

M. Kanzaki, X. Xue, S. Reibstein, E. Berryman and S. Namgung, The crystal structures of two new high-pressure forms of  $\text{AlPO}_4$  by powder X-ray diffraction and NMR spectroscopy: Supplementary Material.

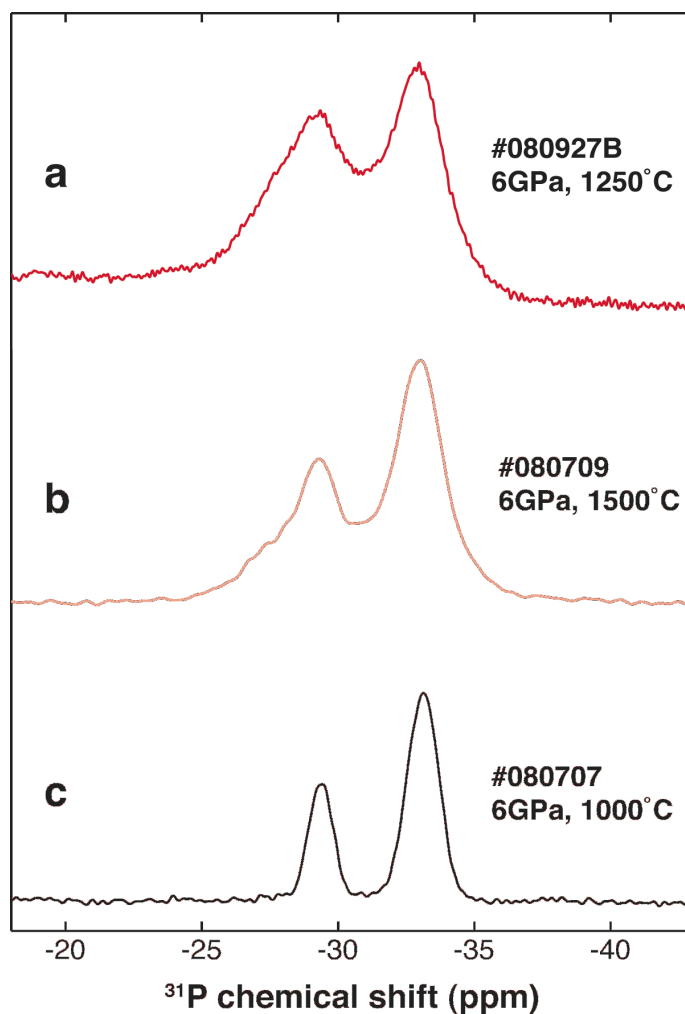


Fig. S1.  $^1\text{H} \rightarrow ^{31}\text{P}$  CP-MAS NMR spectra in the vicinity of peaks for trolleite, all acquired at a resonance frequency of 400.4 MHz for  $^1\text{H}$  and 162.1 MHz for  $^{31}\text{P}$ , and a contact time of 8 ms with no decoupling during acquisition. (a) sample #080927B synthesized at 6 GPa and 1250°C using dried  $\text{AlPO}_4$  starting material (spinning speed: 30 kHz, recycle delay: 10 s); (b) sample #080709 synthesized at 6 GPa and 1500°C using undried  $\text{AlPO}_4$  starting material containing about 2 wt%  $\text{H}_2\text{O}$  (spinning speed: 15 kHz, recycle delay: 5 s); (c) sample #080707 synthesized at 6 GPa and 1000°C using undried  $\text{AlPO}_4$  starting material containing about 2 wt%  $\text{H}_2\text{O}$  (spinning speed: 30 kHz, recycle delay: 60 s). All the spectra have been plotted with the same maximum height. The two peaks of trolleite near -29.3 and -32.9 ppm are narrower and better resolved for (c) than (a,b). This suggests that either trolleite possesses varying degree of disorder depending on temperature, or it could have formed from hydrous melt during quench for samples synthesized at higher temperatures ( $\approx 1250^\circ\text{C}$ ) (a,b).

