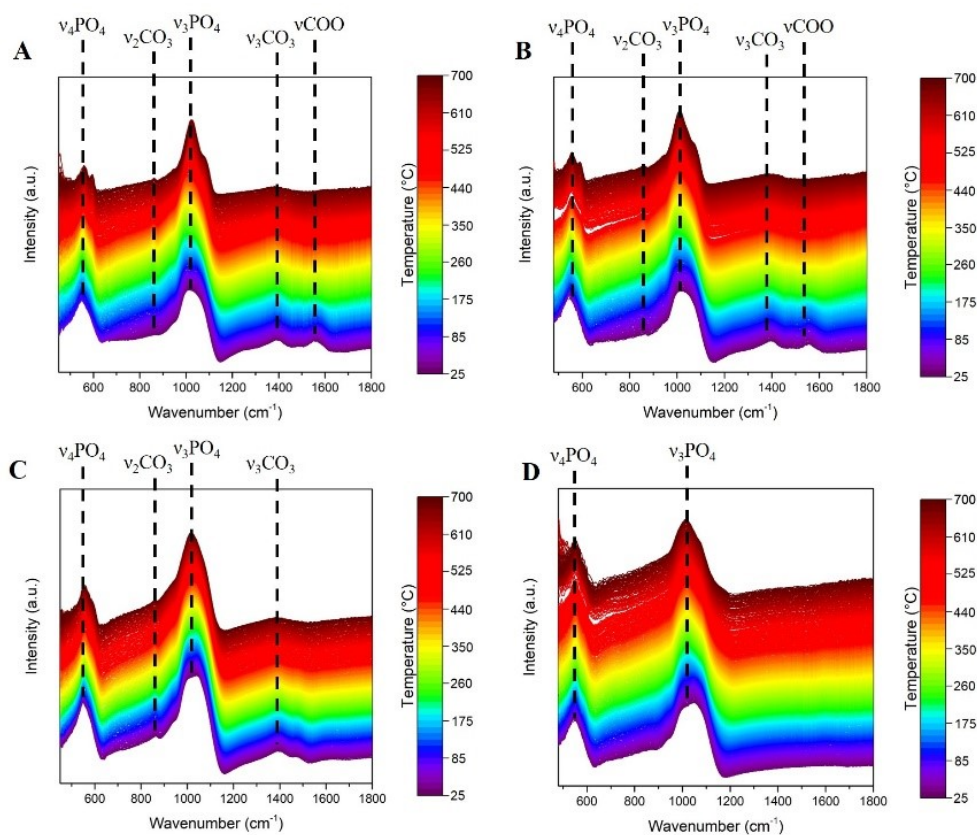
**Supplementary Table 1.** Chemical composition and specific surface area ( $SSA_{BET}$ ) of ACP samples

Sample	Ca (wt%) <sup>a</sup>	P (wt%) <sup>a</sup>	Citrate (wt%) <sup>b</sup>	Carbonate (wt%) <sup>b</sup>	Ca/P (mol)	$SSA_{BET}$ ( $m^2 g^{-1}$ ) <sup>c</sup>
Cit-ACP-4	29.9±0.7*	13.6±0.3*	1.9±0.2*	3.7±0.4*	1.70±0.02*	200±20*
Cit-ACP-1	28.0±0.6*	12.7±0.2*	1.8±0.2*	3.2±0.3*	1.70±0.04*	309±31*
Ref-ACP	27.5±0.4	15.8±0.3	-	0.3±0.1	1.35±0.01	52±5
Ref-CO <sub>3</sub> -ACP	30.0±1.3	14.0±0.6	-	3.4±0.3	1.66±0.01	128±13

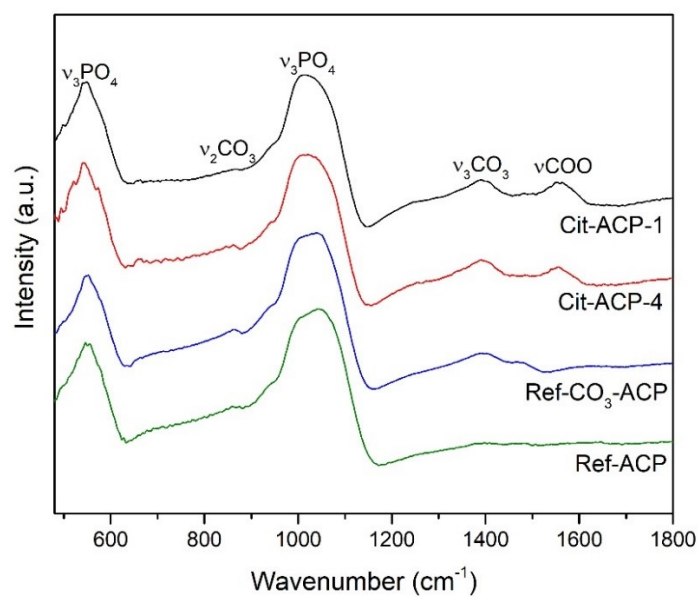
<sup>a</sup>Quantified by ICP-OES; <sup>b</sup>Quantified by TGA; <sup>c</sup>Calculated from BET N<sub>2</sub> adsorption. \*Data from Iafisco et al. [1]**Supplementary Figure 2.** Stack plots of EDXRD patterns, collected as a function of heating temperature of (A) Cit-ACP-1, (B) Cit-ACP-4, (C) Ref-CO<sub>3</sub>-ACP, (D) Ref-ACP. The two peaks at ca. 10° 2θ are due to instrumental contribution and correspond to the anisotropic K<sub>α</sub> and K<sub>β</sub> fluorescence signals of W anode tube.



