A ^{43}Ca NMR perspective on octacalcium phosphate and its hybrid derivatives

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Table S1. *Natural abundance* ^{43}Ca MAS NMR experimental parameters for OCP and OCP intercalated hybrids (D1: recycle delay, NS: number of scans).

Table S2. *Selected Ca…H and Ca…P distances for all eight crystallographically inequivalent calcium sites (noted Ca_n, with n = 1, 3, 5, 7, 9, 11, 13, 15) in OCP (distances are given in Å, geometry optimized at the DFT level)). In blue: the shortest Ca…H distance, in yellow: the shortest Ca…P distance.*

Table S3. *Selected P…Ca distances for all phosphorus sites (P1 to P6) in OCP (distances are given in Å). The P…Ca distances are highlighted in yellow.*

Figure S1. (a) ^{43}Ca{^{1}H} REDOR (with ^{43}Ca detection) and (b) ^{31}P{^{43}Ca} CP REAPDOR (with ^{31}P detection) pulse sequences. L_0 corresponds to the number of recoupling loops. T_R corresponds to the rotor period.

Figure S2. ^{43}Ca{^{1}H} REDOR experiment for *HAp (20.0 T, 14 kHz MAS). Blue spectrum (S_0): ^{43}Ca spin echo, green spectrum (S): REDOR dephased echo, for 24 recoupling loops. L_0 is defined in Figure S1a.

Figure S3. ^{31}P{^{43}Ca} CP REAPDOR experiment for *HAp (20.0 T; 14 kHz MAS). Blue spectra (S_0): ^{31}P CP-echo, with echo delays increasing from bottom to top, green spectra (S): REAPDOR dephased echoes, for 10, 20, 40 and 60 recoupling loops L_0 (as defined in Figure S1b).

Figure S4. ^{31}P{^{43}Ca} CP REAPDOR experiment for *OCP (20.0 T; 14 kHz MAS). Blue spectrum (S_0): ^{31}P CP-echo; green spectrum (S): REAPDOR dephased echo for 20 recoupling loops (see Figure S1b for the definition of L_0). We mention that the ^{31}P CP spectrum presented here is somewhat different from the Bloch-decay spectrum presented in: Y. Li, D.G. Reid, M.J. Duer, J.C.C. Chan, *Solid State Nuclear Magnetic Resonance* **2018**, *95*, 1. Part of the differences are possibly due to isotropic ^{2}J(^{43}Ca-^{31}P) couplings (few Hz) and the large number of ^{43}Ca neighbors for each of the phosphorus sites.

Figure S5. GIPAW calculated $\delta_{iso.}(^{43}Ca)$ for all calcium sites in OCP (red dots) and OCP-citrate (blue dots) models *vs* the average Ca-O distance (with 2 different cut-offs, 2.7 and 2.9 Å). Three groups of ^{43}Ca isotropic chemical shifts are highlighted by red ovals (above 20 ppm, between 0 and 10 ppm, and below 0 ppm).

Figure S6. Analysis of the most extreme *calculated* $\delta_{iso.}(^{43}Ca)$ values calculated for the five OCP-citrate models, showing the corresponding calcium local environments (including Ca…X distances). Ca: green, O: red, P: blue, C: black, H: light pink.

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Sample	**Signal enhancement**	**D1**	**NS**	**Total experimental time**
OCP	RAPT	0.5 s	137864	~ 20h
OCP-citrate	multi-DFS	0.5 s	65500	~ 9h
OCP-succinate	multi-DFS	0.5 s	65500	~ 9h
OCP-formate	multi-DFS	0.5 s	65500	~ 9h
OCP-adipate	multi-DFS	0.5 s	65500	~ 9h
OCP-citrate/formate	multi-DFS	0.5 s	65500	~ 9h

Table S2. *Selected Ca…H and Ca…P distances for all 8 crystallographically inequivalent calcium sites (noted Ca_n, with n = 1, 3, 5, 7, 9, 11, 13, 15) in OCP (distances are given in Å). In blue: the shortest Ca…H distance, in yellow: the shortest Ca…P distance (geometry optimized at the DFT level).*

