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Supporting information for article:

The ambient hydration of the aluminophosphate JDF-2 to AIPO-53(A): insights from NMR crystallography

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S1.

S2. Approximate Errors in $\alpha(t)$

Considering the ^{31}P MAS NMR spectrum of a mixture of JDF-2 and AlPO-53(A) of composition $\phi_{\text{JDF-2}} + \phi_{\text{AlPO-53(A)}}$, where $\phi_{\text{J}} + \phi_{\text{A}} = 1$ (and, hence, $\phi_{\text{A}} = \alpha(t)$), the spectrum can be separated into four distinct regions as shown in [Figure S1](#). Region W (–12.0 to –15.5 ppm) has intensity I_{W} and contains resonances from P2 of JDF-2 and P6 of AlPO-53(A). Region X (–15.5 to –20.0 ppm) has intensity I_{X} and contains only the P5 resonance of AlPO-53(A). Region Y (–22 to –25.8 ppm) has intensity I_{Y} , and contains resonances from P1 and P3 of JDF-2 and P1 and P4 of AlPO-53(A). Region Z (–25.8 to –35 ppm) has intensity I_{Z} and contains the P2 and P3 resonances of AlPO-53(A). Using the notation I_{nM} , where n = the crystallographic P species and M = J or A (denoting JDF-2 or AlPO-53(A), respectively), the intensities of the regions are

$$I_{\text{W}} = I_{2\text{J}} + I_{6\text{A}} , \quad (\text{S1})$$

$$I_{\text{X}} = I_{5\text{A}} , \quad (\text{S2})$$

$$I_{\text{Y}} = I_{1\text{J}} + I_{3\text{J}} + I_{1\text{A}} + I_{4\text{A}} , \quad (\text{S3})$$

and

$$I_{\text{Z}} = I_{2\text{A}} + I_{3\text{A}} . \quad (\text{S4})$$

Given that all P species have equal occupancy in the crystal structures of JDF-2 and AlPO-53(A), and expressing I_{W} , I_{X} , I_{Y} and I_{Z} as a fraction of the total spectral intensity, [Equations S1-S4](#) can be rewritten in terms of $\alpha(t)$, giving theoretical intensities of

$$I_{\text{W}} = \frac{1}{3} \left(1 - \frac{\alpha(t)}{2} \right) , \quad (\text{S5})$$

$$I_{\text{X}} = \frac{\alpha(t)}{6} , \quad (\text{S6})$$

$$I_{\text{Y}} = \frac{2}{3} \left(1 - \frac{\alpha(t)}{2} \right) , \quad (\text{S7})$$

and

$$I_{\text{Z}} = \frac{\alpha(t)}{3} . \quad (\text{S8})$$

The value of $\alpha(t)$ can, therefore, be determined by integration of the quantitative ^{31}P MAS NMR spectrum (including first-order SSBs) of a sample of JDF-2 exposed to ambient moisture for a given time period. The intensities of all four regions can be obtained from one spectrum, allowing four values of $\alpha(t)$ to be determined and providing some indication of the error associated with this approach. Values plotted in Figure 2(a) of the main text represent the mean value of $\alpha(t)$, with the error bars representing the standard deviation of the values obtained from each of the four regions.