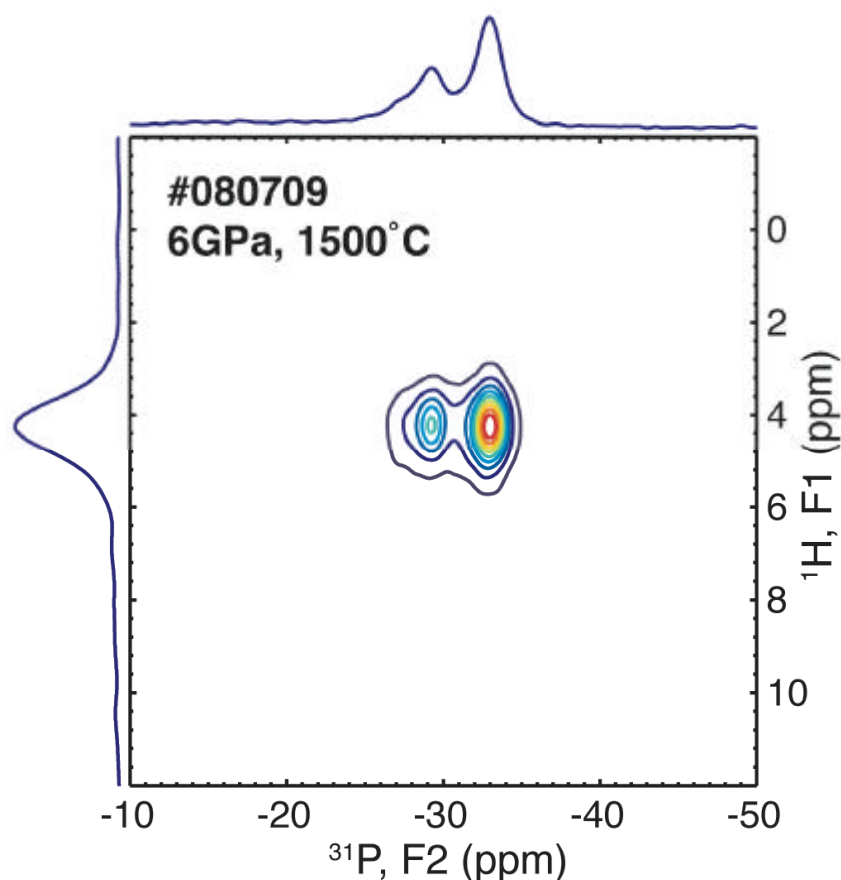


Fig. S2. Rotor-synchronized  $^1\text{H} \rightarrow ^{31}\text{P}$  HETCOR spectrum with total projections along both dimensions for sample #080709 (synthesized at 6 GPa and 1500 °C using undried  $\text{AlPO}_4$  starting material containing about 2 wt%  $\text{H}_2\text{O}$ ), acquired at a resonance frequency of 400.4 MHz for  $^1\text{H}$  and 162.1 MHz for  $^{31}\text{P}$ , a spinning speed of 30 kHz, a contact time of 2 ms, and a recycle delay time of 10 s. No decoupling was applied during acquisition. The  $t_1$  time increment was one rotor period (33  $\mu\text{s}$ ); 24 scans were averaged for each of 64  $t_1$  increments (128 FID). The contours have been plotted with a linear intensity scale from 10% to 100% in increment of 10%. It is clear that the two  $^{31}\text{P}$  peaks of trolleite near -29.3 and -32.9 ppm are both correlated with a  $^1\text{H}$  peak near 4.3 ppm. Other samples described in the main text also gave similar results.