Ca1	O5	2.37688	Ca3	O5	2.35313	Ca5	O21	2.24794	Ca7	O26	2.30977	Ca9	O1	2.31938
Ca1	O14	2.41387	Ca3	O53	2.35409	Ca5	O25	2.35885	Ca7	O34	2.34521	Ca9	O47	2.32703
Ca1	O43	2.42531	Ca3	O14	2.35883	Ca5	O55	2.43867	Ca7	O20	2.40317	Ca9	O23	2.33833
Ca1	O15	2.45129	Ca3	O47	2.37121	Ca5	O35	2.44170	Ca7	O8	2.42810	Ca9	O41	2.39154
Ca1	O53	2.45132	Ca3	O43	2.44471	Ca5	O57	2.48579	Ca7	O56	2.49011	Ca9	O49	2.48853
Ca1	O47	2.52724	Ca3	O15	2.51202	Ca5	O37	2.51845	Ca7	O40	2.51812	Ca9	O51	2.55735
Ca1	O2	2.64489	Ca3	O9	2.61186	Ca5	H17	2.91355	Ca7	O22	2.63194	Ca9	H5	2.73423
Ca1	O51	2.76049	Ca3	O49	3.00357	Ca5	O7	2.95994	Ca7	H24	2.91836	Ca9	O13	2.75038
Ca1	O11	2.85428	Ca3	P4	3.13854	Ca5	H15	2.99606	Ca7	P11	3.08482	Ca9	H3	2.89099
Ca1	P7	3.16379	Ca3	O24	3.15961	Ca5	H13	3.10889	Ca7	H22	3.28359	Ca9	P2	3.12185
Ca1	P4	3.22671	Ca3	P2	3.28112	Ca5	H19	3.12218	Ca7	O50	3.35963	Ca9	O44	3.27054
Ca1	P2	3.23046	Ca3	P7	3.31991	Ca5	O18	3.18256	Ca7	P5	3.43808	Ca9	P7	3.36127
Ca1	H6	5.39327	Ca3	H11	5.10854	Ca5	P3	3.28372	Ca7	P8	3.45711	Ca9	P4	3.42814
						Ca5	P11	3.44455						
						Ca5	P5	3.66854						

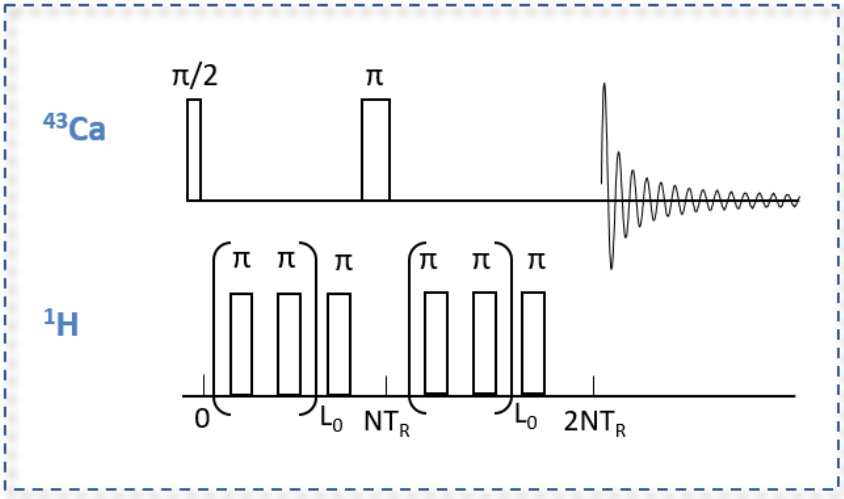
Ca11	O51	2.23811	Ca13	O53	2.30069	Ca15	O11	2.34090
Ca11	O49	2.25031	Ca13	O57	2.33450	Ca15	O9	2.34938
Ca11	O33	2.27282	Ca13	O3	2.33759	Ca15	O16	2.39285
Ca11	O7	2.35658	Ca13	O37	2.41335	Ca15	O27	2.39951
Ca11	O43	2.49745	Ca13	O41	2.46915	Ca15	O23	2.43351
Ca11	O27	2.78822	Ca13	O11	2.51266	Ca15	O1	2.79331
Ca11	O5	2.88203	Ca13	O9	2.60586	Ca15	O5	2.93215
Ca11	O23	3.07836	Ca13	H5	2.74949	Ca15	O3	2.97068
Ca11	P6	3.09382	Ca13	H17	2.78874	Ca15	P1	3.18289
Ca11	P1	3.11421	Ca13	H11	2.97343	Ca15	H5	3.18814
Ca11	P3	3.17691	Ca13	H3	3.04217	Ca15	P3	3.31841
Ca11	O1	3.42160	Ca13	P4	3.13201	Ca15	H11	3.39164
Ca11	Ca8	3.47542	Ca13	H19	3.19164	Ca15	O57	3.51114
Ca11	H5	3.50726	Ca13	O55	3.20045	Ca15	P10	3.53211
Ca11	P2	3.57706	Ca13	P2	3.32442	Ca15	O14	3.54382
Ca11	P2	3.59599	Ca13	P3	3.64232			

