Electronic Supplementary Information

Enhanced Stability and Local Structure in Biologically Relevant Amorphous Materials Containing Pyrophosphate

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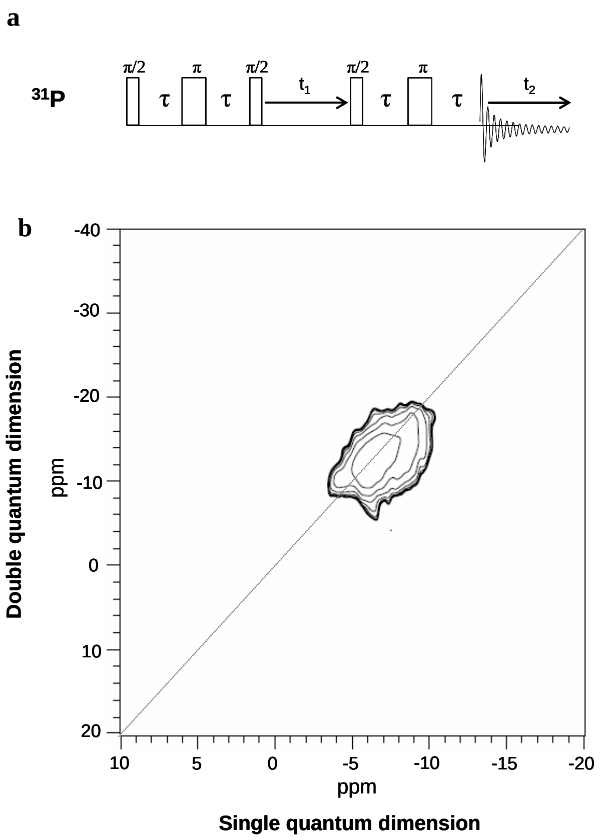
Figure S1: (a) ^{31}P-^{31}P MAS refocused INADEQUATE pulse sequence, (b) INADEQUATE spectrum of ACaPPi.

Figure S2: ^{1}H → ^{31}P CPMAS spectra recorded on crystalline $Ca_2P_2O_7.4H_2O$, using contact times of 0.5, 2.5 and 5.0 ms.

Figure S3. 2D ^{1}H → ^{31}P CPMAS NMR spectrum of ASrPPi, recorded with a contact time of 5 ms.

Figure S1 (a) ^{31}P-^{31}P MAS refocused INADEQUATE pulse sequence, (b) INADEQUATE spectrum of ACaPPi.



