

From crystalline to amorphous Ca-pyrophosphates: a solid state NMR perspective

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Supplementary information

Content	Page
XRD powder patterns of the different hydrated calcium pyrophosphate phases synthesized in this work (Figure S1).	S2
Details on the ^{43}Ca NMR experimental parameters (Table S1).	S3
^{31}P MAS NMR spectra of t-CPPD, m-CPPD, m-CPPT β , m-CPPM and a-CPP, together with their simulation (Figure S2). Exact MAS rotation frequencies are indicated for each experiment.	S4
Evolution of the a-CPP phase after over 4 years of storage at room temperature, as shown by ^{31}P MAS NMR (Figure S3).	S9
^{31}P MAS NMR spectra of a-CPP phases: samples A and B (Figure S4). See section 2.1 for the synthesis of A and B.	S10
^{43}Ca MAS NMR spectra of t-CPPD, m-CPPD, m-CPPT β and m-CPPM, together with their simulation (Figure S5).	S11
Calculated ^{43}Ca isotropic chemical shifts for m-CPPD, t-CPPD and m-CPPT β , and corresponding average Ca...O distances for each phase (Table S2).	S13
Natural abundance ^{43}Ca MAS NMR spectra of a-CPP phases corresponding to two synthetic procedures (samples A and B – see section 2.1) (Figure S6).	S14
Natural abundance ^{43}Ca MAS NMR spectra of a-CPP corresponding to sample B (see section 2.1), before and after different heat-treatments (at 140 °C and 220 °C) (Figure S7).	S14
Calculated ^1H δ_{iso} for m-CPPD, t-CPPD and m-CPPT β (Table S3).	S15
References	S15

Figure S1. XRD powder patterns of the different hydrated calcium pyrophosphate phases synthesized in this work.

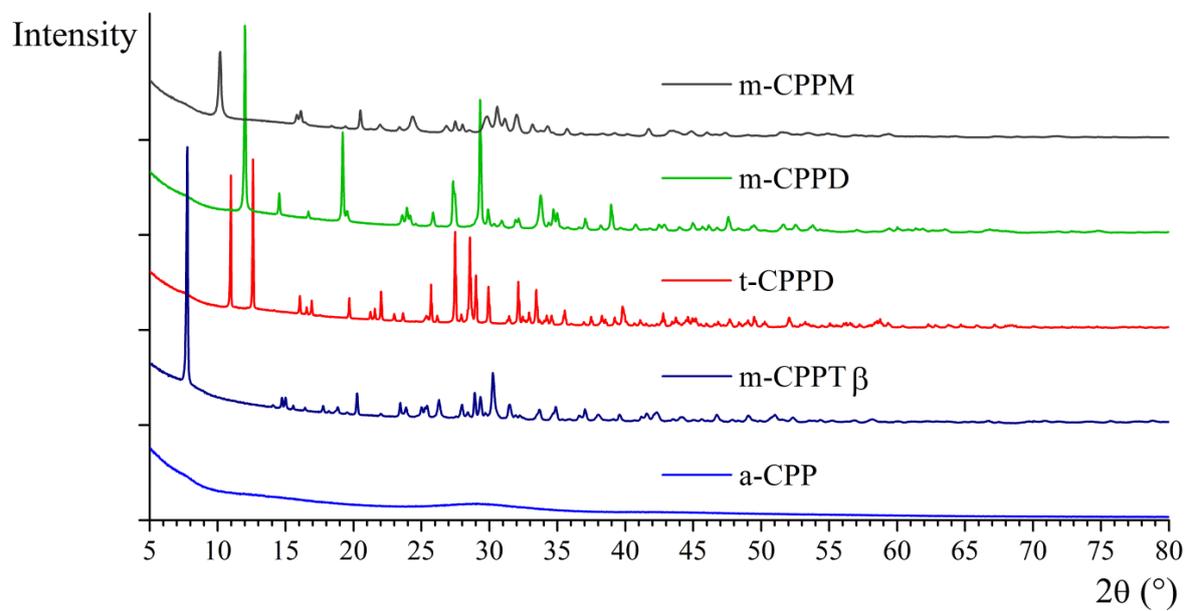
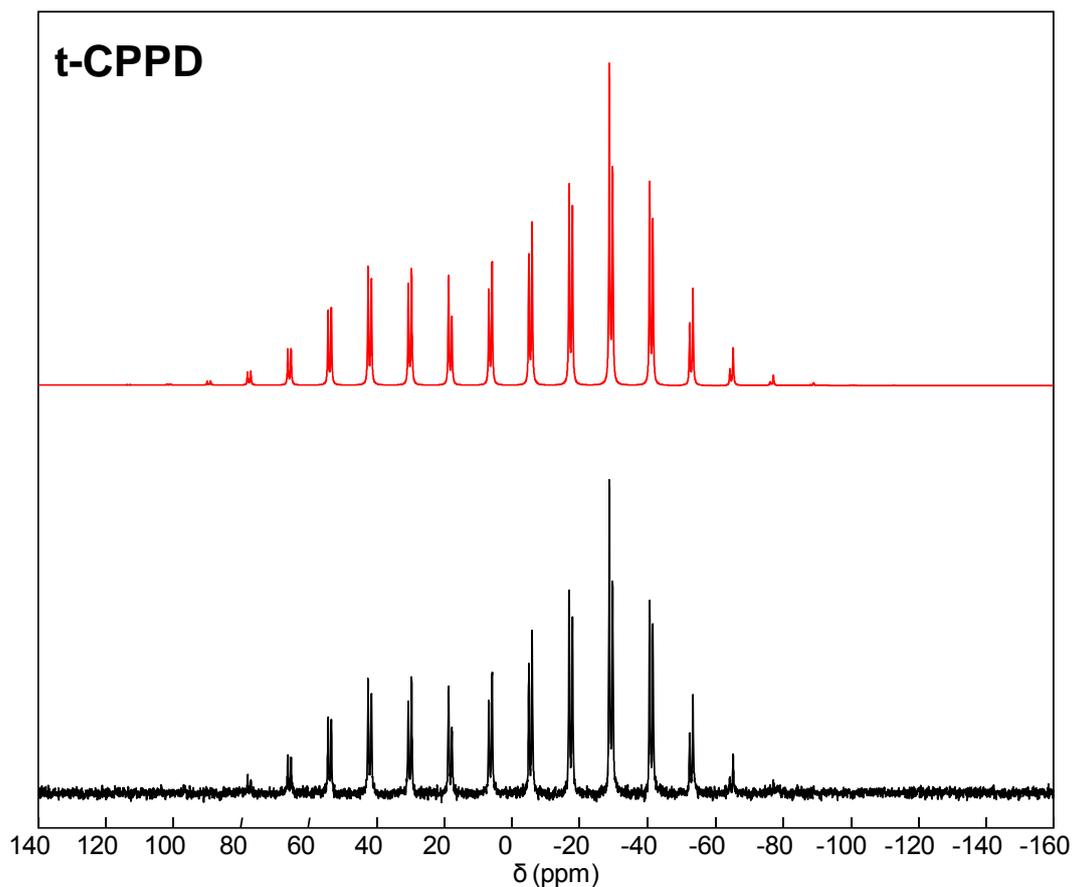