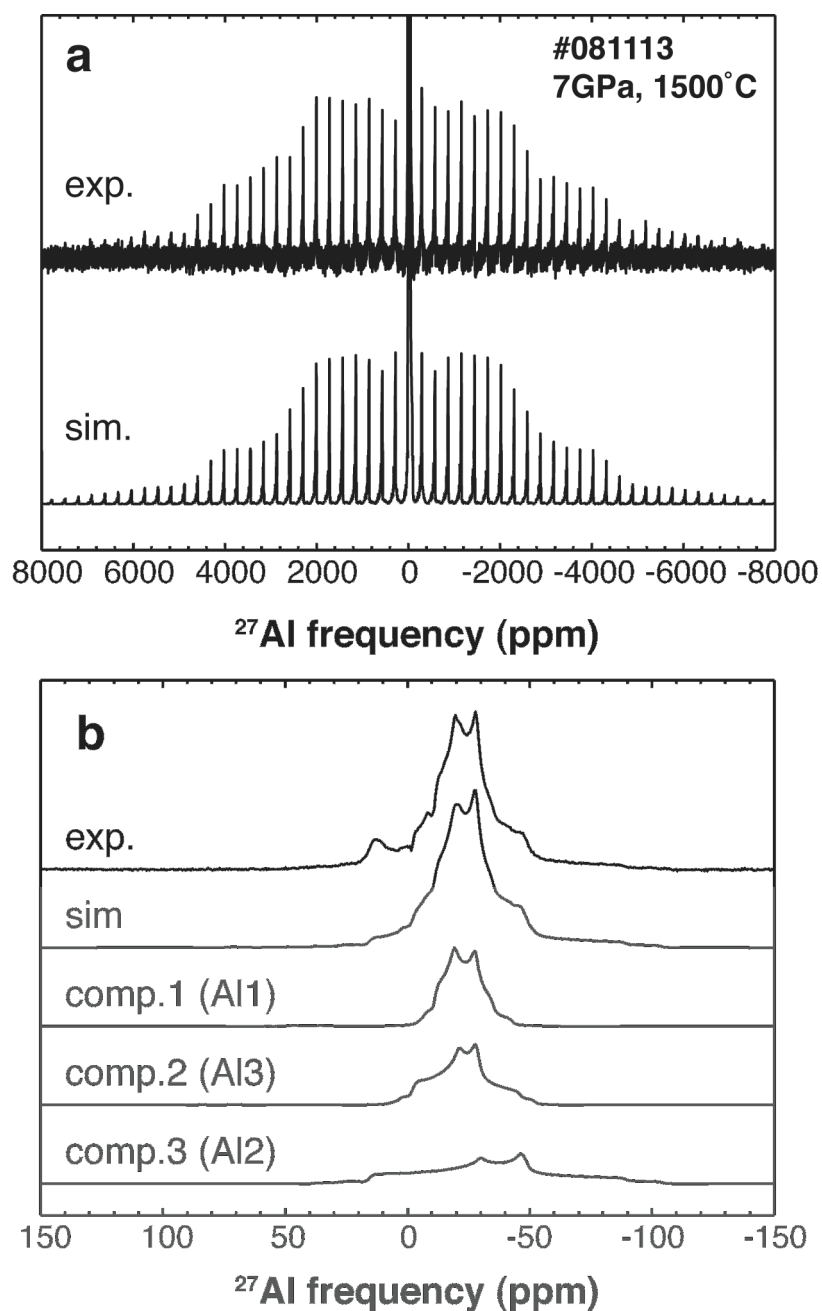


Fig. S3. <sup>27</sup>Al MAS NMR spectra (a: entire frequency range; b: central band) of sample #081113 synthesized at 7 GPa and 1500°C (AlPO<sub>4</sub> P2<sub>1</sub>/c phase + minor corundum), acquired with a spectral width of 2 MHz, a pulse width of 0.5 μs (ca. 30° tip angle for selective central transition), a recycle delay of 3 s and a spinning rate of 30 kHz. A small background signal from the probe/rotor (as measured on the empty rotor under identical conditions) has been subtracted from the reported spectrum. A spline correction has been applied to remove the rolling baseline resulting from spectrometer deadtime (ca. 8 μs). Also shown below the experimental spectra are the simulated spectra for the AlPO<sub>4</sub> P2<sub>1</sub>/c phase with three Al sites of equal abundance using parameters reported in Table 3, as well as the component for each Al site (as labelled).