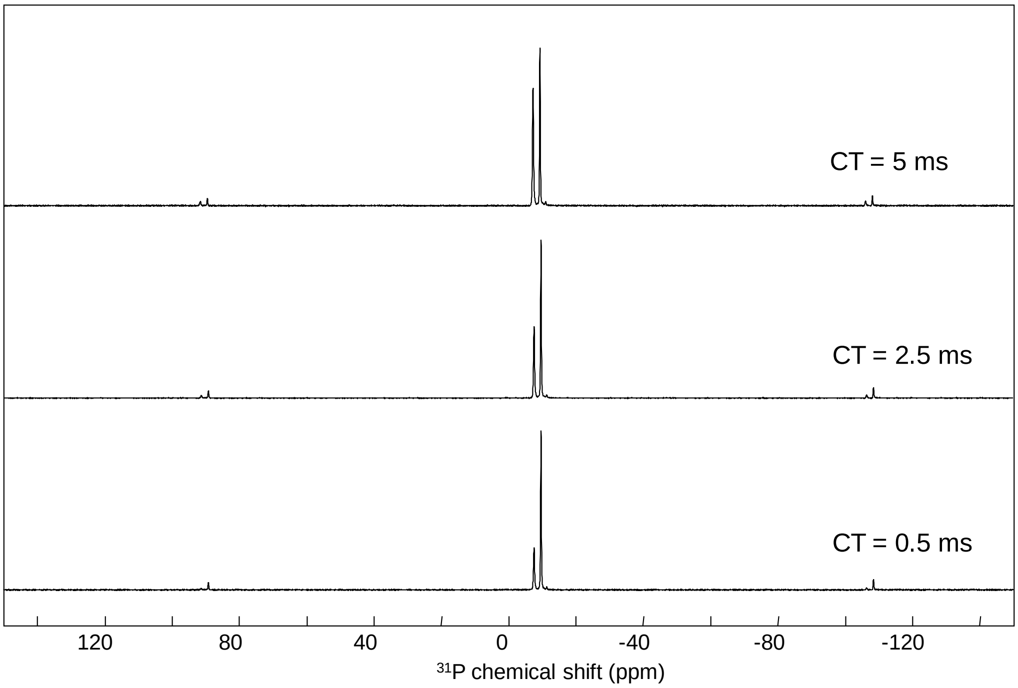
Experimental conditions

The ^{31}P refocused INADEQUATE NMR experiment performed on ACaPPi was carried out at 7.05 T, using a Chemagnetics Infinity Plus spectrometer. A Bruker 4 mm probe was used, with a MAS frequency of 12.5 kHz. The 90° pulse length was 3 μs. The delay τ of the excitation and reconversion periods was synchronized with the rotor period and was set to the optimized value of 4 ms. The recycle delay was set to 60 s. The States acquisition method was used, and 48 acquisitions were co-added for each of the 56 t_1 slices. The F_1 and F_2 spectral widths were both 12.5 kHz. The total experimental time was approximately 45 h. ^{31}P chemical shifts were referenced to solid $NH_4H_2PO_4$ (0.9 ppm with respect to H_3PO_4).

Comment

The presence of a P-O-P bridge in ACaPPi is confirmed by the ^{31}P refocused INADEQUATE experiment. Indeed, a single intense Q^1-Q^1 auto-correlation peak is observed on the 2D map, which proves the through-bond connectivity of the phosphorus atoms in the sample, and thus the presence of $P_2O_7^{4-}$ groups.

Figure S2. $^1H \rightarrow {}^{31}P$ CPMAS NMR spectra recorded on crystalline $Ca_2P_2O_7.4H_2O$ at 9.4 T, using contact times of 0.5, 2.5 and 5.0 ms.



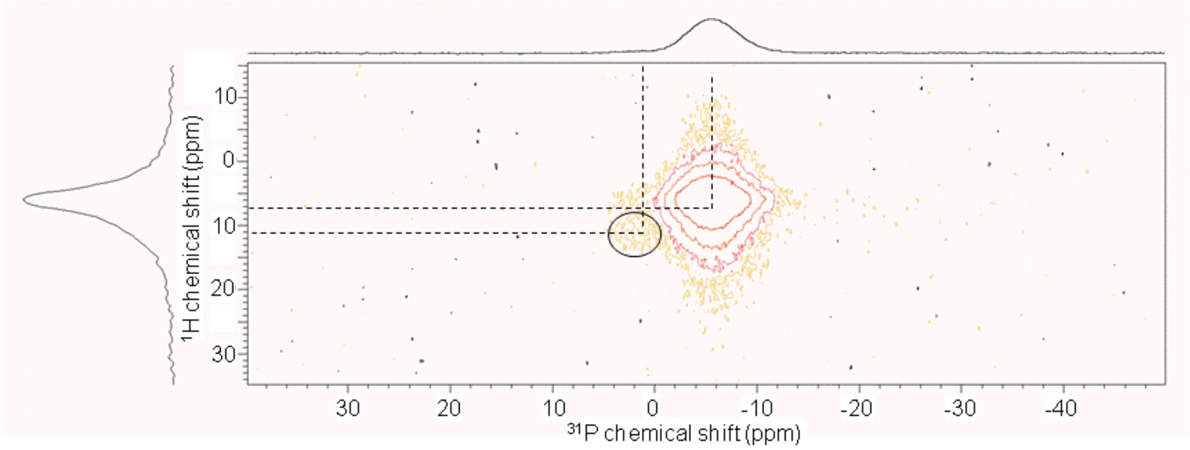
Experimental conditions

$^1H \rightarrow {}^{31}P$ CP MAS NMR experiments were carried out at 9.4 T on a Varian VNMRS 400 MHz, using a 3.2 mm Varian T3 HXY MAS probe spinning at 16 kHz. Spectra were recorded using contact times (CT) of 0.5, 2.5 and 5 ms. 128 transients were acquired, with a recycle delay of 8 s.

Comment

The relative intensity of the two main phosphorus signals in this phase varies with the contact time used, which shows that their relative proximity to the water ligands is different.

Figure S3. 2D ^{1}H → ^{31}P CPMAS NMR spectrum of ASrPPi, recorded with a contact time of 5 ms.



Experimental conditions

^{1}H → ^{31}P CP MAS NMR experiments were carried out at 9.4 T on a Varian VNMRS 400 MHz, using a 3.2 mm Varian T3 HXY MAS probe spinning at 16 kHz. The acquisition conditions are given in more detail in the experimental section of the article.

Comment

The main cross peak shows that the pyrophosphate anions are in close viscinity with the water molecules.

A low intensity cross peak can be noticed, which correlates the ^{31}P shoulder at 2 ppm and a ^{1}H signal at ~11 to 12 ppm, the latter chemical shifts being in the range expected for hydrogen-phosphate protons.