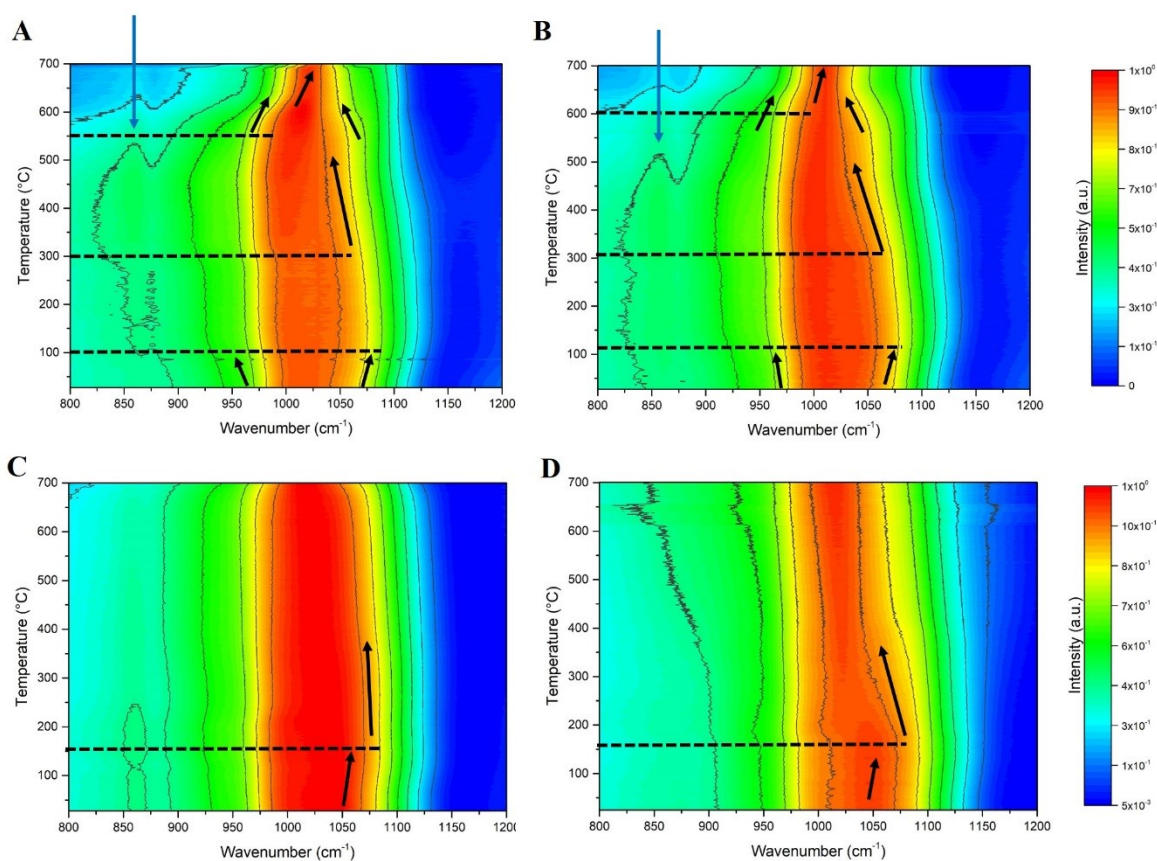
**Supplementary Figure 3.** HT-EDXRD patterns of ACP samples at 700°C. The two small peaks at ca. 10° 2θ are due to instrumental contribution and correspond to the anisotropic  $K_{\alpha}$  and  $K_{\beta}$  fluorescence signals of W anode tube.