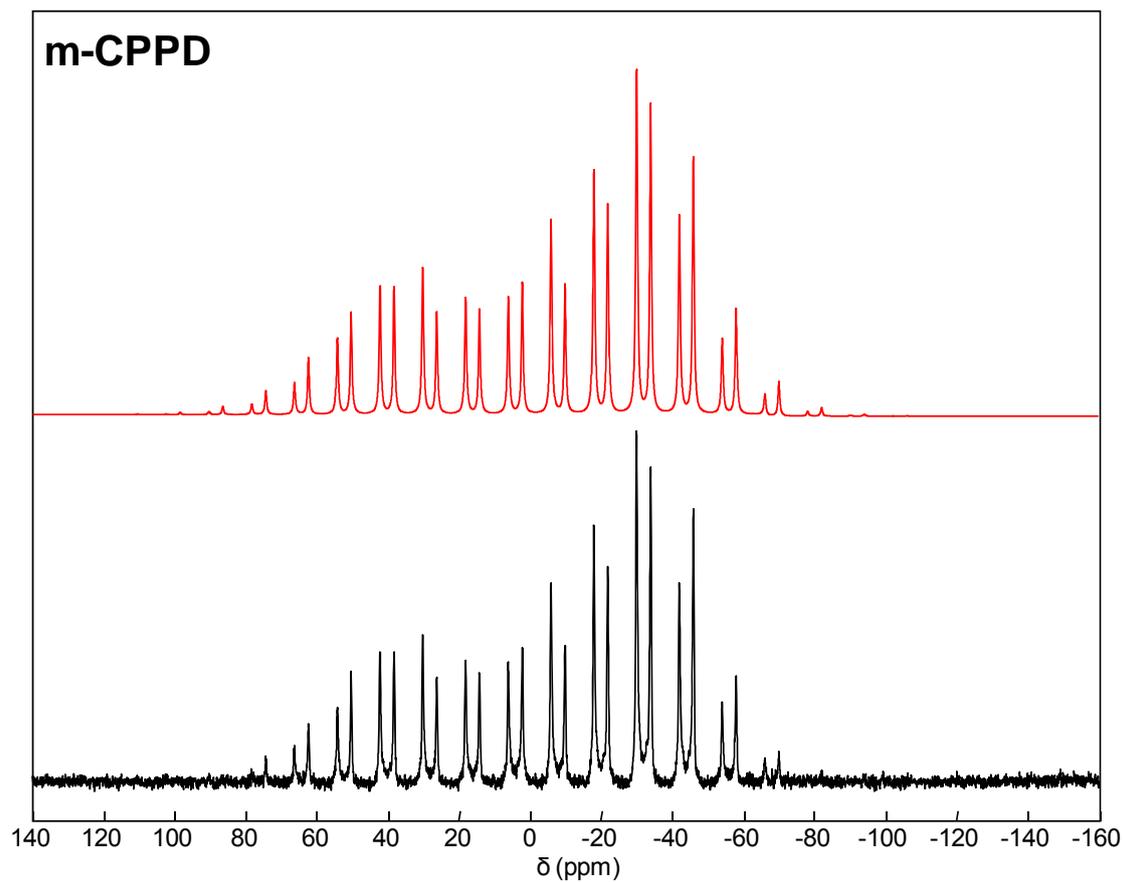
Table S1. ^{43}Ca MAS experimental parameters for m-CPPT β , t-CPPD, m-CPPD, m-CPPM and amorphous samples (a-CPP) at variable temperature (D1: recycle delay, NS: number of scans).