Table S3. *Selected P…Ca distances for all phosphorus sites (P1 to P6) in OCP (distances are given in Å). The P…Ca distances are highlighted in yellow.*

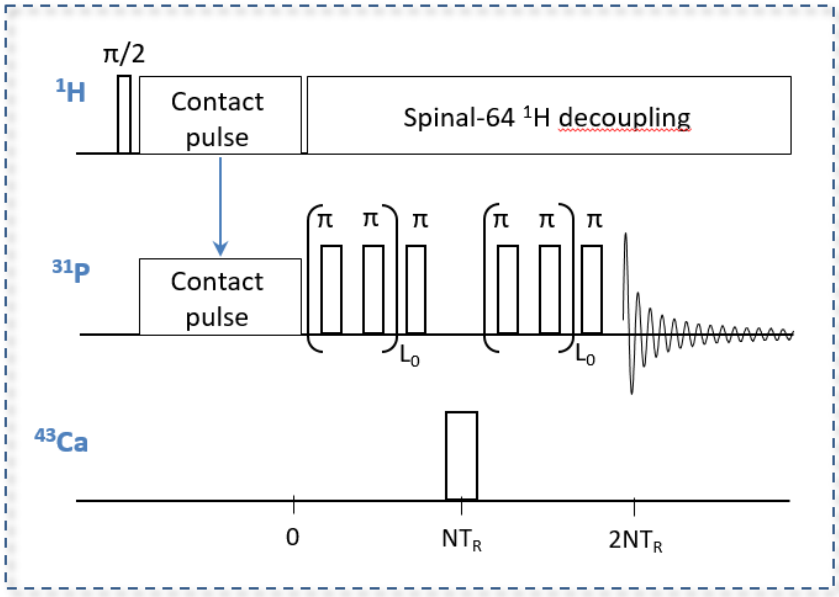
P1	O1	1.53506	P2	O55	1.52231	P3	O57	1.52633	P4	O13	1.53906	P5	O21	1.51899	P6	O33	1.51966
P1	O43	1.54167	P2	O49	1.54237	P3	O7	1.53619	P4	O9	1.54409	P5	O19	1.52811	P6	O31	1.52936
P1	O23	1.54350	P2	O51	1.54591	P3	O3	1.55125	P4	O11	1.54454	P5	O26	1.52960	P6	O27	1.55167
P1	O48	1.54611	P2	O53	1.56278	P3	O5	1.56109	P4	O15	1.55140	P5	O17	1.61772	P6	O29	1.57936
P1	Ca11	3.11421	P2	Ca9	3.12185	P3	H11	2.52773	P4	Ca13	3.13201	P5	H1	2.23963	P6	H11	2.23511
P1	Ca2	3.16378	P2	O47	3.22882	P3	Ca11	3.17691	P4	Ca3	3.13854	P5	H8	2.69921	P6	H5	2.52959
P1	O16	3.17828	P2	Ca1	3.23046	P3	Ca5	3.28372	P4	O53	3.17128	P5	H16	2.77961	P6	H1	2.63118
P1	Ca15	3.18289	P2	Ca3	3.28112	P3	Ca15	3.31841	P4	Ca1	3.22671	P5	Ca8	3.08487	P6	H23	2.78190
P1	Ca4	3.31990	P2	Ca13	3.32442	P3	O29	3.49157	P4	Ca9	3.42814	P5	O20	3.39126	P6	H17	2.80124
P1	Ca10	3.36127	P2	H3	3.34137	P3	H13	3.54055	P4	Ca16	3.53211	P5	O33	3.42391	P6	H21	2.92800
P1	Ca9	3.56781	P2	Ca8	3.45712	P3	Ca3	3.55661	P4	O41	3.53214	P5	Ca7	3.43808	P6	Ca11	3.09382
P1	O47	3.58806	P2	O7	3.51076	P3	Ca13	3.64232	P4	Ca4	3.53451	P5	Ca6	3.44449	P6	H13	3.15134
P1	O51	3.59277	P2	O57	3.53038	P3	O9	3.66817	P4	Ca2	3.57728	P5	O46	3.50296	P6	O41	3.42270
P1	O2	3.62195	P2	Ca11	3.57706	P3	Ca13	3.67348	P4	O1	3.62572	P5	H15	3.66161	P6	O39	3.42602
P1	Ca1	3.62398	P2	O39	3.57916	P3	Ca1	3.67576	P4	O16	3.64560	P5	Ca5	3.66854	P6	O3	3.43287
P1	Ca9	3.68345	P2	Ca11	3.59599	P3	O11	3.70716	P4	O10	3.67989	P5	H20	3.70767	P6	H3	3.44416
P1	O49	3.68832	P2	Ca5	3.74215	P3	O53	3.72073	P4	Ca15	3.69443	P5	O31	3.72995	P6	O17	3.56124
P1	Ca3	3.71006	P2	O41	3.74787	P3	O51	3.72711	P4	Ca15	3.72106	P5	O36	3.75412	P6	O57	3.58275
P1	O27	3.74708	P2	H5	3.88106	P3	O35	3.74819	P4	O23	3.74962	P5	P11	3.92708	P6	H3	3.67373
P1	O47	3.99215	P2	O5	3.88682	P3	O27	3.79614	P4	O16	3.75865	P5	H14	3.95930	P6	Ca8	3.75604
			P2	H21	3.95345	P3	O49	3.81178	P4	O12	3.79699	P5	O22	3.96761	P6	Ca15	3.75667
			P2	O3	3.96596	P3	O53	3.83556	P4	H5	3.80931	P5	H21	3.97856	P6	O37	3.76425
						P3	Ca8	3.85360							P6	O39	3.80075
						P3	O55	3.90019							P6	H8	3.83917
						P3	H17	3.94996							P6	O19	3.90247
															P6	O35	3.91076