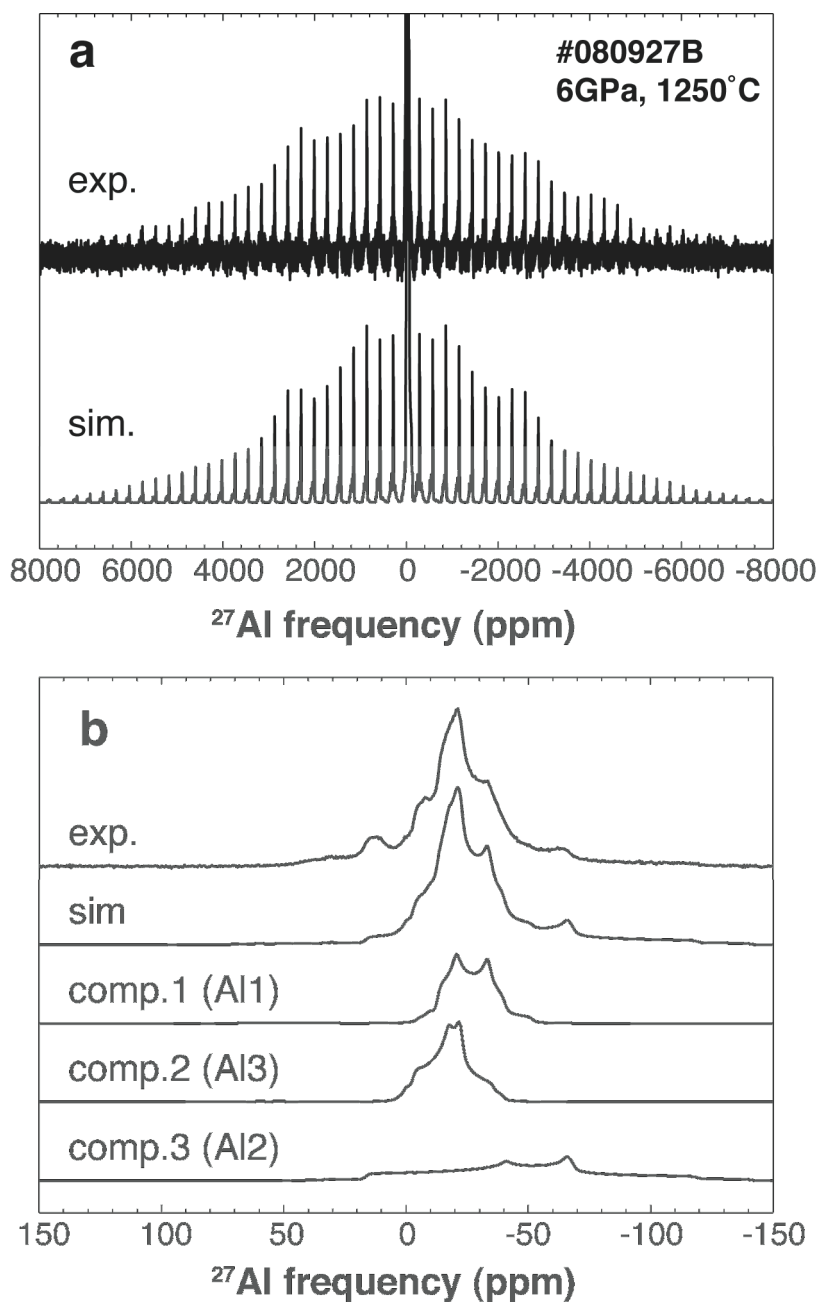


Fig. S4. <sup>27</sup>Al MAS NMR spectra (a: entire frequency range; b: central band) of sample #080927B synthesized at 6 GPa and 1250°C (AlPO<sub>4</sub> P-1 phase + minor trolleite + minor corundum), acquired with a spectral width of 2 MHz, a pulse width of 0.5 μs (ca. 30° tip angle for selective central transition), a recycle delay of 3 s and a spinning rate of 30 kHz. A small background signal from the probe/rotor (as measured on the empty rotor under identical conditions) has been subtracted from the reported spectrum. A spline correction has been applied to remove the rolling baseline resulting from spectrometer deadtime (ca. 8 μs). Also shown below the experimental spectra are the simulated spectra for the AlPO<sub>4</sub> P-1 phase with three Al sites of equal abundance using parameters reported in Table 3, as well as the component for each Al site (as labelled).