Sample	Magnetic Field (probe)	D1	NS	Total experimental time
Crystalline phases				
t-CPPD	850 MHz (7 mm)	1 s	50000	~ 14 h
	600 MHz (7.5 mm)	1 s	144500	~ 41 h
m-CPPD	850 MHz (7 mm)	1 s	20350	~ 6 h
	600 MHz (7.5 mm)	1 s	143300	~ 41 h
m-CPPT β	850 MHz (7 mm)	1 s	15550	~ 4.5 h
	600 MHz (9.5 mm)	2 s	37200	~ 21 h
m-CPPM	850 MHz (7 mm)	1 s	78800	~22 h
	600 MHz (7.5 mm)	1 s	241300	~ 68.5 h
Amorphous phases				
a-CPP sample B	850 MHz (7 mm)	0.5 s	70900	~ 10 h
	600 MHz (7.5 mm)	0.5 s	320000	~ 48 h
a-CPP sample A	850 MHz (7 mm)	0.5 s	38000	~ 5.5 h
a-CPP _{140°} sample B (heated at 140°C)	850 MHz (7 mm)	0.5 s	69000	~ 10 h
a-CPP _{220°} sample B (heated at 220°C)	850 MHz (7 mm)	0.5 s	97600	~ 13.5 h
	600 MHz (7.5 mm)	0.5 s	320000	~ 48 h

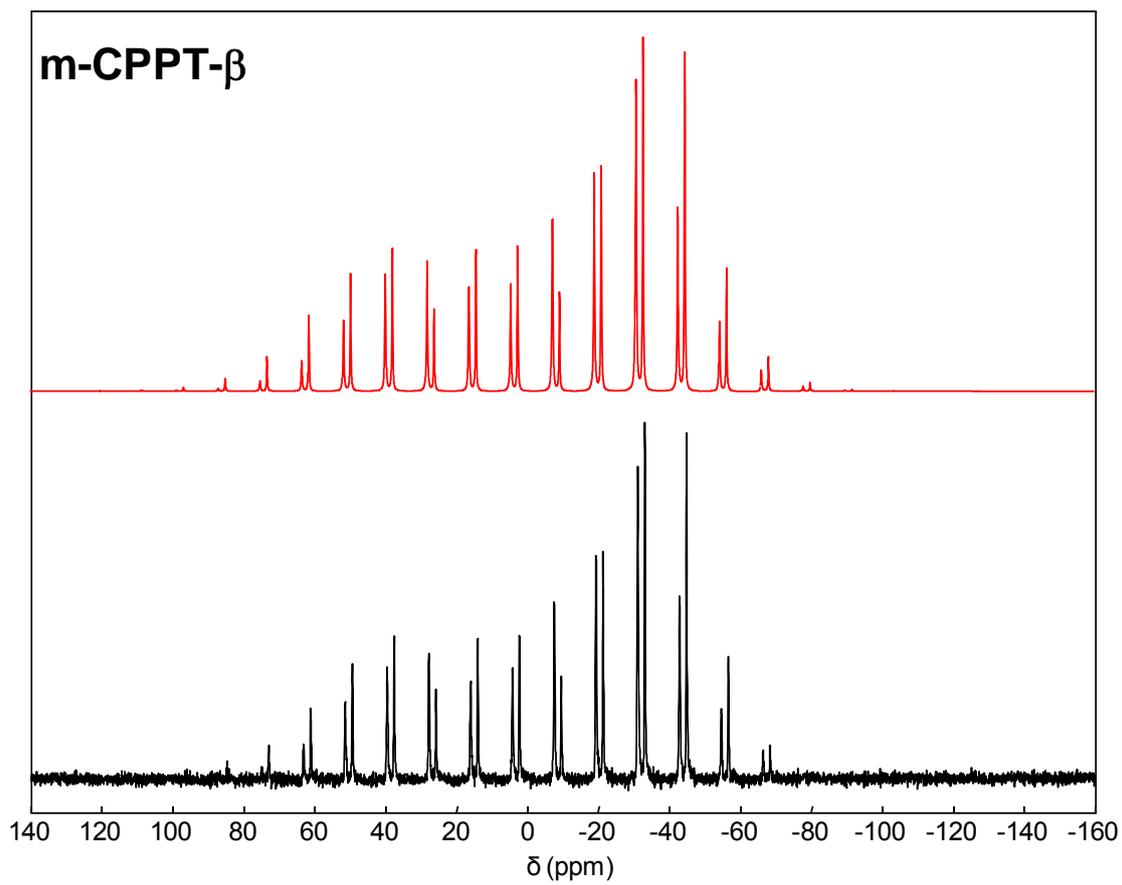
Figure S2: ^{31}P MAS NMR spectra (decoupled from ^1H during the acquisition time) of t-CPPD, m-CPPD, m-CPPT β , m-CPPM and a-CPP (14.1 T, 242.81 MHz, spinal 64 ^1H decoupling, relaxation delay: 128 s, number of scans: 4, regulation of the temperature: 10°C). MAS rotation frequency ν_r : specified for each sample. Experimental spectra are in black; simulated spectra are in red.¹ The extracted CSA parameters are given in the table below each spectrum. The definitions of δ_{CSA} and η_{CSA} are given in the experimental section. The notations P1 and P2 are compatible with those used in Table 1. In the case of a-CPP, the minor component at $\delta_{\text{iso}} \sim 0$ ppm is assigned to orthophosphate species (see main text).



