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Dehydration of $AlPO_4$-34 studied by variable-temperature NMR, XRD and first-principles calculations

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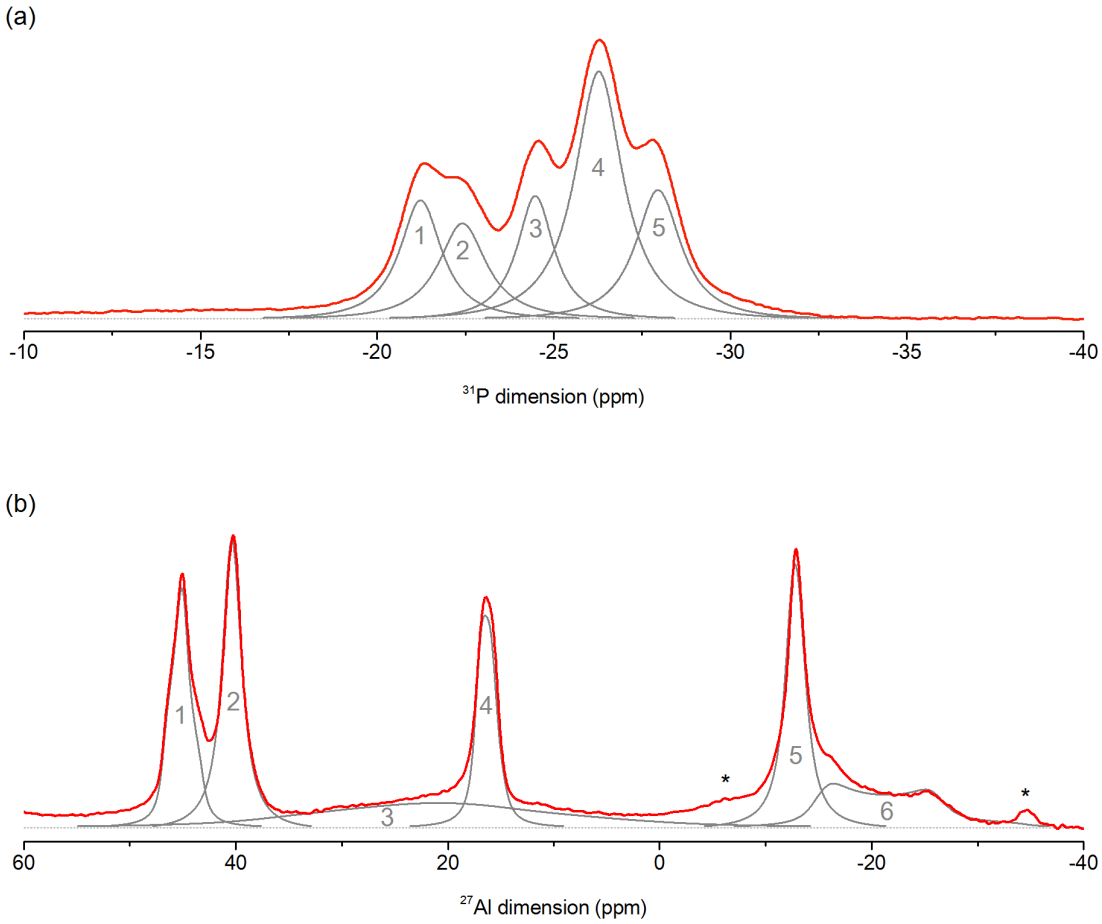

Figure S1: Decomposition of the ^{31}P (a) and ^{27}Al (b) MAS NMR spectra of the hydrated form of $AlPO_4$-34. The parameters of the individual contributions are listed in Table S1. Asterisks in (b) mark spinning sidebands.

Table S1. NMR parameters (isotropic chemical shifts and quadrupolar coupling constants) and intensities of individual contributions in the ^{31}P and ^{27}Al MAS NMR spectra of the hydrated form of $AlPO_4$-34.