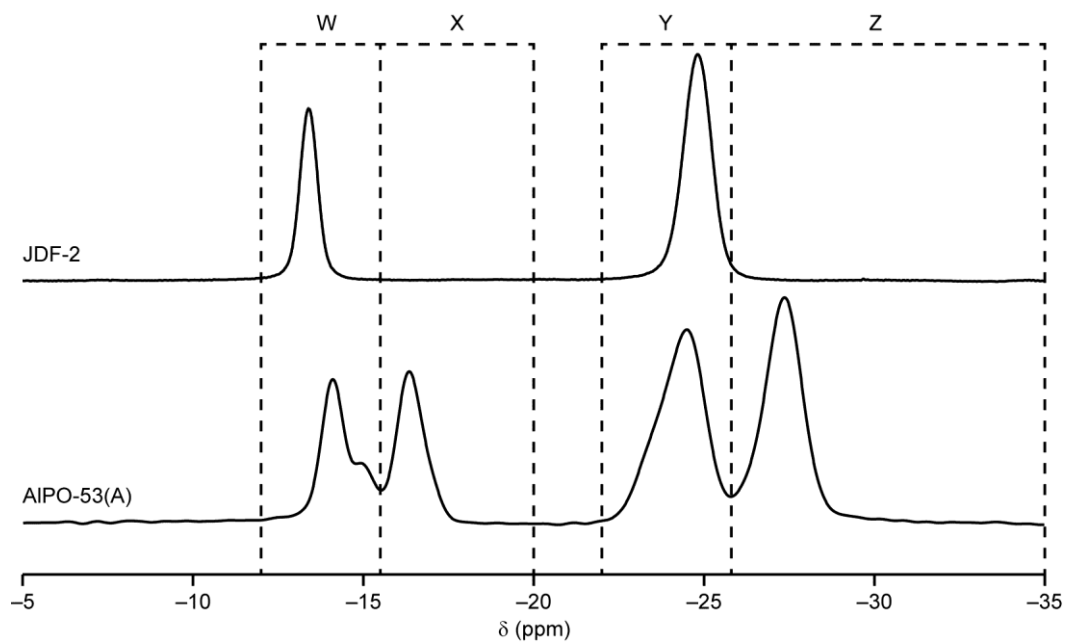


Figure S1 ^{31}P (14.1 T, 12.5 kHz MAS) NMR spectra of JDF-2 and AIPO-53(A). The regions used to determine $\alpha(t)$ are indicated.

S3. Ambient Hydration of Calcined AIPO-53(B)

Figure S2 shows the evolution of the ^{31}P NMR spectra of the calcined AIPOs, AIPO-53(B) (AEN type), and AIPO-34 (CHA type), as a function of time exposed to ambient moisture. It can be seen that the materials reaches an essentially fully-hydrated state within the first 24-48 h and subsequently change very little. An intermediate partially-hydrated state is clearly apparent for AIPO-53(B), but we have not yet identified its nature.

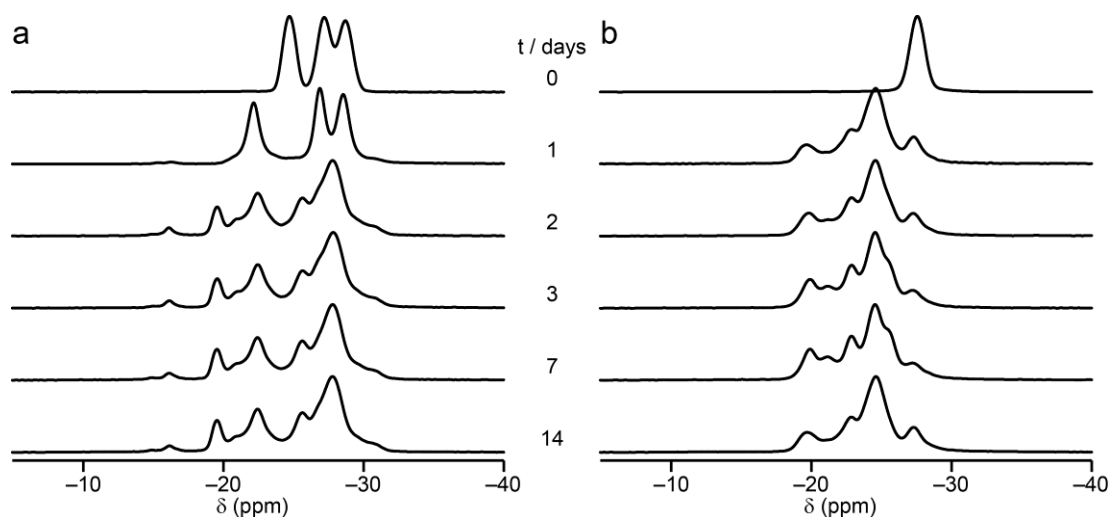


Figure S2 ^{31}P (14.1 T, 12.5 kHz MAS) NMR spectra of calcined AIPOs with (a) AEN framework type (AIPO-53(B)) and (b) CHA framework type (AIPO-34) exposed to ambient conditions for the time indicated.

