

## Supplementary Information

for

### Crystallization of Calcium Carbonate and Calcium Phosphate Phases in Silica Hydrogel: Morphological and Compositional Characterization

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**Table S1.** Raman band assignment for the core

Core (Ca/P ~ 1.75)				
cm-1	Type	Assignement	Phase	Ref
410	sh	O-P-O bending modes (v2) of the HPO4 2- group	OCP	Koutsopoulos 2002
430	p	O-P-O bending modes (v2) of the PO4 group	OCP	Koutsopoulos 2002
		Doubly degenerate bending mode (v2) of the PO4 group (O-P-O bond)	HAP	
447	sh	O-P-O bending modes (v2) of the PO4 group	OCP,	Koutsopoulos 2002
		Doubly degenerate bending mode (v2) of the PO4 group (O-P-O bond)	HAP	
491	p	??	??	
545	p	Bending mode v4 of the HPO4 2- group	OCP	
588	p	P-O and O-P-O stretching and bending modes (v4) of the PO4 group,	OCP	Koutsopoulos 2002
610	sh	Triply degenerate bending mode (v4) of the PO4 group (O-P-O bond)	HAP	
824	w	??	??	??
862	w	CO3 symmetric bending (v2)	Arg	
881	w	P-OH stretching mode (v1) of the HPO4 2- group	OCP	Koutsopoulos 2002
914				
925				
960	p	P-O stretching mode (v1) of the PO4 group,	OCP,	Koutsopoulos 2002
		Totally symmetric stretching mode (v1) of the tetrahedral PO4 group (P-O bond)	HAP	
1000	p	C-H Bonds		Awonusi et al., 2007
1007	p	P-O stretching mode (v3) of the HPO4 2- group	OCP	Koutsopoulos 2002
1043	bp	Triply degenerate asymmetric stretching mode (v3) of the PO4 group (P-O bond)	HAP	Koutsopoulos 2002
1070	sh	CO3 symmetric stretching (v1)	HAP	Awonusi et al. 2007
1074	p	Triply degenerate asymmetric stretching mode (v3) of the PO4 group (P-O bond)	HAP	Koutsopoulos 2002
1079	sh	CO3 symmetric stretching (v1)	Vtr	
1451	bp	CO3 antisymmetric stretching (v3)	Arg	
2876	sh	C-H bonds		
2935	bp			

**Table S2.** Raman band assignment for the fibres

Fibers (Ca/P ~1.7)				
cm-1	Type	Assignment	Phase	Ref
414	Sh	O-P-O bending modes (v2) of the HPO4 2- group	OCP	Koutsopoulos 2002
427	P	O-P-O bending modes (v2) of the PO4 group	OCP	Koutsopoulos 2002
434	P	Doubly degenerate bending mode (v2) of the PO4 group (O-P-O bond)	HAP	Koutsopoulos 2002
450	P	O-P-O bending modes (v2) of the PO4 group	OCP,	Koutsopoulos 2002
		Doubly degenerate bending mode (v2) of the PO4 group (O-P-O bond)	HAP	
481	P	??	??	
492	P	??	??	
540	BP	Bending mode v4 of the HPO4 2- group	OCP	Koutsopoulos 2002
610	P	P-O and O-P-O stretching and bending modes (v4) of the PO4 group,	OCP	Koutsopoulos 2002
		Triply degenerate bending mode (v4) of the PO4 group (O-P-O bond)	HAP	Koutsopoulos 2002
880	BP	P-OH stretching mode (v1) of the HPO4 2- group	OCP	Koutsopoulos 2002
923	P			
959	P	P-O stretching mode (v1) of the PO4 group	OCP	Koutsopoulos 2002
967	Sh			
1011	BP	P-O stretching mode (v3) of the HPO4 2- group	OCP	Koutsopoulos 2002
1037	P	Triply degenerate asymmetric stretching mode (v3) of the PO4 group (P-O bond)	HAP	Koutsopoulos 2002
1049	P	P-O stretching mode (v3) of the PO4 group	OCP	Koutsopoulos 2002
1056	P	Triply degenerate asymmetric stretching mode (v3) of the PO4 group (P-O bond)	HAP	Koutsopoulos 2002
1080	BP	P-O stretching mode (v3) of the PO4 group	OCP	Koutsopoulos 2002

**Table S3.** Raman band assignment for the rim

Rim (Ca/P unreliable)				
cm-1	Type	Assignment	Phase	Ref
427	P	O-P-O bending modes (v2) of the PO4 group	OCP	Koutsopoulos 2002
445	P	O-P-O bending modes (v2) of the PO4 group	OCP	Koutsopoulos 2002
		Doubly degenerate bending mode (v2) of the PO4 group (O-P-O bond)	HAP	Koutsopoulos 2002
573	P	P-O and O-P-O stretching and bending modes (v4) of the PO4 group	OCP,	Koutsopoulos 2002
590		Triply degenerate bending mode (v4) of the PO4 group (O-P-O bond)	HAP	Koutsopoulos 2002
607				
856	P	CO3 symmetric bending (v2)	Arg	
865				
960	P	P-O stretching mode (v1) of the PO4 group,	OCP,	Koutsopoulos 2002
		Totally symmetric stretching mode (v1) of the tetrahedral PO4 group (P-O bond)	HAP	
1032	BP	Triply degenerate asymmetric stretching mode (v3) of the PO4 group (P-O bond)	HAP	Koutsopoulos 2002
1046				
1056				
1070	BP	CO3 symmetric stretching (v1)	HAP	Awonusi et al. 2007
1075	BP	Triply degenerate asymmetric stretching mode (v3) of the PO4 group (P-O bond)	HAP	Koutsopoulos 2002
1452	BP	CO3 antisymmetric stretching (v3)	Arg	
2885	P	C-H bonds		
2936	P			
544	BP	Bending mode v4 of the HPO4 2- group	OCP	Koutsopoulos 2002

**Table S4.** EMP data

	Core			Intermediate area							Rim	
%Ox	126	127	129	Fibers	Fibers	116	118	119	121	122	145	143
CaO	19.773	18.266	19.315	33.702	33.958	43.171	42.008	43.547	42.45	41.973	38.341	44.07
P2O5	17.65	17.589	17.451	17.893	17.609	40.161	39.462	39.022	41.007	39.964	32.336	40.033
Total	37.423	35.855	36.766	86.811	92.019	83.332	81.47	82.569	83.457	81.937	70.677	84.103
%Atm												
Ca	14.132	13.055	13.804	24.087	24.270	30.854	30.023	31.123	30.339	29.998	27.402	31.497
P	7.703	7.676	7.616	7.809	7.685	17.527	17.222	17.030	17.896	17.441	14.112	17.471
Ca/P	1.835	1.701	1.813	3.085	3.158	1.760	1.743	1.828	1.695	1.720	1.942	1.803