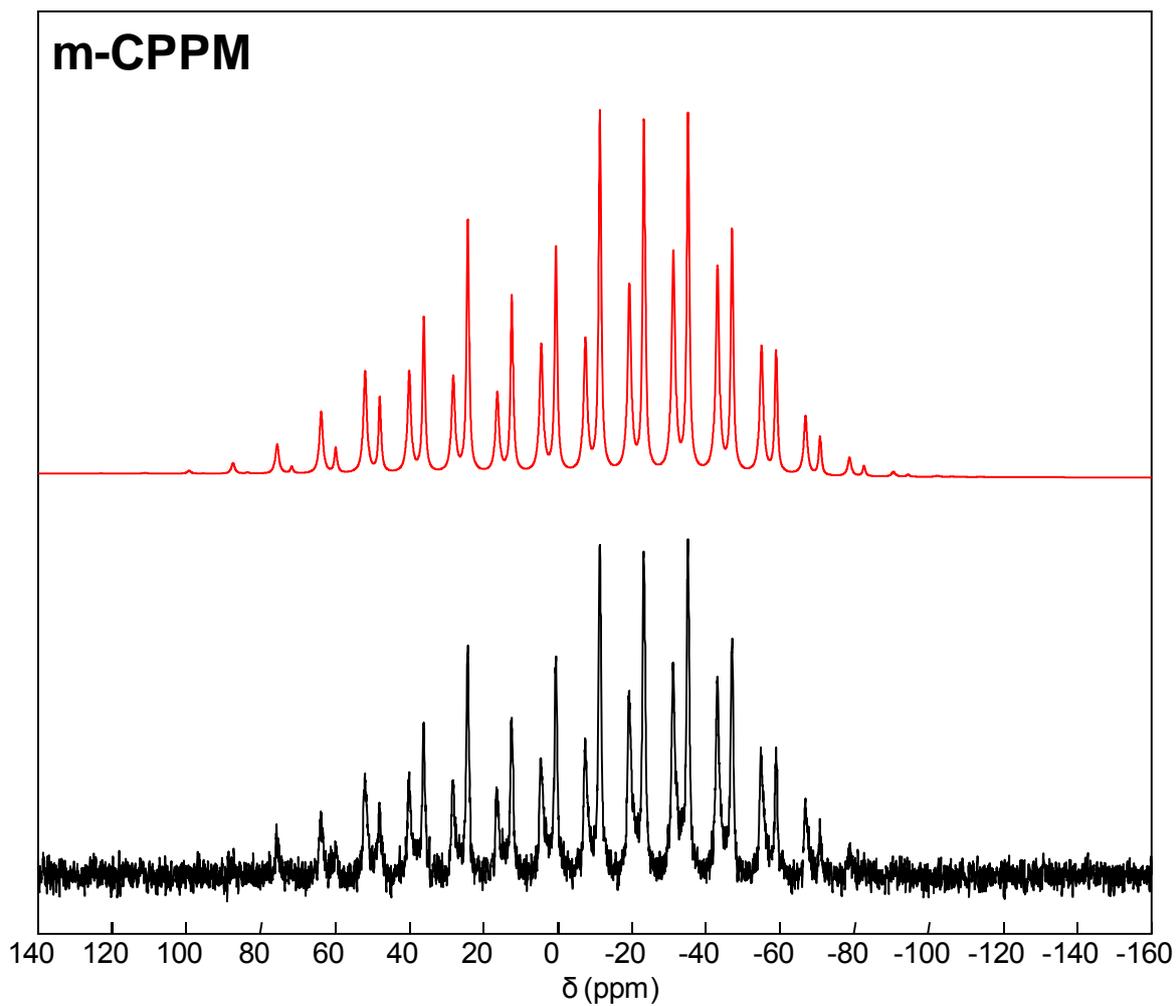
t-CPPD	δ_{iso} (ppm)	δ_{CSA} (ppm)	η_{CSA}	ν_r (Hz)
P1	-5.94	76.6	0.56	2882
P2	-4.97	75.6	0.27	2882



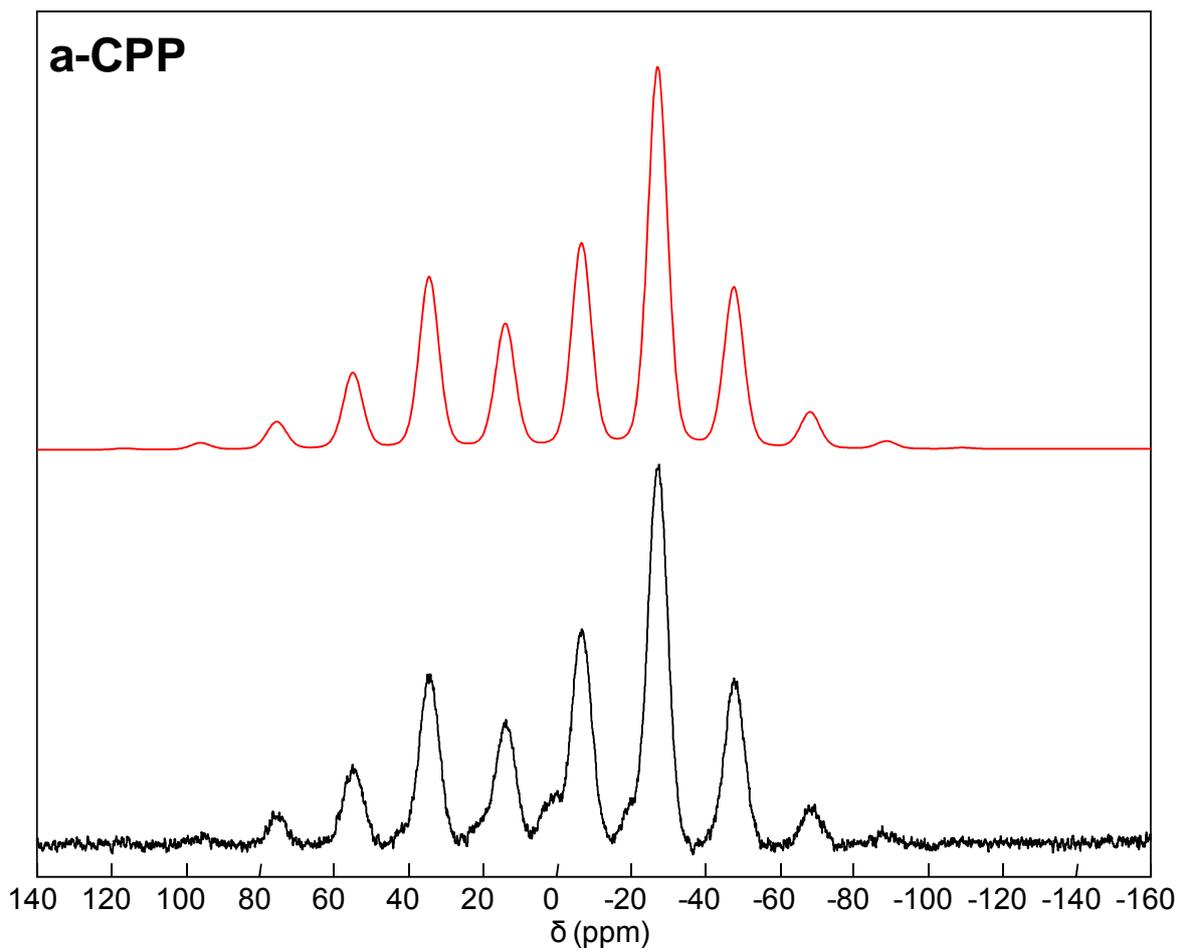
m-CPPD	δ_{iso} (ppm)	δ_{CSA} (ppm)	η_{CSA}	ν_r (Hz)
P1	-5.90	72.5	0.41	2921
P2	-9.70	82.6	0.34	2921