Figure S1. (a) $^{43}Ca\{^{1}H\}$ REDOR (with ^{43}Ca detection) and (b) $^{31}P\{^{43}Ca\}$ CP REAPDOR (with ^{31}P detection) pulse sequences. L_0 corresponds to the number of recoupling loops. T_R corresponds to the rotor period.

(a)



(b)



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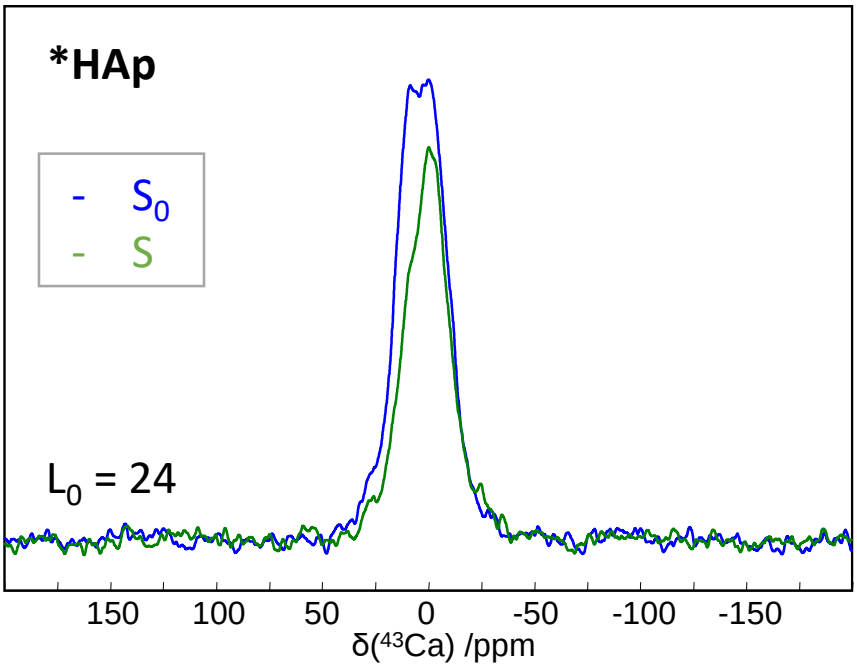