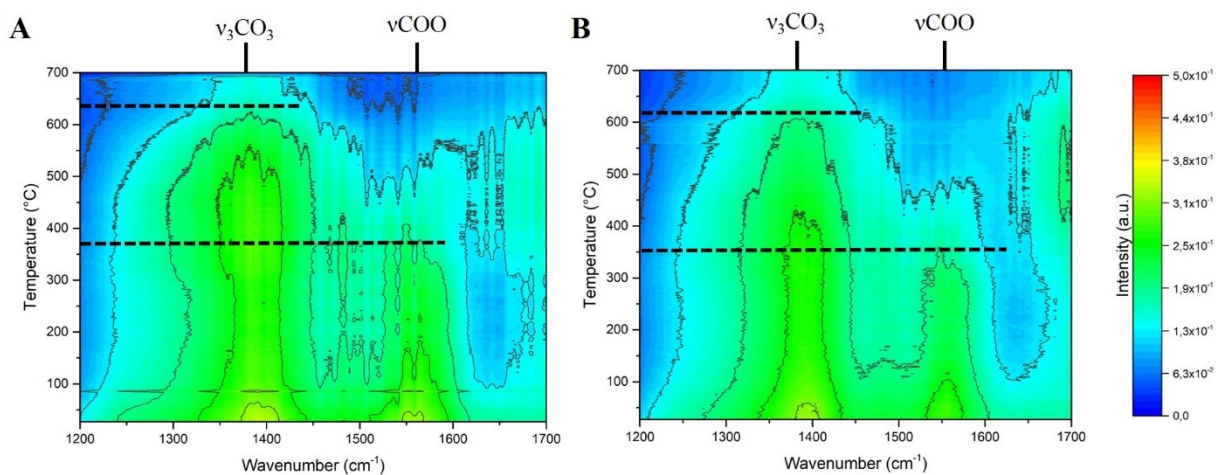
**Supplementary Figure 4.** Stack plot of normalized TD-FTIR spectra, collected as a function of heating temperature of (A) Cit-ACP-1, (B) Cit-ACP-4, (C) Ref-CO<sub>3</sub>-ACP, (D) Ref-ACP.



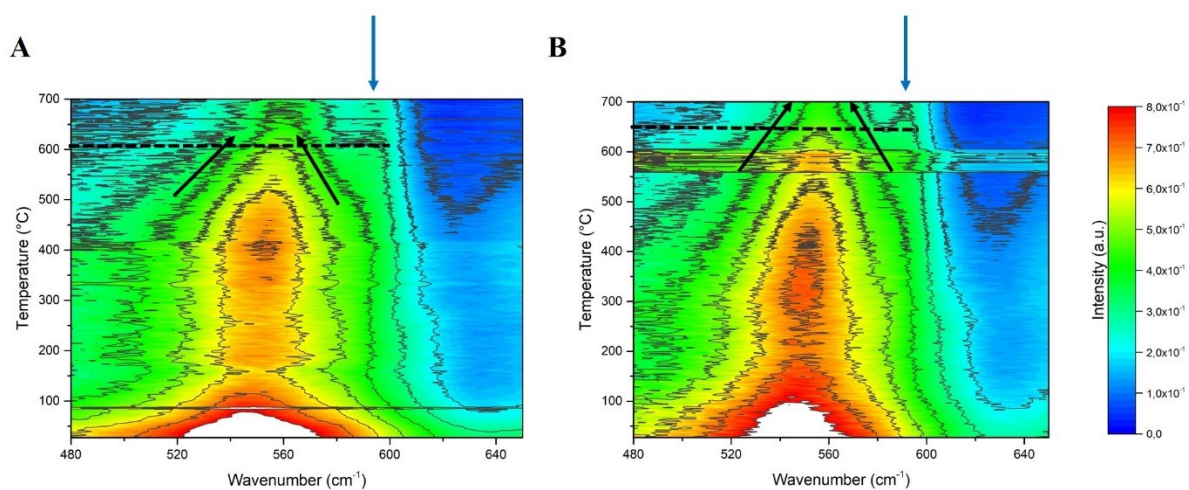
**Supplementary Figure 5.** TD-FTIR spectra of ACP samples at 27°C.