m-CPPT β	δ_{iso} (ppm)	δ_{CSA} (ppm)	η_{CSA}	ν_r (Hz)
P1	-9.31	84.5	0.21	2858
P2	-7.33	71.6	0.41	2858



m-CPPM	δ_{iso} (ppm)	δ_{CSA} (ppm)	η_{CSA}	ν_r (Hz)
P1	-11.27	64.0	0.80	2877
P2	-7.34	85.7	0.48	2877



a-CPP	δ_{iso} (ppm)	δ_{CSA} (ppm)	η_{CSA}	ν_r (Hz)
P	-6.7	78.2	0.80	4984

Figure S3: Evolution of the a-CPP phase after over 4 years of storage at room temperature, as shown by ^{31}P MAS NMR (experiments performed at 14.1 T, with a rotation frequency of 16 kHz).

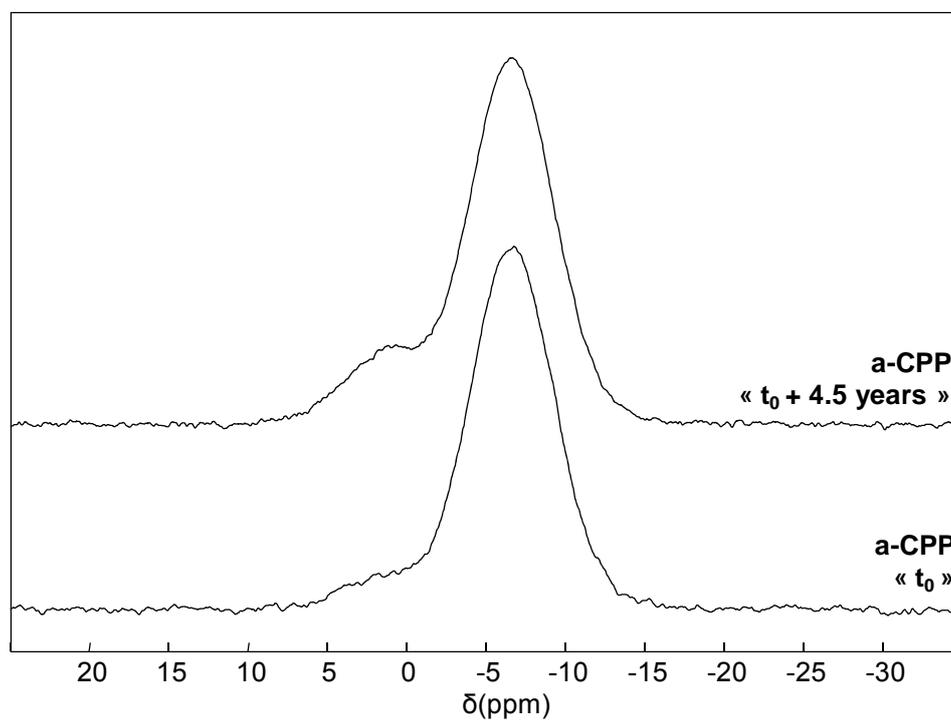


Figure S4: ^{31}P MAS NMR spectra of α -CPP phases corresponding to two synthetic procedures (samples A and B – see section 2.1 in the main text) at 14.1 T. MAS rotation frequency: 16 kHz.