S4. ^1H DQMAS NMR Spectra of JDF-2 and AIPO-53(A)

Assignment of the ^1H NMR spectra of JDF-2 and AIPO-53(A), shown in Figure 3, was confirmed by ^1H DQMAS spectra, shown in Figure S2. For JDF-2, the spectrum contains only one pair of off-diagonal resonances, with shifts of (3.0, 9.1) and (6.1, 9.1) ppm, confirming the close spatial proximity of the two H species with shifts of 3.0 and 6.1 ppm, previously assigned to CH_3 and NH_3 , respectively. On-diagonal resonances are also observed at (3.0, 6.0) and (6.1, 12.2) ppm, as would be expected for both CH_3 and NH_3 . The resonance at 5.3 ppm, assigned to OH^- does not appear in the DQMAS NMR spectrum, confirming that this resonance arises from spatially isolated ^1H nuclei, as would be expected from the structure of JDF-2.

For AIPO-53(A), the ^1H DQMAS spectrum contains sets of on- and off-diagonal resonances that can be traced out to give CH_3 and NH_3 shifts of 2.8 and 6.6 ppm for one MA and 3.0 and 6.3 ppm for the other (indicated by solid red and blue lines, respectively). DQCs are also observed at (5.2, 8.0) and (2.8, 8.0) ppm, corresponding to a close $\text{CH}_3\text{-HO}^-$ distance. There is also a weak correlation between H_2O and NH_3 (although only one of the pair of expected DQCs is observed in each case), supporting the idea that there is a close spatial proximity between H_2O and the NH_3 groups, as discussed in the text.