^{31}P

Line	δ_{iso} (ppm) ±0.1	Intensity ±1
1	-21.2	17
2	-22.5	14
3	-24.5	16
4	-26.3	34
5	-28.0	19

^{27}Al

Line	δ_{iso} (ppm) ±0.1	C_Q (kHz) ±10	η_Q ±0.01	Intensity ±1
1	46.9	2390	0.83	16
2	40.9	1470	0.01	19
3*	33.8	6940	0.80	19
4	17.6	2220	0.42	14
5	-12.1	1670	0.03	18
6	-12.1	6030	0.12	14

*NMR parameters for line 3 are not as well defined as NMR parameters for other lines in the ^{27}Al MAS NMR spectrum. Because the line is severely smeared, the quadrupolar coupling constant and the asymmetry parameter cannot be determined reliably. Certain ambiguity of the quadrupolar coupling constant affects also the reliability of the determined isotropic chemical shift.

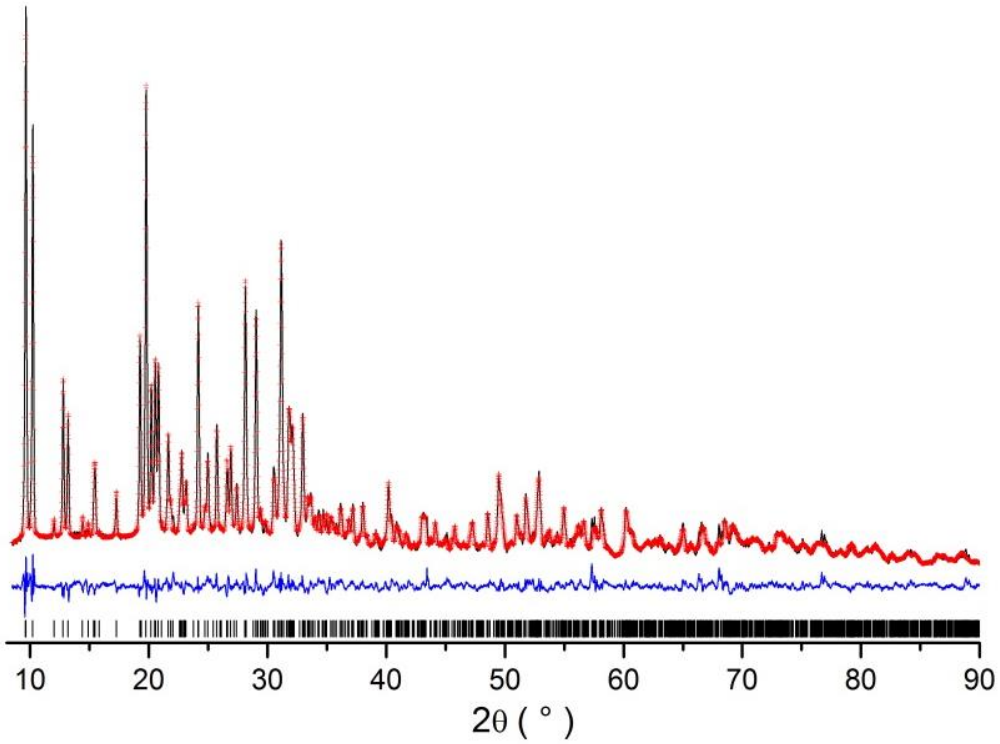

Figure S2: Rietveld plot of the partly dehydrated phase I based on the XRD pattern measured at 50 °C. Black line – experimental plot, red crosses – calculated pattern, blue line – differential plot, black ticks – calculated positions of reflections.

Table S2. Crystal structure refinement data of partly dehydrated phase I.

Chemical formula	$Al_6O_{35}P_6$
Formula weight (g/mol)	907.71
Temperature (°C)	50
Wavelength (Å)	1.5418
symmetry	triclinic
Space group	P1 (No. 1)
a (Å)	9.0197(2)
b (Å)	9.2738(2)
c (Å)	9.5994(2)
α (°)	95.217(2)
β (°)	104.901(2)
γ (°)	95.270(3)
V (Å^3)	767.19(4)
Z, calculated density	1, 1.965
2θ range (°)	8.5 to 90.0
No Reflections	145
No. non hydrogen atoms	47
GoF	1.36
No structural parameters	163
R_{wp}, R_p	0.081, 0.072
R_{Bragg}	0.046

Table S3. Atomic coordinates and temperature factors for partly dehydrated phase I.