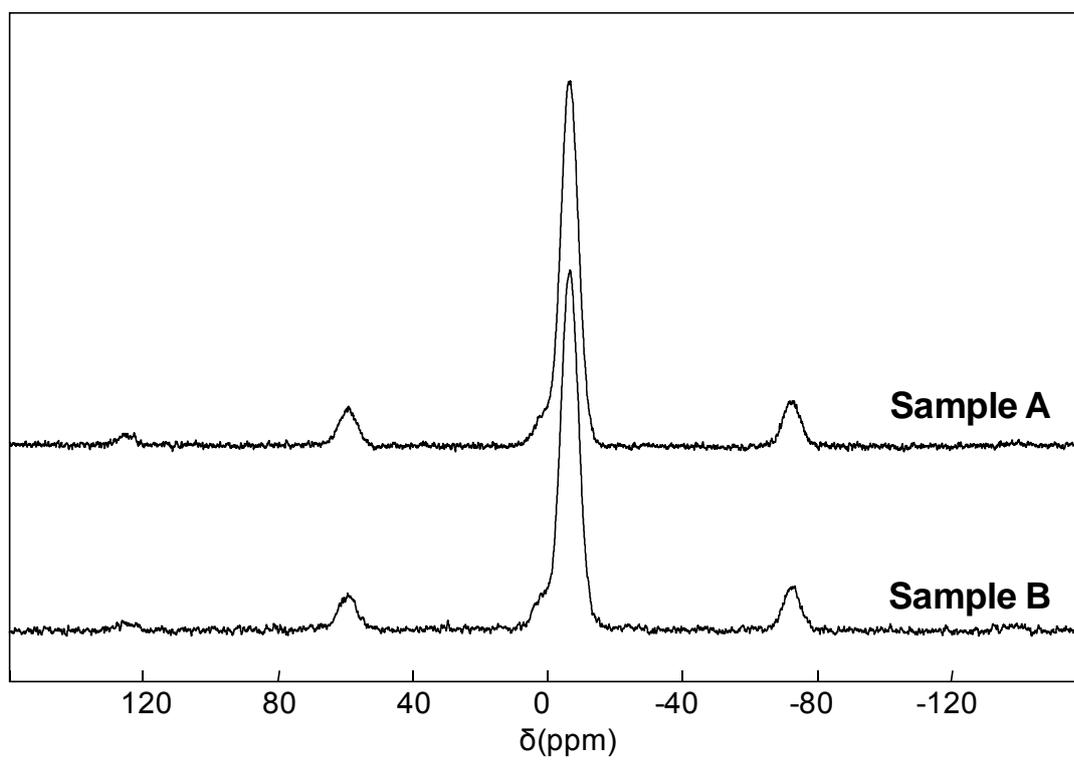
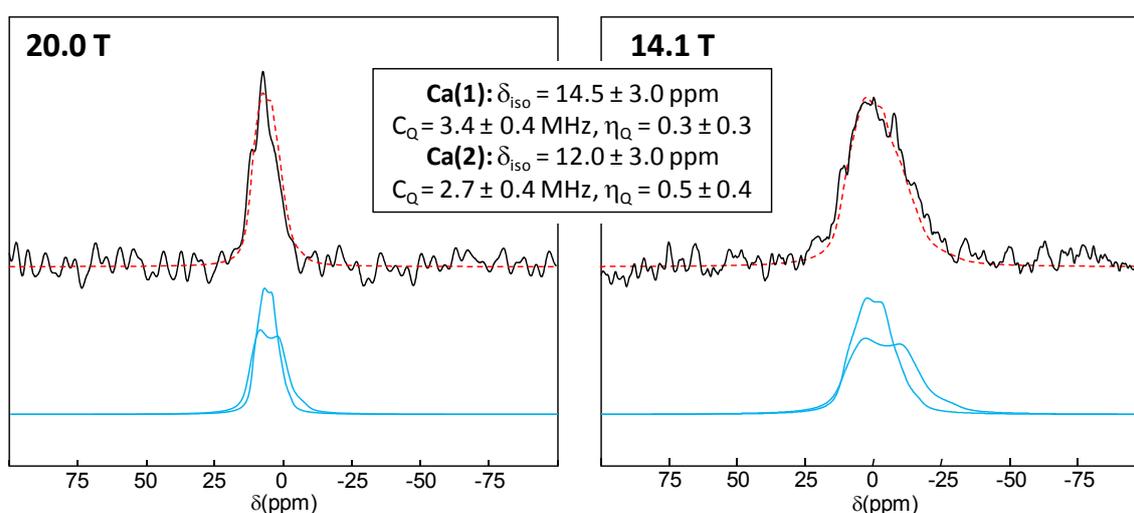
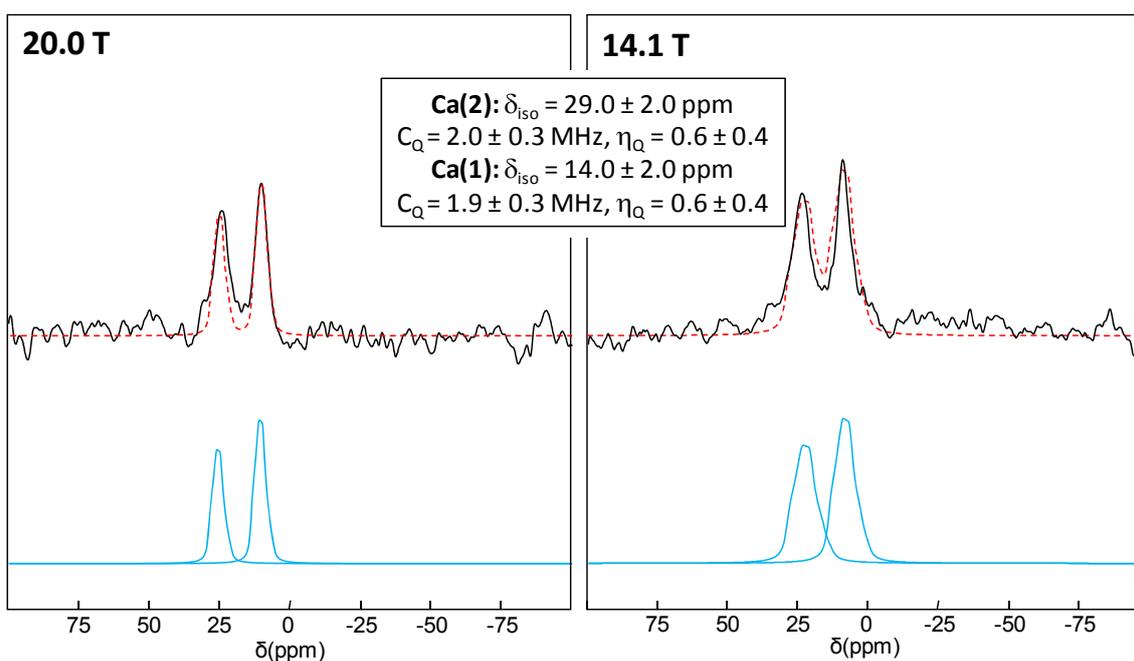


