

Supporting Information

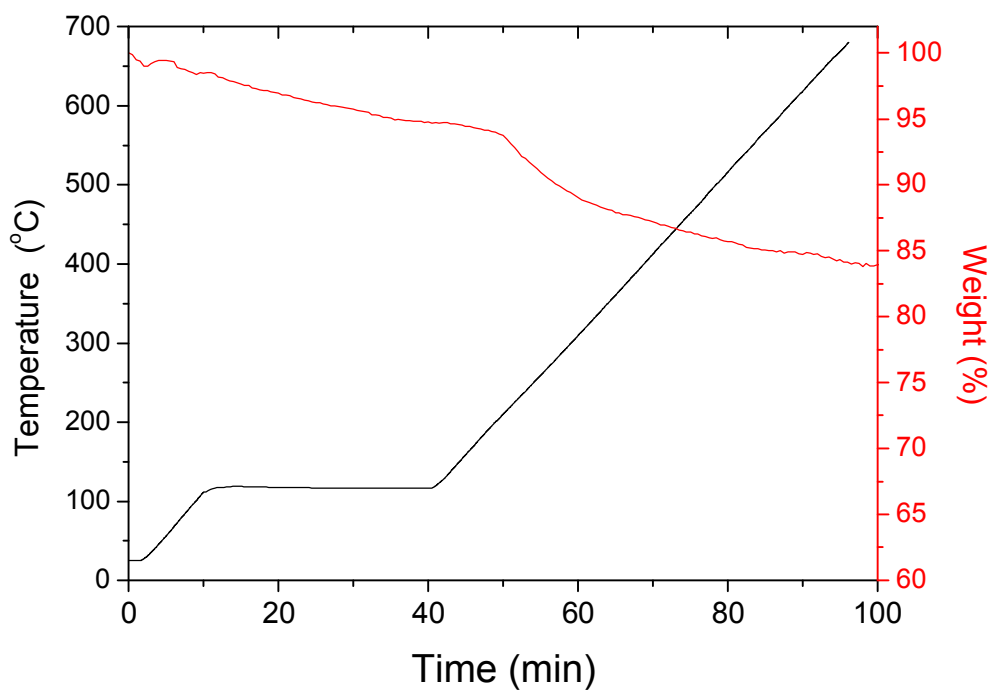


Figure S1. TGA results obtained for OCP.

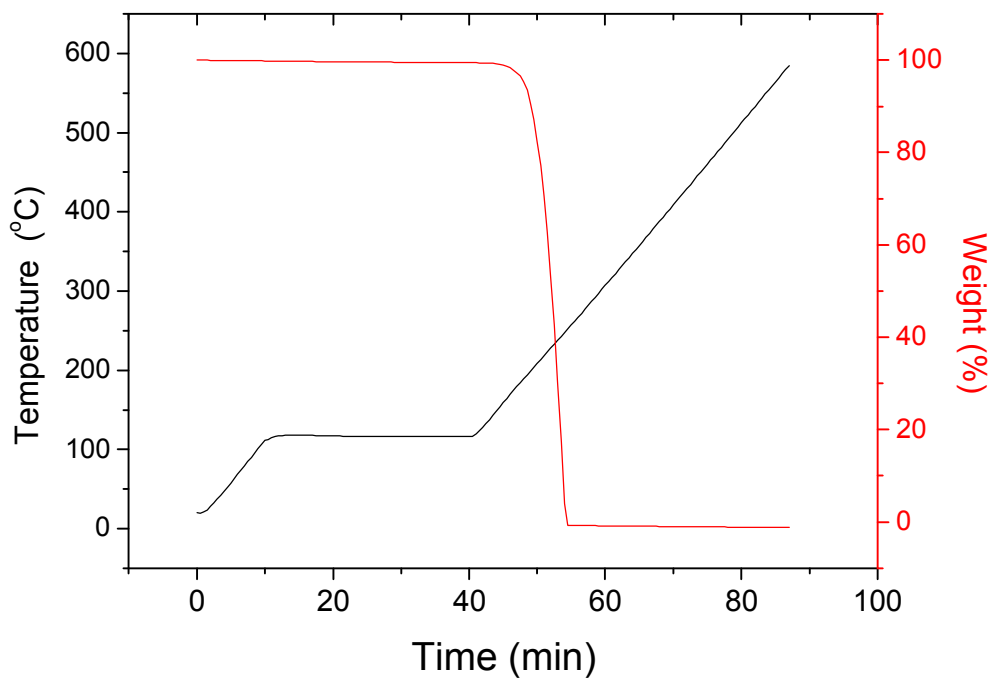


Figure S2. TGA results obtained for succinic acid.