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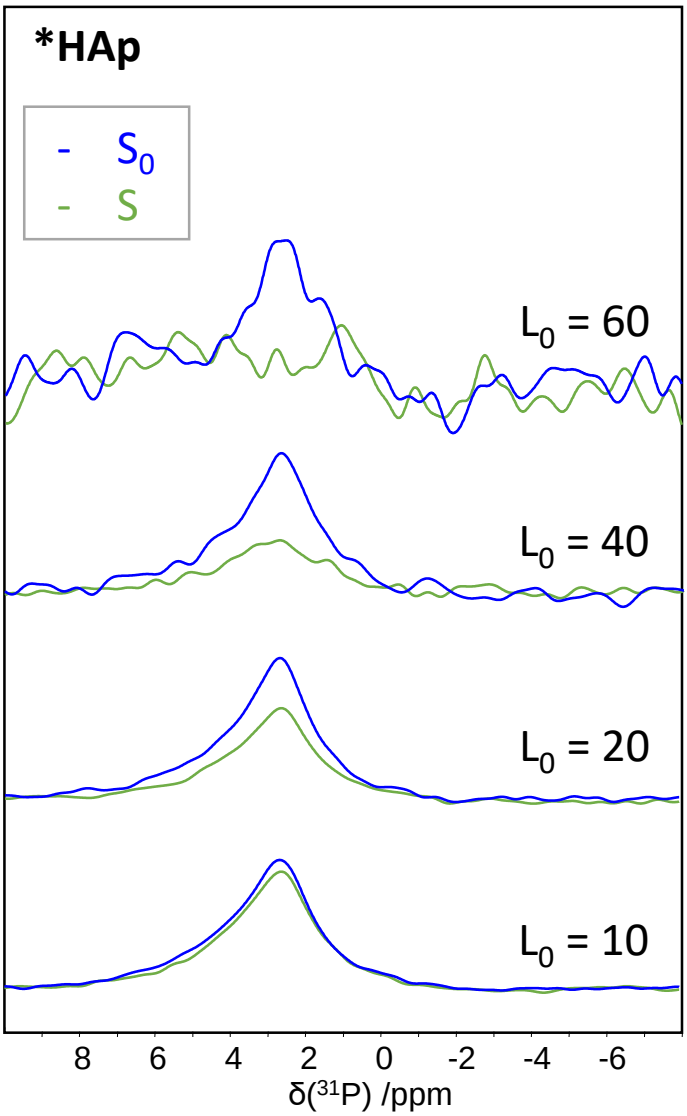


Figure S4. $^{31}P\{^{43}Ca\}$ CP REAPDOR experiment for *OCP (20.0 T; 14 kHz MAS). Blue spectrum (S_0): ^{31}P CP-echo; green spectrum (S): REAPDOR dephased echo for 20 recoupling loops (see Figure S1b for the definition of L_0). We mention that the ^{31}P CP spectrum presented here is somewhat different from the Bloch-decay spectrum presented in: Y. Li, D.G. Reid, M.J. Duer, J.C.C. Chan, *Solid State Nuclear Magnetic Resonance* **2018**, *95*, 1. Part of the differences are possibly due to isotropic $^{2}J(^{43}Ca\text{-}^{31}P)$ couplings (few Hz) and the large number of ^{43}Ca neighbors for each of the phosphorus sites.