Figure S5: ^{43}Ca MAS NMR spectra of t-CPPD, m-CPPD, m-CPPT β and m-CPPM at 20.0 T [$\nu_0(^{43}\text{Ca}) = 57.22$ MHz] and 14.1 T [$\nu_0(^{43}\text{Ca}) = 40.37$ MHz]. The relaxation delay and number of scans for each sample are given in Table S1. MAS rotation frequency: 4 to 6 kHz. Experimental spectra are in black, the simulation1 of the Ca sites is in blue (in agreement with the presence of 2 inequivalent Ca atoms in the asymmetric unit), and the sum of the contributions is shown as a dashed red line. The extracted quadrupolar parameters are given in an insert for each sample. The definitions of C_Q and η_Q are given in the experimental section. The notations Ca1 and Ca2 are compatible with those used in Table 2. For m-CPPM, only the data at 20.0 T was simulated due to the high level of noise in the data recorded at 14.1 T (this means that the accuracy of the ^{43}Ca NMR parameters for this phase is lower, especially for the Ca(2) site).

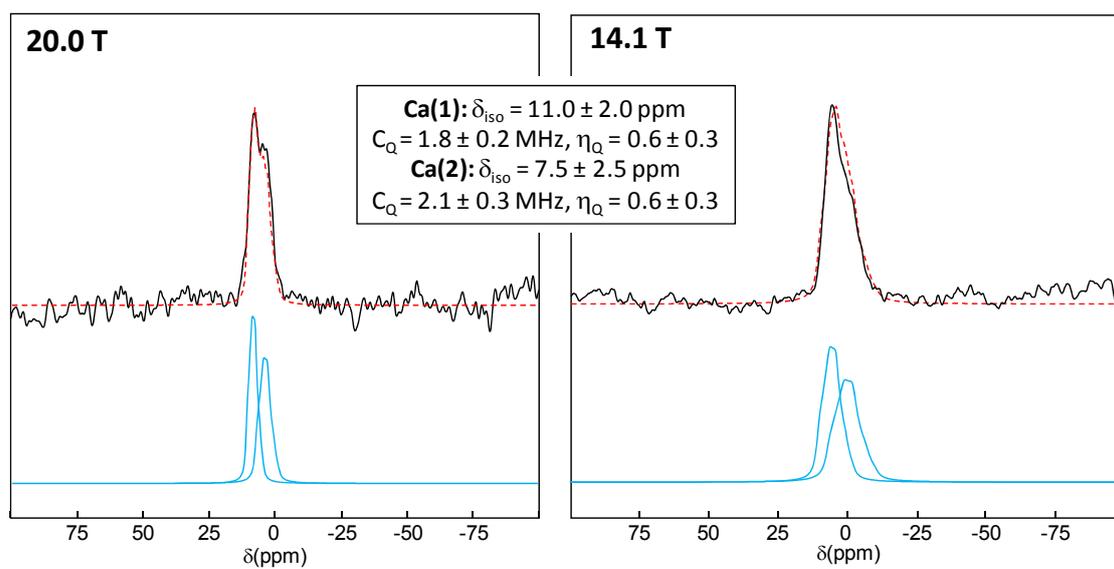
a/ t-CPPD



b/ m-CPPD



c/ m-CPPT β



d/ m-CPPM

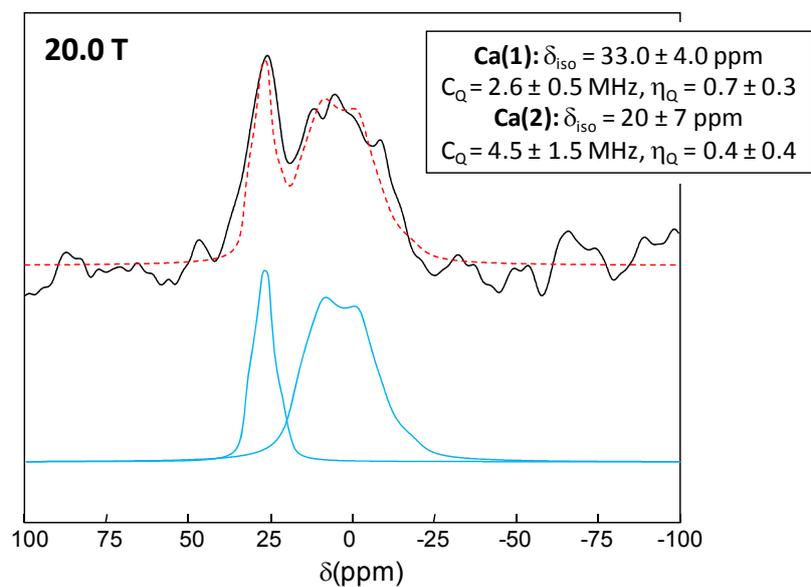


Table S2: Calculated ^{43}Ca δ_{iso} for m-CPPD, t-CPPD and m-CPPT β and corresponding average distance calculated taking into account the oxygen atoms situated at distances ≤ 2.7 Å.

		δ_{iso} (ppm) calc	d(Ca...O) (Å)	Coordination number	Number of H ₂ O in the coordination Sphere
m-CPPD	Ca1	14.9	2.405	6	1
Rel H	Ca2	17.6	2.414	7	1
t-CPPD	Ca1	13.8	2.453	7	1
Rel H	Ca2	12.0	2.443	7	2
m-CPPT β	Ca1	11.9	2.431	7	1
Rel H	Ca2	11.4	2.422	7	3
m-CPPM	Ca1	15.2	2.443	7	1
Rel tot	Ca2	5.3	2.426	6	1
$\alpha\text{-Ca}_2\text{P}_2\text{O}_7$	Ca1	-22.1	2.470	6	0
	Ca2	6.4	2.496	8	0

Figure S6: Natural abundance ^{43}Ca MAS NMR spectra of a-CPP phases corresponding to two synthetic procedures (samples A and B – see section 2.1) at 20.0 T ($\nu_0(^{43}\text{Ca}) = 57.22$ MHz). MAS rotation frequency: 5 kHz. For the relaxation delay and number of scans used for each sample, see Table S1.