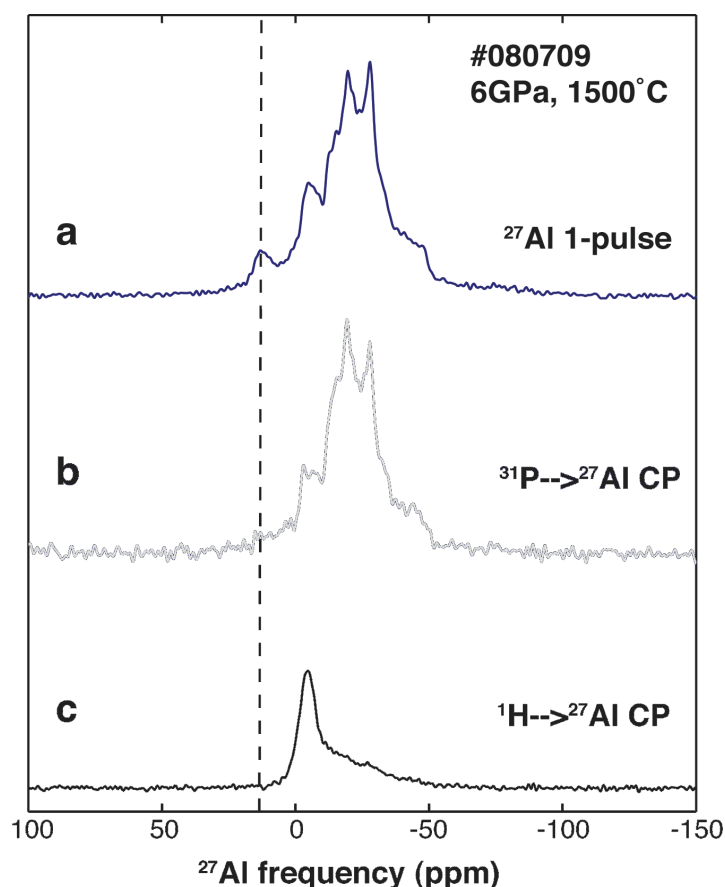


Fig. S5. Comparison of  $^{27}\text{Al}$  single-pulse MAS NMR spectrum (pulse width:  $0.5\ \mu\text{s}$  (ca.  $30^\circ$  tip angle for selective central transition), recycle delay: 3 s, 3172 scans) (a),  $^{31}\text{P} \rightarrow ^{27}\text{Al}$  CP-MAS NMR spectrum (contact time: 8 ms, recycle delay: 80 s, 768 scans) (b), and  $^1\text{H} \rightarrow ^{27}\text{Al}$  CP-MAS NMR spectrum (contact time: 8 ms, recycle delay: 5 s, 800 scans) (c) for sample #080709 synthesized at 6 GPa and  $1500^\circ\text{C}$  using undried  $\text{AlPO}_4$  starting material containing about 2 wt%  $\text{H}_2\text{O}$  ( $\text{AlPO}_4$  P2<sub>1</sub>/c phase + minor trolleite + minor corundum). All the spectra have been obtained with a spectral width of 2 MHz, a spinning rate of 30 kHz, and no decoupling applied during acquisition. A small background signal from the probe/rotor (as measured on the empty rotor under identical conditions) has been subtracted from the reported spectrum in (a). The vertical scale is arbitrary. A small peak near 14 ppm (delineated by a dashed line) is visible in the single-pulse spectrum (a), but is absent in both types of CP spectra (b,c), and may be attributed to a small amount of  $\text{Al}_2\text{O}_3$  corundum. All the other components in the single-pulse spectrum (a) are also present in the  $^{31}\text{P} \rightarrow ^{27}\text{Al}$  CP spectrum (b), and may be attributed to aluminophosphate phases ( $\text{AlPO}_4$  P2<sub>1</sub>/c phase + minor trolleite). The  $^1\text{H} \rightarrow ^{27}\text{Al}$  CP spectrum (c) reveals a narrower  $^{27}\text{Al}$  component with a maximum near -4.1 ppm and a broader component at lower frequency, which most likely correspond to the two Al sites in trolleite. Similar  $^{27}\text{Al}$  peaks have also been observed in the  $^1\text{H} \rightarrow ^{27}\text{Al}$  CP-MAS and 2D HETCOR spectra for other samples synthesized from water-bearing starting materials (as described in the main text) and have been confirmed to both correlate with a  $^1\text{H}$  peak near 4.3 ppm (for trolleite).