	x	*y*	*z*	Beq
Al1	0.348(1)	0.148(1)	0.918(2)	1.15(6)
Al2	0.946(2)	0.371(1)	0.109(2)	1.15(6)
Al3	0.225(1)	0.892(1)	0.408(1)	1.15(6)
Al4	0.715(1)	0.929(2)	0.112(2)	1.15(6)
Al5	0.119(2)	0.704(1)	0.902(2)	1.15(6)
Al6	0.857(1)	0.157(1)	0.641(1)	1.15(6)
P1	0.3627(8)	0.9195(8)	0.1157(8)	1.15(6)
P2	0.1290(8)	0.3646(8)	0.8848(8)	1.15(6)
P3	0.9689(8)	0.1278(8)	0.3296(9)	1.15(6)
P4	0.6737(8)	0.1409(8)	0.8710(8)	1.15(6)
P5	0.9347(8)	0.6898(8)	0.1406(8)	1.15(6)
P6	0.0771(8)	0.9077(8)	0.6657(8)	1.15(6)
O1	0.223(2)	0.008(2)	0.744(2)	0.7(1)
O2	0.253(2)	0.775(2)	0.020(2)	0.7(1)
O3	0.027(2)	0.243(2)	0.770(2)	0.7(1)
O4	0.732(2)	0.271(2)	0.978(2)	0.7(1)
O5	0.813(2)	0.026(2)	0.252(2)	0.7(1)
O6	0.072(2)	0.752(2)	0.254(2)	0.7(1)
O7	0.321(2)	0.049(2)	0.041(1)	0.7(1)
O8	0.295(2)	0.327(1)	0.930(2)	0.7(1)
O9	0.072(2)	0.374(2)	0.027(2)	0.7(1)
O1	0.992(2)	0.265(2)	0.253(2)	0.7(1)
O1	0.105(2)	0.050(2)	0.322(2)	0.7(1)
O1	0.333(2)	0.931(2)	0.262(2)	0.7(1)
O1	0.741(2)	0.006(2)	0.937(2)	0.7(1)
O1	0.801(2)	0.781(1)	0.135(2)	0.7(1)
O1	0.967(2)	0.689(2)	-0.014(2)	0.7(1)
O1	0.055(2)	0.779(2)	0.748(2)	0.7(1)
O1	-0.075(2)	0.984(2)	0.654(2)	0.7(1)
O1	0.718(2)	0.155(2)	0.738(2)	0.7(1)
O1	0.502(2)	0.118(2)	0.838(1)	0.7(1)
O2	0.529(2)	0.886(2)	0.136(1)	0.7(1)
O2	0.893(2)	0.537(2)	0.172(1)	0.7(1)
O2	0.126(2)	0.522(2)	0.826(2)	0.7(1)
O2	0.087(2)	0.853(1)	0.525(2)	0.7(1)
O2	0.971(2)	0.175(2)	0.480(2)	0.7(1)
O2	0.243(2)	0.683(2)	0.406(2)	0.9(3)
O2	0.404(2)	0.020(2)	0.522(3)	0.9(3)
O2	0.738(2)	0.325(1)	0.540(2)	0.9(3)
O2	0.713(2)	0.009(2)	0.496(2)	0.9(3)
O2	0.601(2)	0.808(2)	-0.118(2)	0.9(3)
O3	0.683(3)	0.645(3)	0.573(2)	2.1(3)
O3	-0.044(2)	0.553(2)	0.460(3)	2.1(3)
O3	0.541(3)	0.493(2)	-0.078(3)	2.1(3)
O3	0.465(3)	0.569(2)	0.293(2)	2.1(3)
O3	0.401(3)	0.269(2)	0.393(2)	2.1(3)
O3	0.271(2)	0.452(2)	0.584(2)	2.1(3)