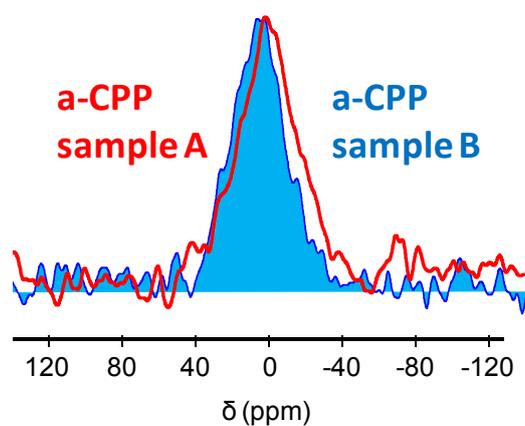


Figure S7: Natural abundance ^{43}Ca MAS NMR spectra of a-CPP corresponding to sample B (see section 2.1), before (RT) and after different heat-treatments (at 140 °C and 220 °C). Spectra recorded at 20.0 T [$\nu_0(^{43}\text{Ca}) = 57.22$ MHz] and at 14.1 T [$\nu_0(^{43}\text{Ca}) = 40.37$ MHz]. For the relaxation delay and number of scans, see Table S1. MAS rotation frequency: 5 kHz. For T = 140 °C, a unique spectrum at 20.0 T was recorded.

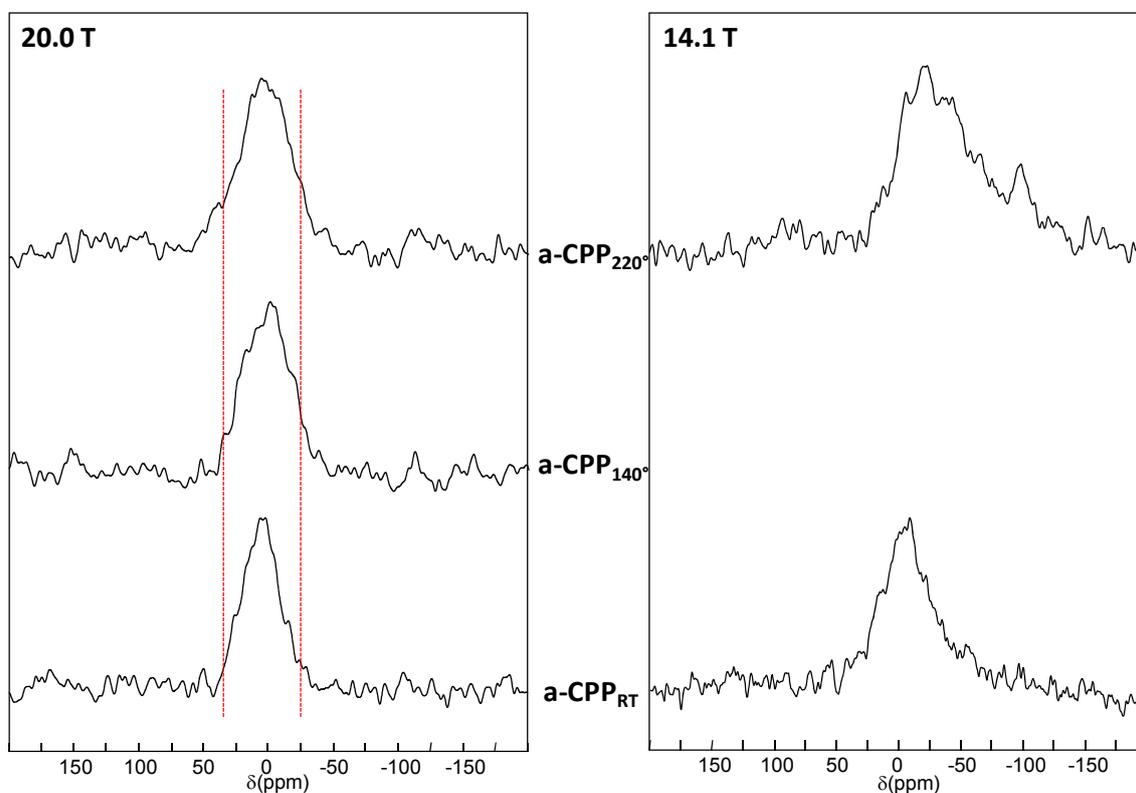


Table S3: Calculated ^1H δ_{iso} for m-CPPD, t-CPPD and m-CPPT β and m-CPPM. All calculations were performed starting from H relaxed structures (Rel H), except for m-CPPM, for which a fully relaxed structural model was used.

		δ_{iso} (ppm) Calc
m-CPPD Rel H	H1	4.26
	H2	3.05
	H3	8.32
	H4	3.95
t-CPPD Rel H	H1	5.10
	H2	4.89
	H3	5.85
	H4	4.74
m-CPPT β Rel H	H1	5.17
	H2	2.85
	H3	6.27
	H4	4.31
	H5	5.78
	H6	2.58
	H7	4.33
	H8	7.93
m-CPPM Rel tot	H1	4.03
	H2	7.41

¹ Massiot D, Fayon F, Capron M, King I, Le Calvé S, Alonso B, Durand J-O, Bujoli B, Gan Z, Hoatson G. Modelling one- and two-dimensional solid-state NMR spectra. *Magn Reson Chem* 2002;20:70-6.