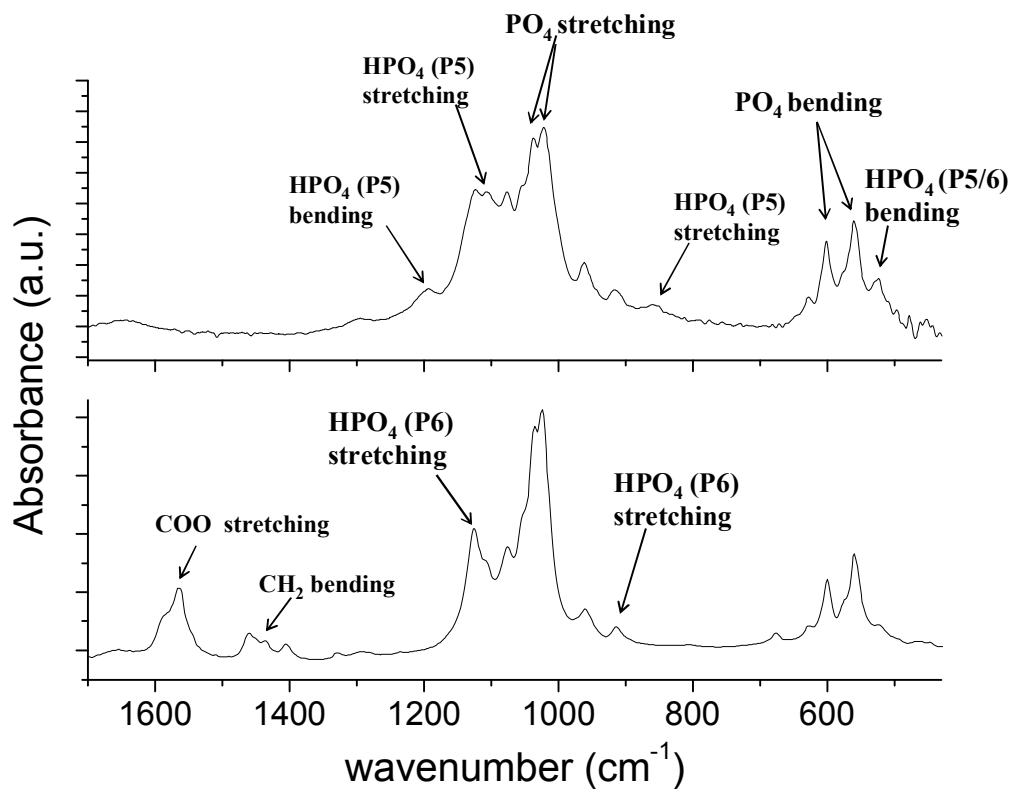


Figure S3. FT-IR spectra of OCP (upper trace) and OCPS (lower trace).