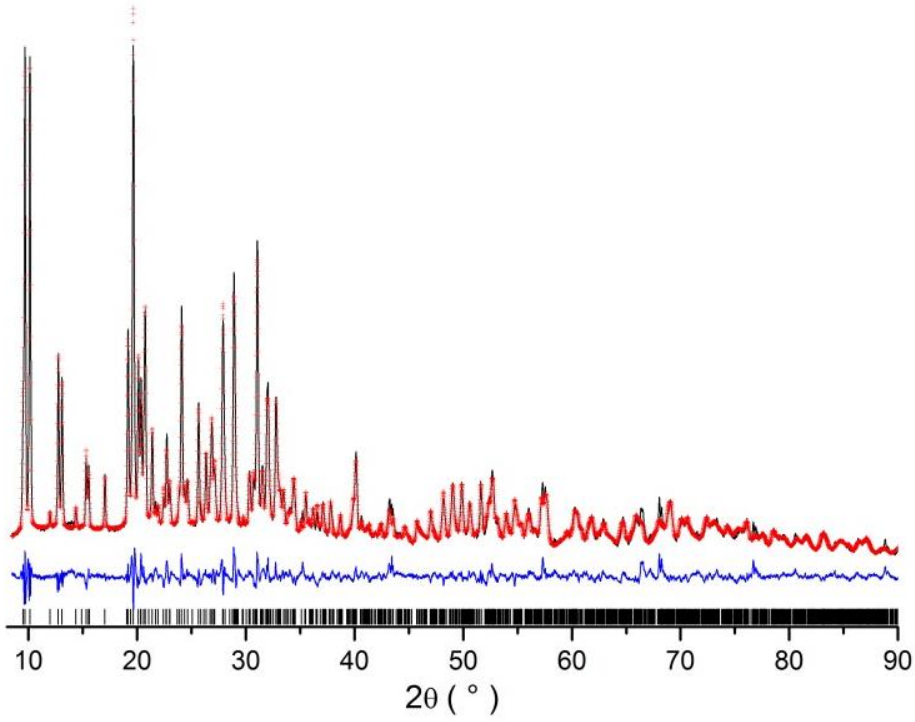

Figure S3: Rietveld plot of the partly dehydrate phase II based on the XRD pattern measured at 56 °C. Black line – experimental plot, red crosses – calculated pattern, blue line – differential plot, black ticks – calculated positions of reflections.

Table S4. Crystal structure refinement data of partly dehydrated phase II.

Chemical formula	$Al_3O_{17}P_3$
Formula weight (g/mol)	445.85
Temperature (°C)	56
Wavelength (Å)	1.5418
symmetry	triclinic
Space group	P-1 (No. 2)
a (Å)	9.0832(3)
b (Å)	9.2516(2)
c (Å)	9.6682(3)
α (°)	95.098(3)
β (°)	104.216(2)
γ (°)	95.889(3)
V (Å^3)	777.92(4)
Z, calculated density	2, 1.903
2θ range (°)	8.5 to 90.0
No Reflections	129
No. non hydrogen atoms	23
GoF	1.36
No structural parameters	104
R_{wp}, R_p	0.097, 0.108
R_{Bragg}	0.051

Table S5. Atomic coordinates and temperature factors for partly dehydrated phase II.

	x	*y*	*z*	Beq
Al1	0.6875(9)	0.8927(8)	0.1084(8)	1.26(6)
Al2	0.0861(8)	0.6697(9)	0.8895(7)	1.26(6)
Al3	0.8282(9)	0.1371(8)	0.6184(8)	1.26(6)
P1	0.3443(8)	0.8855(7)	0.1144(7)	1.26(6)
P2	0.0918(8)	0.3355(8)	0.8704(7)	1.26(6)
P3	0.9417(8)	0.1103(8)	0.3351(7)	1.26(6)
O1	-0.033(1)	0.238(2)	0.755(1)	0.81(9)
O2	0.758(1)	0.246(1)	0.004(1)	0.81(9)
O3	0.791(1)	0.008(2)	0.253(1)	0.81(9)
O4	0.983(1)	0.243(1)	0.276(1)	0.81(9)
O5	0.079(1)	0.043(1)	0.327(1)	0.81(9)
O6	0.679(1)	-0.038(1)	0.946(1)	0.81(9)
O7	0.752(1)	0.723(1)	0.104(1)	0.81(9)
O8	0.949(1)	0.675(1)	-0.012(1)	0.81(9)
O9	0.695(1)	0.087(1)	0.748(1)	0.81(9)
O1	0.507(2)	0.863(1)	0.144(1)	0.81(9)
O1	0.115(2)	0.499(1)	0.851(1)	0.81(9)
O1	0.932(1)	0.164(1)	0.479(1)	0.81(9)
O1	0.276(1)	0.713(1)	0.418(1)	4.3(4)
O1	0.649(1)	-0.008(2)	0.491(2)	4.3(4)
O1	0.603(1)	0.719(2)	0.574(2)	4.3(4)
O1	0.466(2)	0.517(2)	0.259(2)	4.3(4)
O1	0.173(2)	0.468(1)	0.555(1)	4.3(4)