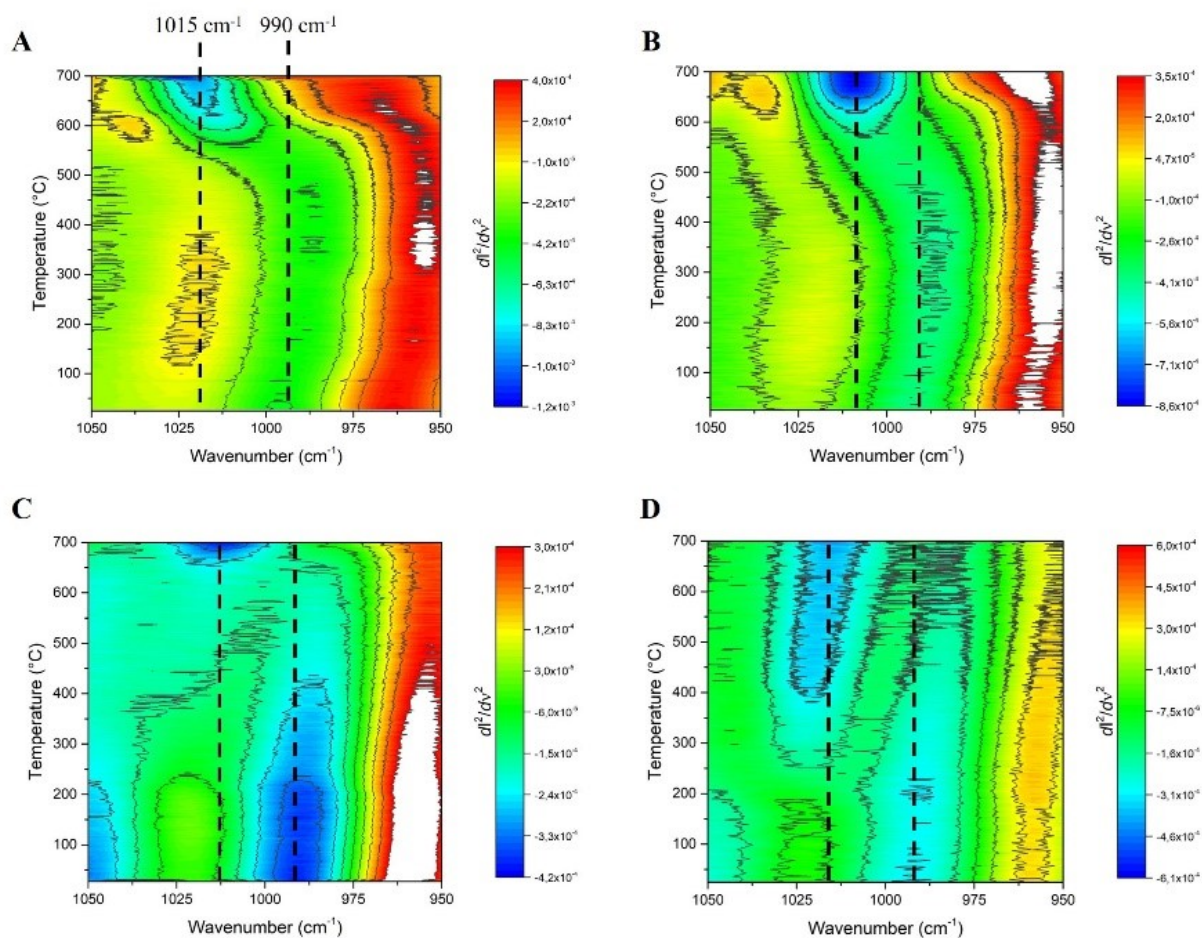
**Supplementary Figure 6.** Enlargement of TD-FTIR contour plots as a function of temperature in the range 800-1200  $\text{cm}^{-1}$  for (A) Cit-ACP-1, (B) Cit-ACP-4, (C) Ref-CO<sub>3</sub>-ACP, and (D) Ref-ACP. The black arrows highlight the peak shifts and change in FWHM. The blue arrows point the 865  $\text{cm}^{-1}$   $\nu_2\text{CO}_3$  peak. The dotted lines highlight initial or final temperatures of peak shifts.



**Supplementary Figure 7.** Enlargement of TD-FTIR contour plots as a function of temperature in the range 1200-1700  $\text{cm}^{-1}$  for (A) Cit-ACP-1, and (B) Cit-ACP-4. The dotted line highlight temperatures of  $\nu_3\text{CO}_3$  and  $\nu\text{COO}$  disappearance.



**Supplementary Figure 8.** Enlargement of TD-FTIR contour plots as a function of temperature in the range 480-650 $\text{cm}^{-1}$  for (A) Cit-ACP-1, and (B) Cit-ACP-4. The black arrows highlight the peak shifts and change in FWHM. The blue arrows point the 595  $\text{cm}^{-1}$   $\nu_4\text{PO}_4$  peak. The dotted line highlight the initial temperatures of  $\nu_4\text{PO}_4$  appearance.



**Supplementary Figure 9.** Enlargement of second derivative of TD-FTIR contour plots as a function of temperature in the range 950-1050 cm<sup>-1</sup> for (A) Cit-ACP-1, and (B) Cit-ACP-4. The dotted lines highlight the negative peaks at 990 and 1015 cm<sup>-1</sup>.

## References

1. Iafisco, M., et al., *Fluoride-doped amorphous calcium phosphate nanoparticles as a promising biomimetic material for dental remineralization*. Scientific Reports, 2018. **8**(1): p. 17016.