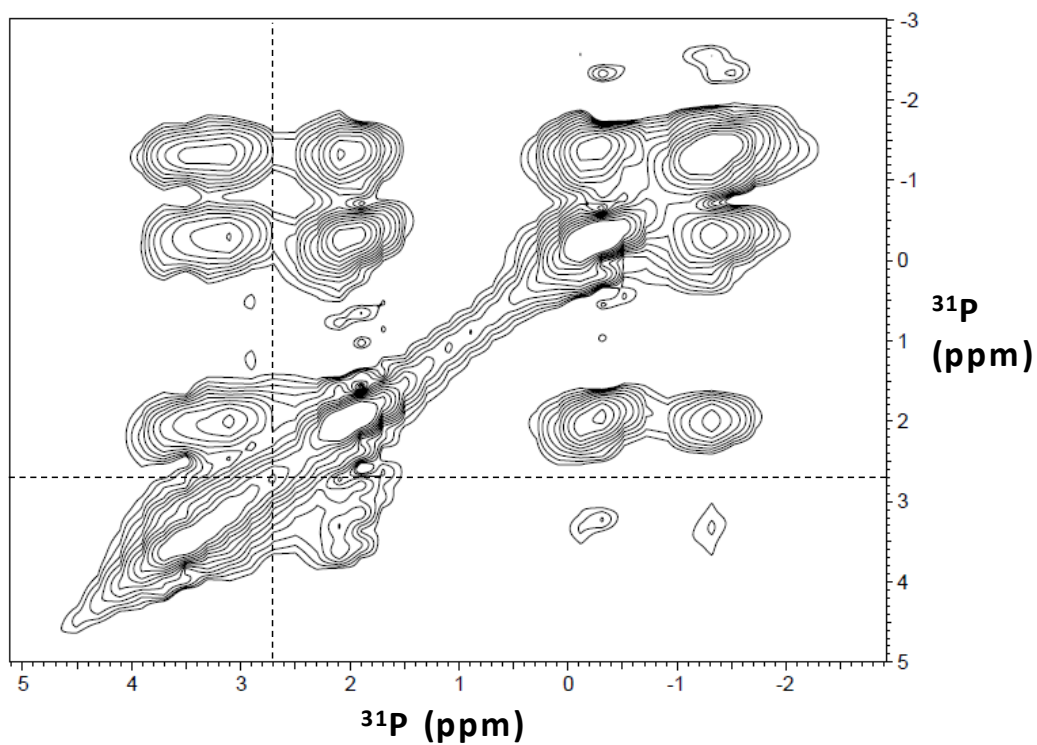


Figure S4. ³¹P-³¹P DARR measurements with a mixing time of 300 ms. The dashed lines show the chemical shift of the HAp impurity phase.

Determination of the proportionality constants between the van Vleck's second moment and the experimental DQ build-up rates for OCP

The proportionality constants between the van Vleck's second moment and the experimental DQ build-up rates were determined for OCP in the following way. Firstly, we made an assignment of the peak at -0.2 ppm. Then we calculated the corresponding M_2 values based on the X-ray crystal structure. Because there are three possible assignments of the peak at -0.2 ppm for OCP, viz. P5/P6, P4/P5/P6, and P2/P5/P6, we had calculated three sets of proportionality constants as shown in Table S1 to S3.

Table S1. Proportionality constants between the van Vleck's second moment and the experimental DQ build-up rates determined for OCP. The signal at -0.2 ppm is assigned to P5 and P6.

Correlation peaks (ppm, ppm)	Assignments	A	Calculated M_2 ($\times 10^6$ rad ² sec ⁻²)	M_2/A ($\times 10^6$ rad ² sec ⁻²)
3.7, -0.2	P1-P5/6	0.926	0.347	0.375
3.3, -0.2	P2-P5/6	0.840	0.696	0.828
2.0, -0.2	P3-P5/6	0.710	1.076	1.516
-0.2, -0.2	P5/6-P5/6	0.639	2.1082	3.301
3.7, 3.7	P1-P1	1.148	3.222	2.806
3.7, 2.0	P1-P3	0.819	0.581	0.710

Table S2. Proportionality constants between the van Vleck's second moment and the experimental DQ build-up rates determined for OCP. The signal at -0.2 ppm is assigned to P4, P5, and P6.

Correlation peaks (ppm, ppm)	Assignments	A	Calculated M_2 ($\times 10^6$ rad ² sec ⁻²)	M_2/A ($\times 10^6$ rad ² sec ⁻²)
3.7, -0.2	P1-P4/5/6	0.926	0.894	0.966
3.3, -0.2	P2-P4/5/6	0.840	0.789	0.939
2.0, -0.2	P3-P4/5/6	0.710	1.100	1.550
-0.2, -0.2	P4/5/6-P4/5/6	0.639	1.405	2.200
3.7, 3.7	P1-P1	1.148	3.222	2.806
3.7, 2.0	P1-P3	0.819	0.581	0.710

Table S3. Proportionality constants between the van Vleck's second moment and the experimental DQ build-up rates determined for OCP. The signal at -0.2 ppm is assigned to P2, P5, and P6.

Correlation peaks (ppm, ppm)	Assignments	A	Calculated M_2 ($\times 10^6$ rad ² sec ⁻²)	M_2/A ($\times 10^6$ rad ² sec ⁻²)
3.7, -0.2	P1-P2/5/6	0.926	0.759	0.819
3.3, -0.2	P2-P2/5/6	0.840	0.536	0.638
2.0, -0.2	P3-P2/5/6	0.710	1.815	2.557
-0.2, -0.2	P2/5/6-P2/5/6	0.639	1.270	1.989
3.7, 3.7	P1-P1	1.148	3.222	2.806
3.7, 2.0	P1-P3	0.819	0.581	0.710

Table S4. The calculated M_2 of OCPS based on the assignment of $P_A \rightarrow P6$ and $P_B \rightarrow P5$.