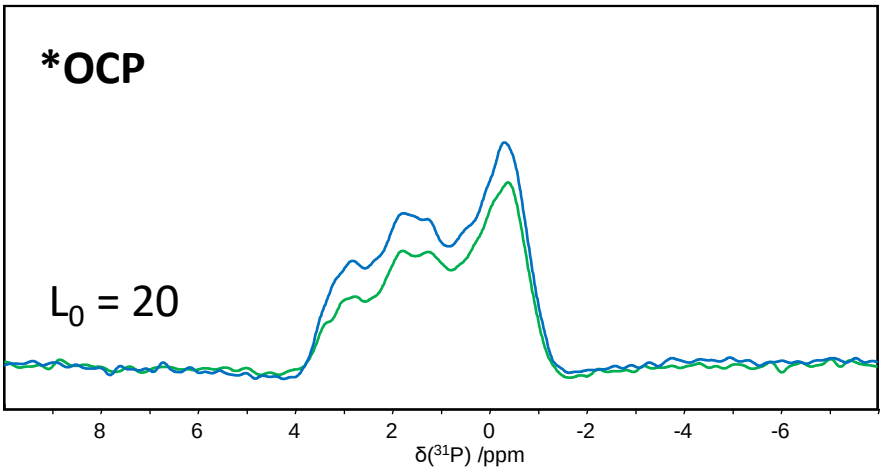
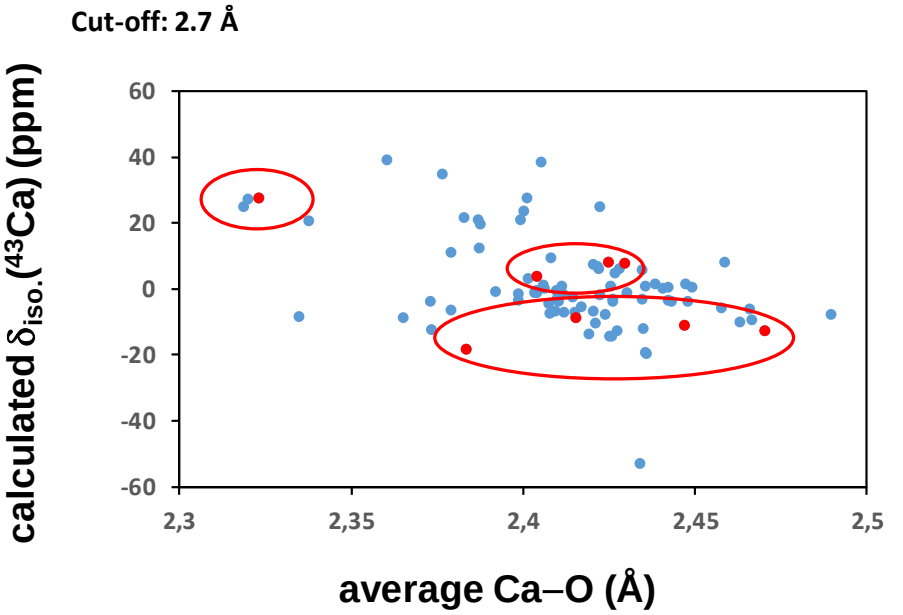


Figure S5. GIPAW calculated $\delta_{iso.}(^{43}Ca)$ for all calcium sites in OCP (red dots) and OCP-citrate (blue dots) models *vs* the average Ca-O distance (with 2 different cut-offs, 2.7 and 2.9 Å. Three groups of ^{43}Ca isotropic chemical shifts are highlighted by red ovals (above 20 ppm, between 0 and 10 ppm, and below 0 ppm).



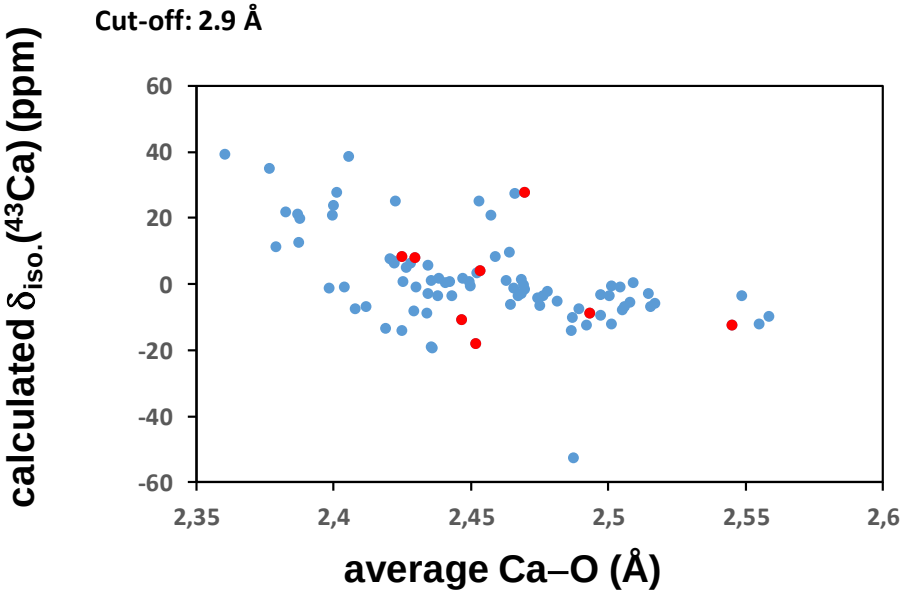


Figure S6. Analysis of the most extreme *calculated* $\delta_{iso.}(^{43}Ca)$ values calculated for the five OCP-citrate models, showing the corresponding calcium local environments (including Ca…X distances). Ca: green, O: red, P: blue, C: black, H: light pink.