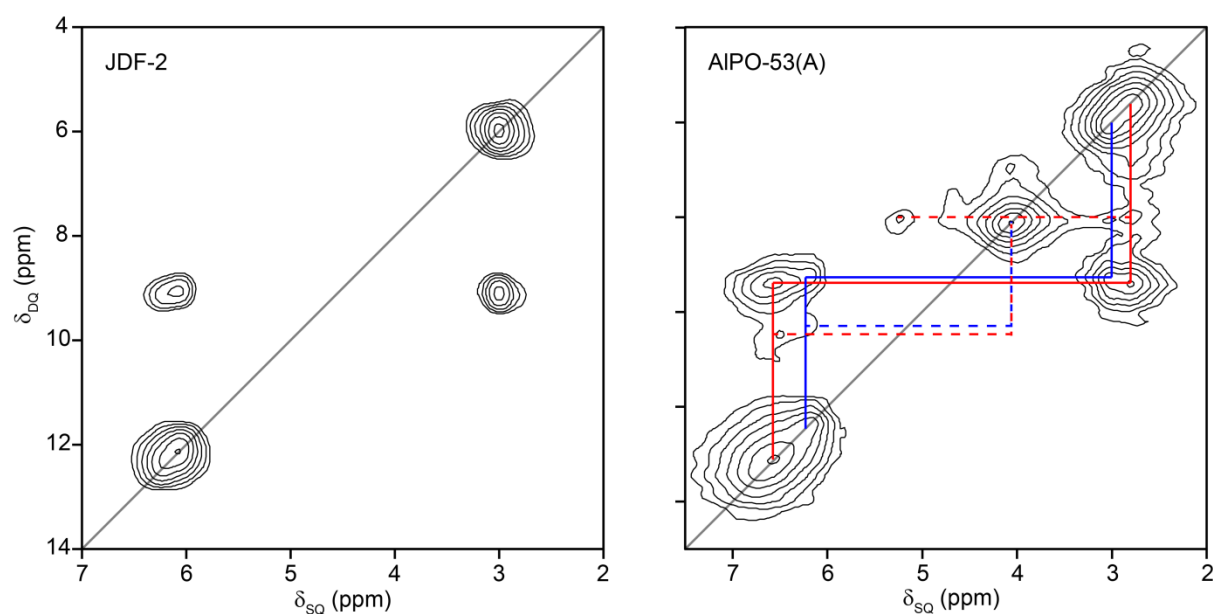


Figure S3 ^1H (14.1 T, 60 kHz MAS) double-quantum/single-quantum correlation spectra of JDF-2 and AIPO-53(A). In both parts, the $\delta_{\text{DQ}} = 2\delta_{\text{SQ}}$ diagonal is indicated in grey. For AIPO-53(A), sets of resonances arising from the same MAH^+ species are indicated with red and blue lines. $\text{CH}_3\text{-OH}$ and $\text{NH}_3\text{-H}_2\text{O}$ correlations are indicated with broken lines.

S5. ^{27}Al MQMAS NMR Spectra

^{27}Al MQMAS NMR spectra of JDF-2 and AIPO-53(A) are shown in Figure S3. The spectrum of JDF-2 contains three clear resonances with NMR parameters (given in Table 4) extracted from cross-sections of each ridge. The spectrum of AIPO-53(A) contains five clear resonances, with the NMR parameters (given in Table 4) extracted from cross sections of each ridge. As observed by Ashbrook *et al.* (2009), the resonances attributed to Al2 and Al4 are overlapped at 14.1 T.

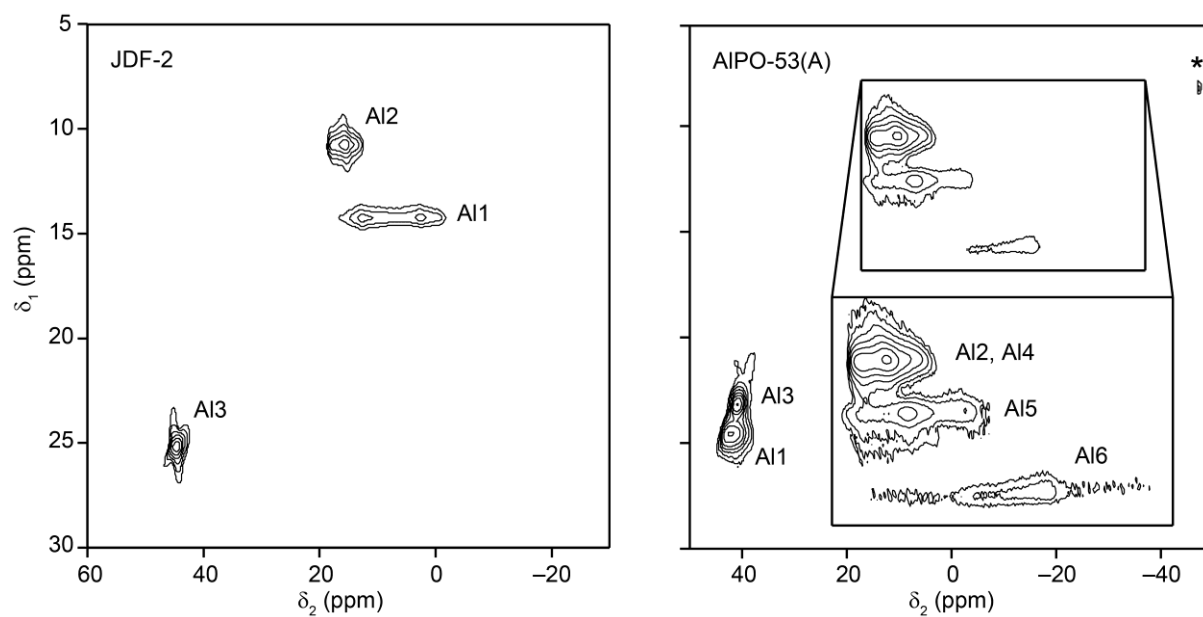


Figure S4 ^{27}Al (14.1 T, 14 kHz MQMAS) NMR spectra of JDF-2 and AIPO-53(A).