Site	Assignment	A	Extracted M_2 of OCPS [†] ($\times 10^6$ rad ² sec ⁻²)	Calculated M_2 of OCP [†] ($\times 10^6$ rad ² sec ⁻²)
P1- P_A	P1-P6	0.706	0.682	0.60889
P1- P_B	P1-P5	0.490	0.473	0.0847
P3- P_A	P3-P6	0.599	0.929	1.5891
P3- P_B	P3-P5	0.346	0.537	0.5623
P_A - P_B	P5-P6	0.397	0.873	1.3509

[†] The proportionality constants (M_2/A) were taken from Table S2. [‡] The M_2 values were calculated based on the X-ray crystal structure.

Table S5. The calculated M_2 of OCPS based on the assignment of $P_A \rightarrow P5$ and $P_B \rightarrow P6$.

Site	Assignment	A	Extracted M_2 of OCPS [†] ($\times 10^6$ rad ² sec ⁻²)	Calculated M_2 of OCP [†] ($\times 10^6$ rad ² sec ⁻²)
P1- P_A	P1-P5	0.706	0.682	0.0847
P1- P_B	P1-P6	0.490	0.473	0.60889
P3- P_A	P3-P5	0.599	0.929	0.5623
P3- P_B	P3-P6	0.346	0.537	1.5891
P_A - P_B	P5-P6	0.397	0.873	1.3509

[†] The proportionality constants (M_2/A) were taken from Table S2. [‡] The M_2 values were calculated based on the X-ray crystal structure.

As shown in the crystal structure of OCP, P4 is more likely to react with water to form the species of HPO_4^{2-} . Therefore, in the main text of our manuscript, we chose to employ the entries of Table S2 to calculate the M_2 values of OCPS. Nevertheless, the same conclusion shown in Figure 7 was obtained when we employed the entries of Table S1 or S3.

Determination of the chemical formula of OCPS and the overall Ca/P ratio

Table S6. Summary of the ^{31}P NMR spin counting data.

	HAp	OCP	OCPS
P-31 signal integral (a.u.)	1.0	2.3	1.1 ^a
Sample mass (mg)	37.9	26.9	15.0
Mw (g/mol)	1004.0	982.6	--
Number of scan	4	12	12
# of P-31 per formula unit	6	6	
# of mole of P-31 (10^{-3})	0.22649	0.16426	
Integral per scan per mole of P-31 spins (10^3)	1.1038	1.16684	

^a The contribution of the impurity phase has been subtracted.

The average integral per scan per mole of P-31 spins was equal to 1.135×10^3 , from which the number of mole of P-31 spins per unit mg of OCPS was calculated as $1.1 / 12 / (1.135 \times 10^3) / 15 = 5.38 \times 10^{-6}$.

By comparing the ^{13}C Bloch decay spectra of OCPS and L-alanine, the number of mole of succinate ions per unit mg of OCPS was found to be 5.49×10^{-7} .

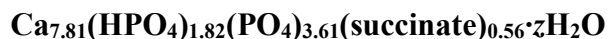
Assuming that the formula of OCPS is $\text{Ca}_{8-y/2}(\text{HPO}_4)_{2-x}(\text{PO}_4)_{4-y}(\text{succinate})_{x+y} \cdot z\text{H}_2\text{O}$:
 $5.49 \times 10^{-7} : 5.38 \times 10^{-6} = (x + y) : [6 - (x + y)]$
 $\Rightarrow x + y = 0.56$

From the deconvolution data, the ratio of the integrals of $\text{HPO}_4^{2-} : \text{PO}_4^{3-}$ is calculated as

$$\frac{1.38}{2.72} = \frac{2-x}{4-y}$$

$$\Rightarrow x = \mathbf{0.17} \quad \text{and} \quad y = \mathbf{0.39}$$

Therefore, the molecular formula of OCPS is found to be:



Hence the amount of Ca^{2+} due to OCPS is calculated as $5.38 \times 10^{-6} \times 7.81 / (1.82 + 3.61) = \mathbf{7.74 \times 10^{-6}}$.

Based on ^{31}P integral ratio of the HAp (impurity phase) and OCPS, the amount of ^{31}P due to HAp is calculated as $5.38 \times 10^{-6} \times 0.64 / 4.10 = \mathbf{8.40 \times 10^{-7}}$.

Assuming that the HAp phase has a perfect stoichiometry, the amount of Ca ions due to HAp is then calculated as $8.40 \times 10^{-7} \times 1.67 = \mathbf{1.40 \times 10^{-6}}$.

Overall, the Ca/P ratio of our OCPS sample is calculated as

$$\frac{(7.74 + 1.40)}{(5.44 + 0.84)} = \mathbf{1.46}$$