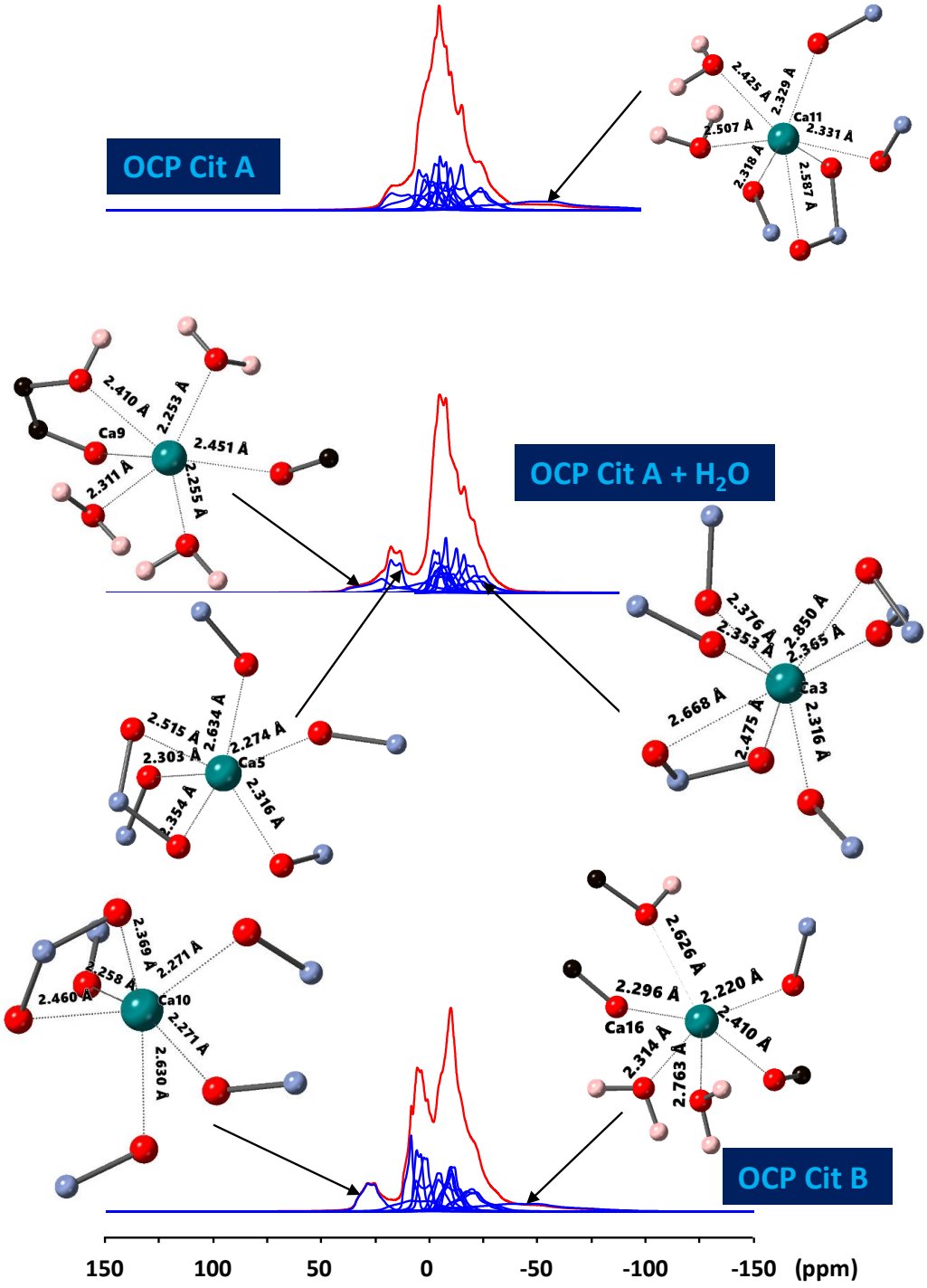


Figure S6. Continued.