S6. Structural Models of Disorder in AIPO-53(A)

Table S1 summarises the numbering scheme used for the different models of disorder in AIPO-53(A). The input and output files for the CASTEP calculations have been uploaded separately as part of the underpinning data (see the main text for details).

Table S1 Summary of the models of JDF-2 and AIPO-53(A) considered in this work.

Model	Description	Total Energy / eV ^a
J1	Literature structure of JDF-2 (Chippindale <i>et al.</i> , 1994)	-58257.298
J2	JDF-2 with the C and N of each MAH ⁺ reversed	-58256.335
A1	Literature structure of AIPO-53(A) (Kirchner <i>et al.</i> , 2000)	-62037.578
A2	Literature structure of AIPO-53(A) with all water removed	-58256.446
A3	As A2 but with the C and N of each MAH ⁺¹ and MAH ⁺² reversed	-58257.290
A4	As A1 but with the C and N of each MAH ⁺¹ and MAH ⁺² reversed	-62037.612
A5	Removal of a single W1 from model A1 (before optimisation)	-61565.182
A6	Removal of a single W2 from model A1 (before optimisation)	-61565.142
A7	Removal of a single W1 from model A4 (before optimisation)	-61565.066
A8	Removal of a single W2 from model A4 (before optimisation)	-61564.687
A9	Removal of all W1 from model A1 (before optimisation)	-60147.507
A10	Removal of all W2 from model A1 (before optimisation)	-60147.320
A11	Removal of all W1 from model A4 (before optimisation)	-60146.676
A12	Removal of all W2 from model A4 (before optimisation)	-60146.536
A13	A3 containing a single W1	-58729.193
A14	A3 containing a single W2	-58729.156

a. Dispersion-corrected total energy after full geometry optimisation.

S7. Calculated ^{31}P Chemical Shifts

Figure S4 shows the calculated ^{31}P chemical shifts for the different models of AIPO-53(A) and JDF-2 discussed in the text. It can be seen that no one model is a clear match for the experimental ^{31}P NMR spectrum of AIPO-53(A). However, for JDF-2, the agreement is much better for model J1 than J2.

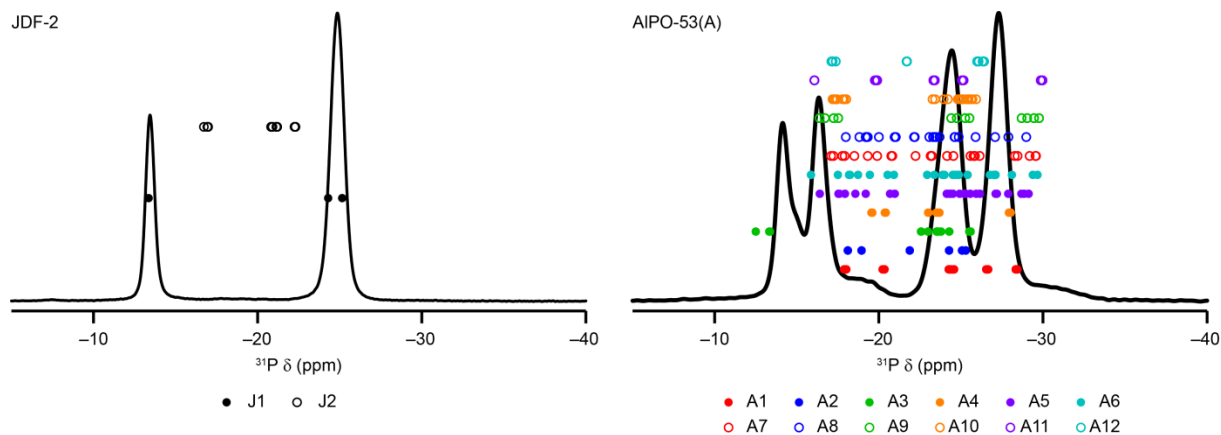


Figure S5 Experimental ^{31}P NMR spectra of AIPO-53(A) and JDF-2 overlaid with data points representing the calculated isotropic chemical shifts for the structural models discussed in the text (see Section S4 for details).